THEORY OF RADIATIONLESS TRANSITIONS, LIGHT SCATTERING AND FLUORESCENCE

Thesis by

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In Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

California Institute of Technology
Pasadena, California

1977
(Submitted September 20, 1976)

To Art, my parents, and sister

ACKNOWLEDGMENTS

First, I wish to thank my research advisor, Professor G. Wilse Robinson, for many of the research ideas and for giving me confidence to work independently. I learned a lot from interacting with him and am grateful for the time he spent teaching me.

Second, I thank my "substitute advisor", Professor Vince McKoy, for help with several mathematical problems. Thanks also go to several other professors for discussions on various topics, in particular to Professor Ahmed Zewail for educational discussions on several areas of spectroscopy.

Third, I wish to acknowledge the friendship and help of present and past members of my group--Dr. Graham Fleming, Tom Orlowski, Bob Reiner, Mark Allen, and also to Professor Charles Langhoff for long-distance help. A very special thank you goes to Professor Ken Kaufman for his friendship, support and encouragement when I got depressed about my work.

Fourth, thanks go to Adria McMillan, for being a superb secretary, and to Henriette Wymar for typing this thesis.

Fifth, I gratefully acknowledge financial support from an NSF fellowship and from a grant from the Army Research Office.

Finally, all my love and thanks go to the four people to whom this thesis is dedicated. To my parents and sister, thank you for never-ending encouragement and for never trying to limit my dreams or aspirations. To my husband Art, whose love and patience has kept me going during these past four years and especially for these last three months, thank you so much--I don't know how to repay you.

ABSTRACT

In the first part of this thesis a purely electronic mechanism by which ~ 20 eV excitations in condensed non-metallic phases relax to lower energy states is described. The mechanism utilizes an "energy fission" process whereby an ionic or excitonic state splits into two lower energy states, at least one being of the Frenkel exciton variety. These relaxation processes should be important in the pre-chemical stage in the radiation chemistry of condensed phases. The mechanism explains not only the known rapidity of such processes but also suggests an explanation for the proportionation of the chemistry between ionic and electronically excited states.

In the second part of this thesis, Green's functions are used to discuss the time and frequency dependence of light scattering and fluorescence from model systems. In the first section of this part, time-dependent scattering from a single resonance using an uncertainty-limited light pulse is described. Three terms occur in the time dependence--one which decays as the resonance, one which decays like the light source and a beat term between them which beats at the frequency difference between the exciting pulse and the resonance.

In the next section the model is extended to scattering from a two-level system. The frequency dependence of the Rayleigh and Raman scattering is described, again using excitation from an uncertainty-limited light pulse.

The effects of the two-photon states, which lead to the antiresonance terms in time-independent light scattering, have been evaluated for time-dependent light scattering in the next section. Thus a unified theory is obtained for time-dependent light scattering of an uncertainty-limited pulse from far off-resonance into the resonance region. The theory reduces to the conventional Kramers-Heisenberg second-order results if a monochromatic light source is used. The two-photon states' contribution to the scattering cross section has the same time dependence as the light source while the zero-photon state has the time-dependence previously calculated for near-resonance light scattering.

In the next section excitation profiles for Rayleigh and Raman cross sections have been calculated using the formalism of the previous section for an actual diatomic molecule from over 8000 cm^{-1} off resonance into the resonance region. Several interference effects are discussed. The usual formula for the scattering cross sections is shown to lead to errors off resonance if the basis set is truncated.

Finally, a new method of calculating the zero-order density function directly from the absorption spectrum has been found and applied to the origin region of naphthalene's second excited singlet state. Results are in good agreement with previous trial-and-error methods.

Mathematical appendices are given which derive the key formulae needed in the second part of this thesis.

TABLE OF CONTENTS

PART I The Radiationless Relaxation of High-Energy States in the Radiation Chemistry of Condensed Phases

PART II Use of Green's Functions to Study Radiationless Transitions, Light Scattering and Fluorescence in Model Systems

PROPOSITIONS

PART I

THE RADIATIONLESS RELAXATION OF HIGH-ENERGY STATES IN THE RADIATION CHEMISTRY OF CONDENSED PHASES

INTRODUCTION

In radiation chemistry a high-energy particle or photon is shot into the system. A high-energy photon loses most of its energy to the electrons in the system by the photoelectric effect or by Compton scattering.[1,2] The photoelectric effect dominates for photon energies below about 20 keV; Compton scattering dominates above 40 keV.[2] The main effect of these two processes is to produce high-energy electrons. Thus in studying radiation chemistry one can limit oneself to the discussion of the interaction of high-energy particles with matter. These particles lose energy mainly to the electrons in the medium creating ionizations and electronic excitations.[1,2] In condensed systems these excited states cannot, in general, be considered states of single, isolated molecules, due to the overlap (non-orthogonality) of the wavefunctions of neighboring molecules. In general, the higher the energy of the excitation, the larger the spatial extent of the excited electron's wavefunction and thus the larger the overlap of its wavefunctions with that of neighboring molecules. A large proportion of energy losses fall in the 10-30 eV[3,4] range and for this range non-localized states will, at least initially, play a very important role.[3,5]

The excited electronic states that are important in the radiation chemistry of condensed systems are plasmons, excitons and ionizations (conduction band states).[6-8] Plasmons are collective longitudinal density excitations of free electrons. These excitations have been extensively studied in metals,[9] where they are well-defined, relatively long-lived and easily excited by high-energy charged particles. In insulators the concept of a plasmon is not well-defined since the electrons cannot behave as if they were free as they can in metals. Although peaks around 20 eV in the energy loss spectra of high-energy electrons passing through thin films of insulators have often been assigned as plasmons,[8,10-12] they are more likely to be oscillations of single electrons having frequencies different from that of the isolated molecule due to the interactions between molecules.[13,14] Even if the peaks in the energy loss spectra were plasmons, their widths are several eV's wide implying that the lifetime of these states is on the order of 10^{-15} to 10^{-16} seconds. They would decay into single particle excitations--excitons and conduction band states--in this period of time.[6,8] Thus we can consider the states initially formed in the radiation chemistry of condensed materials to be excitons and conduction band states.

Excitons are electron-hole pairs which migrate through a crystal with well-defined momenta (due to the periodicity of the crystal). The two extreme types are Frenkel excitons where the hole and electron are always on the same site and Wannier excitons where the electron is in a large-radius orbit around the hole and feels the hole's Coulomb attraction modified by the dielectric constant of the medium.[15] Naturally, intermediate states between these two limits also exist--for instance, ion-pair states. In organic molecular crystals and rare gas crystals the lowest excited states are in the Frenkel limit while the higher ones are of the intermediate kind or even in the Wannier limit.[15,16] This is due to the larger spread of higher energy wavefunctions and their non-orthogonality.

An important problem in the radiation chemistry of condensed materials is how these initially formed conduction band and exciton states having energies in the 10 eV to 30 eV range electronically relax. The time scale of interest is 10^{-14}–10^{-16} seconds, before the nuclei have time to respond to the changing fields since vibrational times are on the order of 10^{-13}–10^{-14} seconds.[3] It has been suggested[6,7,17] that an exciton fission process should be an important electronic relaxation process. Voltz[6] and Klein and Voltz[7] considered the fission of a high-energy Frenkel exciton to form two Frenkel excitons on neighboring sites. However, as discussed above, a Frenkel exciton is only one possibility for the initial state.

The relaxation of a conduction band state and of a general exciton state will be discussed in sections A and B respectively. In both cases an energy fission process was found which yielded a Frenkel exciton and a conduction band state in the former case and a Frenkel exciton and a general exciton of the same type as the initial exciton in the latter case. These relaxation processes should be important in the pre-chemical stage of the radiation chemistry of condensed materials and show that the energy can relax very efficiently on this time scale.

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Section A

AN APPROACH TO THE UNDERSTANDING OF RADIATION CHEMISTRY IN THE CONDENSED PHASE*

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*Chemical Physics Letters 34, 211 (1975).

†Contribution No. 5069.

Radiationless transition theory[1,2] has been applied successfully to various aspects of ordinary photochemistry, which usually involves the lowest lying excited electronic states of a system. Little effort, however, has been made so far to apply these concepts to higher electronic states--those which are inevitably involved in radiation chemistry and radiation biology from ionizing radiation.

Because of the possibility of the existence of rather extensive energy relaxation in a condensed phase, as compared with the gaseous phase, one might guess that lower energy, more specific processes would tend to dominate the former and make it simpler to interpret.[†]

[†] This seemingly antithetical idea is analogous to that which applies to the transfer of low-energy electronic excitation. In a crystalline solid, particularly at very low temperatures, molecules have more uniform environments than in the gas phase, and energy relaxation tends to follow a better defined path, leading to fewer quantum states involved in the initial processes. To some extent this could also be true for certain types of mixed crystals. Experimental data seem to support this idea.[3] For example, in the X-irradiation of mixed crystals of various rare gases at 4.2° K diluted with a small amount of molecular N_2, transfer of excitation from the rare gas to the N_2 appears to occur from the lowest exciton band of the rare gas since only in neon is the band-energy sufficiently high to excite the $C^3\Pi_u$ state of N_2 at ~ 11 eV. The other process that leads to N_2 light emission in this system occurs in all the rare gases and is also

In addition, because radiation biology is a condensed phase problem, it seems not only more reasonable but also more important to direct attention to solid state radiation chemistry in searching for a better understanding of this seemingly complex phenomenon.

In this communication we will suggest a scheme for relaxation and localization of energy in solid state radiation chemistry. The concepts may also be applied to the liquid state. Our model is physically a simple one and is relevant to the pre-chemical relaxation stage* of radiation chemistry, taking place roughly in the time domain 10^{-16} - 10^{-12} sec. It is conceivable that an understanding of this realm could allow some external control over the chemical pathways taken by the system in radiation chemistry or radiation biology experiments. Thus our preliminary results seem worth reporting at this time.

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interesting from a radiation chemistry point of view. This process excites only $\upsilon \leq 6$ quanta of vibration in the $A^3\Sigma_u^+$ state of N_2. Since no higher quanta can be observed, it is implied that the energy transfer process occurs cleanly from the $\upsilon = 0$ vibrational level of the $B^3\Pi_g$ state, which is approximately isoenergetic with $\upsilon = 6$ of $A^3\Sigma_u^+$. Thus, even though the complexity of states in this mixed crystal system defies enumeration, the energy relaxation paths appear simple and well defined.

*We would prefer to call this the "physicochemical" stage, but that term has been used for the time interval 10^{-13} - 10^{-10} sec[4] where chemistry is already taking place.

Even though the high energies of the exciting particles used in radiation chemistry are mind-boggling to the photochemist, a simplifying feature is the fact that most of the energy loss occurs near a few relatively low-energy ($\lesssim$ 40 eV) "resonances" in the energy spectrum.[5-9] For systems containing only first-row elements and hydrogen, these resonances must arise through promotion of electrons having 2s and 2p parentage. Molecular ionization limits in gaseous molecules become the conduction bands (CB's) of the condensed phase. Because of the dielectric constant of the medium, these CB's may lie at very low energies, perhaps as low as half the ionization potential of the free molecule.[10] Other gross changes occur in the condensed phase. For instance, most Rydberg states of the gas are thought[10,11] to be embedded in and strongly mixed with the CB's of the solid, losing their identity except in rare cases where the lowest energy ones appear as Wannier exciton states[12] of the solid. However, excited valence states of molecules are better able to retain their identity in the condensed phase and often appear as sharp, localized, relatively long-lived Frenkel exciton states[13] of the solid.

Energy loss resulting from the passage of high energy ($\gtrsim$ 500 eV) primary and secondary particles through the medium may excite any of the states in the condensed phase, but experimental data[5-9] show that most of the loss occurs at energies above that of the first CB. The generation of charge carriers in the solid is most probably not a "one-step" process, but rather more like an autoionization where the original excitation is relatively localized but mixes very strongly with wavefunctions on neighboring sites.[10]

The most intense energy loss peak for condensed systems of first-row atoms (plus hydrogen) occurs around 20 eV[5-9] and has been attributed by some workers[5,8,14] to the plasma frequency of collective electron oscillations. We do not concur with this description for systems that are basically insulators,* but would rather attribute this loss peak to ionization or to excitation of single electrons of relatively deep valence levels having substantially 2s + 2p parentage. For instance, both in ice[9] and liquid water[8] there is a broad energy loss peak centered at approximately 22 eV with no further maxima in the valence electron region at higher energy. Energy loss is proportional to $\epsilon_2(\epsilon_1^2 + \epsilon_2^2)^{-1}$, where ϵ_1 and ϵ_2 are the real and imaginary parts, respectively, of the dielectric constant function $\epsilon(\omega)$.[15-17] The condition for the existence of a plasmon is that ϵ_1 and ϵ_2 be very

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*R. L. Platzman's comments following the paper by W. Brandt and R. H. Ritchie (Ref. 14) are relevant to this point: "Metals are very different from the systems we are interested in here. I do not believe there is good evidence for collective oscillations in many of the systems we are concerned with... No, I do not [think that the peak found in liquid water is caused by collective oscillations]. I think that your single oscillator model is too simple and is very misleading for these systems. I just picture what is found as the typical oscillation of single electrons in a Coulomb field with an effective charge somewhat greater than one so the loss will be 20 to 25 eV."

small.[18] The 22 eV[8] peak has been assigned to a plasmon for liquid water but not for ice, owing to differences of opinion[8, 9] as to whether ϵ_1 and ϵ_2 are sufficiently small in the region of the peak. For liquid water there is a peak in the absorption cross section $\sigma(\omega) \propto \omega[-\epsilon_1 + \sqrt{\epsilon_1^2 + \epsilon_2^2}]^{\frac{1}{2}}$ near 20 eV.[8] Similar results would be expected for ice due to the similarity in the plots of ϵ_1 and ϵ_2 as a function of ω for ice and water.[8, 9] If the loss peak were assigned as a plasmon for water, then $\sigma(\omega)$ would have a minimum near 20 eV rather than the maximum that is observed. Thus the plasmon idea seems unnecessary for water and probably for most other insulating systems as well.[†]

Even though ionic states may be responsible for the major energy loss peak in low molecular weight solids, it is known that they play only a partial role in radiation chemistry. The low-lying excited electronic states of the system also substantially contribute to the chemistry,[20, 21] in fact of the same order of importance as the ionic ones. Clearly there must be relaxation mechanisms that create these excited states from the initially formed states. More important, the relaxation process must be fast in order to compete efficiently with the chemistry from initially formed ionized states. Experimental evidence[22] suggests that this latter process can be extremely fast

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[†] Even if the original state were a plasmon, it would decay in 10^{-15} to 10^{-16} seconds into single particle states having the same energy.[19] These latter states are the ones we will consider in this paper.

($< 10^{-11}$ sec). It would be unreasonable to expect a pure electron-phonon mechanism to be able to explain such a fast relaxation.*

A better model for relaxation between the conduction band and the low-lying excited states of a condensed medium is an energy fission process[19,23] analogous to exciton fission in organic crystals,[24,25] but different from it because here we are dealing with CB states of the system with energies quite a bit higher than those energies.

As we mentioned above, the initial state to consider has an excited ion, that is, one having a hole in a relatively deep orbital, and an excited electron in the CB. This excited ion can relax to give some of its energy to another electron, forming either another hole and a CB electron, a charge transfer state or an excited molecule (exciton). The most general way of writing this process is

$$A^{+*}BCD \rightarrow AB^{+}C^{+}D^{-} , \tag{1}$$

where A, B, C, and D schematically stand for sites and any of the final species may be in an excited state, the asterisk standing for a state of higher excitation. However, our calculations, which will be outlined below, show that the most likely process involves only two sites,

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*For a CB at 20 eV and an excited state at 6 eV, 14 eV must be converted into lattice energy. The process then corresponds to well over 1000 phonons and, assuming 10^{-12} sec per relaxation step, would take longer than 10^{-9} sec to complete.

$$A^{+*}B \rightarrow A^{+}B^{*} . \qquad (2)$$

Figure 1 gives an example of process (2). If the system is solid water, the 22 eV energy loss corresponds to ionization of an electron from the deep valence level $2a_1 \equiv \varphi_0$ at site A producing a hole in φ_0 and an excited electron in φ_{CB} (Fig. 1b). The final state produced by the "fission" process must conserve energy. One possibility (Fig. 1c) promotes the hole from φ_0 to φ_1 ($\equiv 1b_2$) at site A while simultaneously promoting an electron from φ_3 ($\equiv 1b_1$) to φ_4 ($\equiv 4a_1$) at site B. Processes (1) and (2) are intended to be schematic; in a crystal the eigenfunctions must satisfy Bloch's theorem[26] and thus are linear combinations of the states given above. Even if the energy were not exactly conserved in the purely electronic process, creation of a small number of phonons or vibrons could complete the energy conservation process.

The part of the Hamiltonian that connects these orbital configurations is the electron-electron interaction term $\frac{1}{2}\sum_{i,j}' \frac{e^2}{|\underset{\sim}{r}_i - \underset{\sim}{r}_j|}$. Here i and j sum over all electrons and $i \neq j$. Assuming the orbitals to be real and orthonormal and neglecting spin and Bloch's theorem,* the matrix element between the initial and final states for process (1) is

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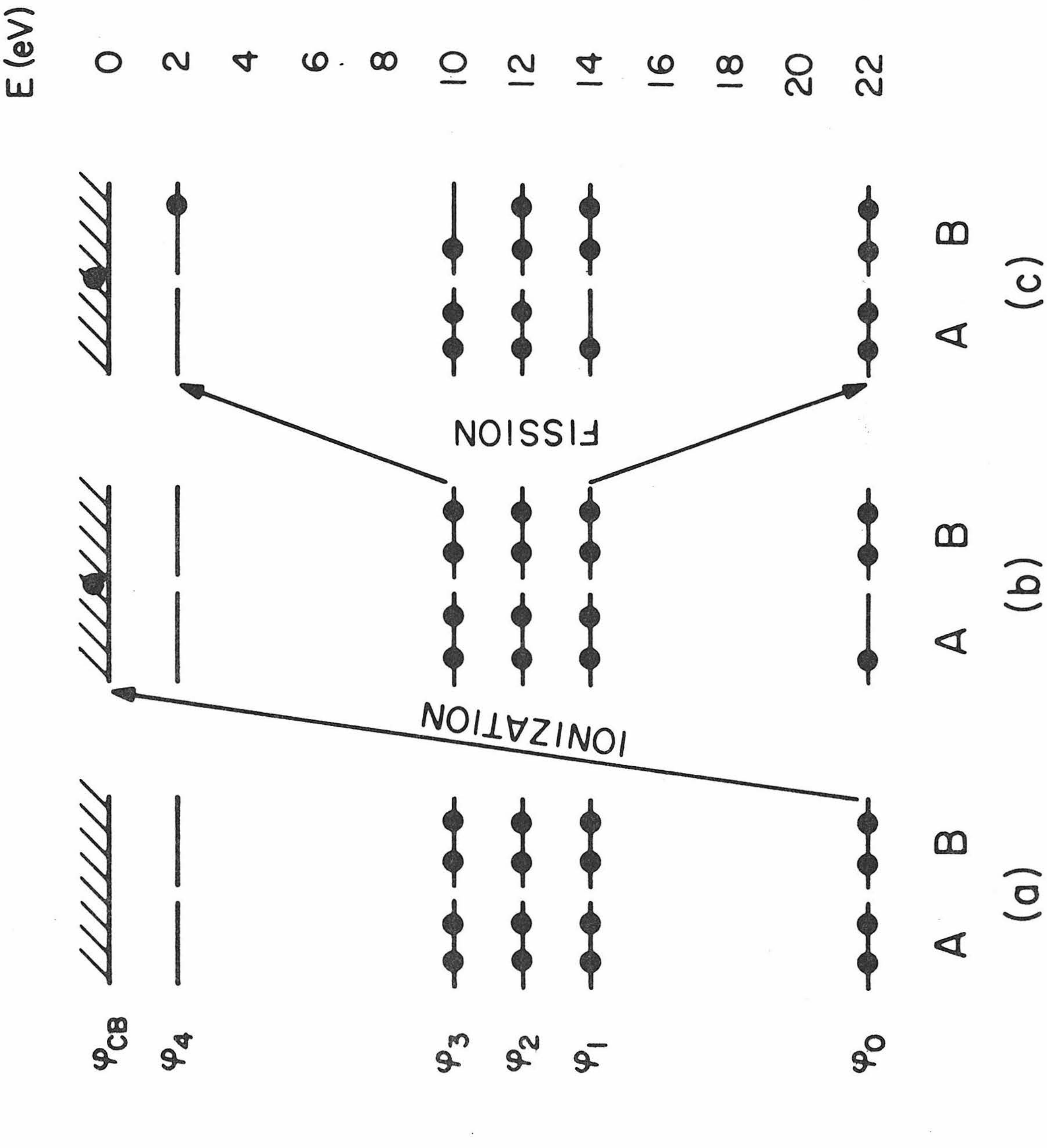
*To be more rigorous, since molecular orbitals on neighboring sites are not strictly orthogonal, Wannier functions[27] can be used. This has no qualitative effect on our arguments. Neither do the neglect of spin and translational symmetry.[28]

Figure 1. (a) Filled localized valence bands in the vicinity of sites A and B. (b) Arrow indicates creation of deep hole in the φ_0 orbital at A by the primary energy loss mechanism. (c) Spontaneous inter-valence-band Auger process, indicated by the two arrows, excites hole at site A to φ_1 at site A simultaneously creating tightly bound exciton at site B. This process is analogous to "exciton fission" in the organic solid state.


E (eV)
0
2
4
6
8
10
12
14
16
18
20
22
φ_{CB}
φ_4
φ_3
φ_2
φ_1
φ_0
A B
(a)
A B
(b)
A B
(c)
IONIZATION
FISSION

$$\langle \varphi_{0A}(\underset{\sim}{r}_1)\varphi_{4D}(\underset{\sim}{r}_2) \left| \frac{e^2}{|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|} \right| \varphi_{1B}(\underset{\sim}{r}_1)\varphi_{3C}(\underset{\sim}{r}_2)\rangle \; - \tag{3}$$

$$\langle \varphi_{0A}(\underset{\sim}{r}_1)\varphi_{4D}(\underset{\sim}{r}_2) \left| \frac{e^2}{|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|} \right| \varphi_{3C}(\underset{\sim}{r}_1)\varphi_{1B}(\underset{\sim}{r}_2)\rangle \; ,$$

where again A, B, C, D represent sites and φ_j ($j = 0, 1 \ldots$) have a similar meaning as in Fig. 1; the second term is an exchange term arising from antisymmetrization. For an insulator, the valence band orbitals, φ_{0A}, φ_{1B}, and φ_{3C}, are localized around their respective sites. The argument below will show that this matrix element will be largest when φ_{4D} is also localized and more particularly when it is localized around one of the sites that has a hole, thus forming an exciton or excited state rather than an ion and a CB electron.

The first matrix element in (3) represents the Coulomb interaction of the charge cloud $\varphi_{0A}\varphi_{1B}$ with the cloud $\varphi_{4D}\varphi_{3C}$. This term is very small unless the overlaps of φ_{0A} with φ_{1B} and of φ_{4D} with φ_{3C} are large. Now, due to the localization of the valence band orbitals, site A must be equal to site B and φ_{4D} must be reasonably well localized around site C. Thus the process that is most likely to occur is (2), and the system is left with a shallow hole at the original site and an exciton state (or localized excited state) at another site, as in Fig. 1. (For the exchange term to be large it would be necessary to interchange the holes in the final state.)

The energy of the first excited state in water is around 8 eV,[29] but the other energies in Fig. 1 are not known and are thus only approximate. The ionization potentials of the valence orbitals in water vapor are 36 eV ($2a_1$), 18 eV ($1b_2$), 15 eV ($3a_1$), and 13 eV ($1b_1$).[30] X-ray photoelectron spectroscopy data (XPS) of ice[30] indicate that the $2a_1$ ionization limit moves down to about 27 eV and that the other limits also move down, but how far seems uncertain because there are several possibly extraneous peaks in the valence electron region below 18 eV. Also, one must know the work function for ice to determine the CB energy levels. However, XPS might be an unreliable way of measuring ionization energies of the bulk material anyway because it samples only the surface regions.

The ionized electron will be left in the CB. It could, in a separate interaction, pair with the hole to form a charge-transfer complex or a more weakly bound exciton, the remaining energy going to phonons.[31] These processes are much more likely to happen in a non-polar solid where the electron-hole interaction is stronger, while the inverse processes may be expected to occur in ionic or highly polar solids leading to qualitatively different excitations.

The relaxation process described in this paper is applicable to any molecular solid or liquid. It requires only the conservation of energy and a localized final state. If the final state ion does not have sufficient energy to repeat the process (as in Fig. 1) then the net result is one ion and one excited state giving a possible explanation for the nearly equal distribution of chemistry between ions and excitations in some systems.

The above process whereby an excited ion goes to an ion having a lower degree of excitation plus an additional neutral excited state should be very rapid, requiring as it does only a purely electronic relaxation process together with at most a low-order phonon process for detailed energy conservation. Due to the form of the matrix element, the exciton or excited state will most likely form near the original ion. Equation (3) also predicts that the excited state formed by the relaxation process will be the one that carries the most oscillator strength, not necessarily the lowest excited state. This is easily seen by expanding the matrix element of $e^2 (|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|)^{-1}$ in multipoles and retaining the leading dipole term,

$$\frac{1}{|A - B|^3} \langle \varphi_{0A} | e \underset{\sim}{r} | \varphi_{1A} \rangle \langle \varphi_{4B} | e \underset{\sim}{r} | \varphi_{3B} \rangle ,$$

where A - B stands for the distance between the sites A and B. These higher lying states, with greater oscillator strength, may perform different chemistry than the lowest excited state. Thus ultraviolet excitation into lower excited states may produce different products than ionizing radiation excitation, even if one neglects the products formed from ionic states.

Throughout this paper we have assumed that the initial state is an ionic one. However, the general relaxation process discussed is applicable also if the initial state is an exciton having a hole in a deep valence level.[28] Naturally in this case neither the initial nor the final state is ionic.

In summary then, the mechanism by which an initial formed $\sim$20 eV ionic state of a solid splits by a purely electronic mechanism into a lower energy ionic state plus a localized excited state can explain not only the rapidity of the energy relaxation process in radiation chemistry but also the proportionation of the energy into partly ionic and partly excited states.

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Section B

THE RELAXATION OF A HIGH ENERGY EXCITON

In the last section, the relaxation of a conduction band (CB) state was considered. The key steps in the determination of the states into which the CB state would decay were shown. In this section a more detailed calculation for the relaxation of a high-energy exciton will be given. The model that will be used is that of a perfect crystal having one molecule per unit cell with each molecule contributing a pair of electrons to each filled band. All wavefunctions for this model must satisfy Bloch's theorem[1] for a periodic lattice with periodic boundary conditions.

Two basic approximations will be made. The first is the static lattice approximation which says that the electrons move in the potential given by the equilibrium position of the nuclei. This approximation is certainly valid for the time scale of interest--10^{-14}-10^{-16} seconds (see Part I, Introduction)--during which the nuclei do not move. The other approximation is the one electron approximation which states that the wavefunction for the electrons can be written as

$$\psi(\underset{\sim}{r}) = \mathcal{A}\,\psi_1(\underset{\sim}{r}_1)\,\psi_2(\underset{\sim}{r}_2)\cdots\psi_N(\underset{\sim}{r}_N) \qquad (1)$$

where $\mathcal{A}$ is the antisymmetrizer, the ψ_i's are spin orbitals for one electron and $\underset{\sim}{r}_i$ represents the spatial and spin coordinates for the ith electron. To say that eq. (1) is valid is equivalent to stating that the total potential is the sum of one-electron potentials, where somehow these one-electron potentials take into account self-consistently the potential due to all the other electrons as well as the nuclei. This approximation is obviously poorer for the valence electrons than for the core electrons since it omits the instantaneous correlations due to the other electrons which is most important for the valence or outer electrons. Thus, in reality, wavefunctions of the form (1) will not be exact solutions of the Schrödinger equation, but will be coupled together by electron-electron interaction terms.

The one-electron wavefunctions that will be used in this section are Wannier functions $a_{n\mathbf{R}}(\mathbf{r}_i)$, where n is a band index and $\mathbf{R}$ represents the position of a molecular site. These functions are defined by[2,3]

$$a_{n\mathbf{R}}(\mathbf{r}_i) = N^{-\frac{1}{2}} \sum_{\mathbf{k}} e^{-i\mathbf{k}\cdot\mathbf{R}} \psi_{\mathbf{k}n}(\mathbf{r}_i) \qquad (2)$$

where N is the number of cells in the periodic parallelpiped, $\mathbf{k}$ is a reciprocal lattice vector and the $\psi_{\mathbf{k}n}(\mathbf{r}_i)$'s are Bloch functions for the nth band which are eigenfunctions of the one-electron Hamiltonian (kinetic energy plus one electron self-consistent potential). The Wannier functions $a_{n\mathbf{R}}(\mathbf{r}_i)$ are localized around the molecule at $\mathbf{R}$,[3-7] ones centered on different sites $\mathbf{R}$ are orthogonal, and ones for different bands are also orthogonal.

The ground-state wavefunction can be represented by[2]

$$\psi(\mathbf{r}) = \mathcal{A}\, a^{\alpha}_{m'\mathbf{R}_1}(\mathbf{r}_1)\, a^{\beta}_{m'\mathbf{R}_1}(\mathbf{r}_2)\, a^{\alpha}_{m''\mathbf{R}_1}(\mathbf{r}_3) \cdots a^{\beta}_{M\mathbf{R}_1}(\mathbf{r}_{2M})\, a^{\alpha}_{m'\mathbf{R}_2}(\mathbf{r}_{2M+1}) \cdots$$

$$a^{\beta}_{M\mathbf{R}_2}(\mathbf{r}_{4M}) \cdots a^{\beta}_{M\mathbf{R}_N}(\mathbf{r}_{2NM}) \qquad (3)$$

where M represents the number of filled bands (each molecule is assumed to have 2M electrons) and α and β are the spin projections

$\frac{1}{2}$ and $-\frac{1}{2}$ respectively. $\psi(\underset{\wedge}{r})$ can be shown to satisfy Bloch's theorem with $\underset{\wedge}{k} = 0$.

The wavefunction for a general exciton can be written as[2, 3]

$$\psi^{\sigma\sigma'}_{mn\nu}(\underset{\wedge}{K}) = \sum_{\underset{\wedge}{B}} U_{mn\nu \underset{\wedge}{K}}(\underset{\wedge}{B})\ \Phi^{\sigma\sigma'}_{mn}(\underset{\wedge}{K}, \underset{\wedge}{B}) \tag{4}$$

where

$$\Phi^{\sigma\sigma'}_{mn}(\underset{\wedge}{K}, \underset{\wedge}{B}) = N^{-\frac{1}{2}} \sum_{\underset{\wedge}{R}} e^{i\underset{\wedge}{K}\cdot\underset{\wedge}{R}}\, \mathcal{A}\, a^{\alpha}_{m\underset{\wedge}{R}_1} \cdots a^{\sigma}_{m\underset{\wedge}{R}}\, a^{\sigma'}_{n\underset{\wedge}{R}+\underset{\wedge}{B}} \cdots a^{\beta}_{m\underset{\wedge}{R}_N} \tag{5}$$

where an electron from $a_{m\underset{\wedge}{R}}$ with spin $-\sigma$ has been placed in $a_{n\underset{\wedge}{R}+\underset{\wedge}{B}}$ with spin σ', $\underset{\wedge}{B}$ represents the electron-hole separation, $\underset{\wedge}{K}$ is the wavevector of the excitation, and ν is some new quantum number. For Wannier excitons $U_{mn\nu\underset{\wedge}{K}}(\underset{\wedge}{B})$ is a hydrogenic-like wavefunction;[2, 3] for Frenkel excitons $U_{mn\nu\underset{\wedge}{K}}(\underset{\wedge}{B})$ is zero for $\underset{\wedge}{B} \neq 0$.[2] Both kinds of excitons, as well as intermediate ones, can be excited by high-energy electrons.[8, 9] $\psi^{\sigma\sigma'}_{mn\nu}(\underset{\wedge}{K})$ satisfies Bloch's theorem, has a wavevector $\underset{\wedge}{K}$, and is assumed to be an eigenfunction of the total Hamiltonian. In reality, these wavefunctions never are eigenfunctions of the total Hamiltonian since only two bands m and n have been included and because $U_{mn\nu\underset{\wedge}{K}}(\underset{\wedge}{B})$ is generally calculated by omitting several terms from the total Hamiltonian.[2]

The final states of interest to us in considering the relaxation of a high-energy exciton are double excitation states having two holes and two excited electrons. A state of this form that satisfies Bloch's theorem is

$$\psi^{\omega\omega'\eta\eta'}_{m'n'm''n''}(\underset{\sim}{R}_0,\underset{\sim}{\gamma},\underset{\sim}{\gamma}',\underset{\sim}{K}) = N^{-\frac{1}{2}}\sum_{\underset{\sim}{T}} e^{i\underset{\sim}{K}\cdot\underset{\sim}{T}}\mathcal{A}\, a^{\alpha}_{m\underset{\sim}{R}_1}\, a^{\beta}_{m\underset{\sim}{R}_1}\cdots a^{\omega}_{m'\underset{\sim}{T}}\, a^{\omega'}_{n'\underset{\sim}{T}+\underset{\sim}{\gamma}} \cdots a^{\eta}_{m''\underset{\sim}{T}+\underset{\sim}{R}_0}\, a^{\eta'}_{n''\underset{\sim}{T}+\underset{\sim}{\gamma}'}\cdots a^{\beta}_{m\underset{\sim}{R}_N} \tag{6}$$

where the holes are $\underset{\sim}{R}_0$ apart and the electrons are located $\underset{\sim}{\gamma}$ and $\underset{\sim}{\gamma}'$ from one of the holes, $\underset{\sim}{\gamma}-\underset{\sim}{R}_0$ and $\underset{\sim}{\gamma}'-\underset{\sim}{R}_0$ from the other hole, and $\underset{\sim}{\gamma}-\underset{\sim}{\gamma}'$ from each other. To get the eigenfunctions of the total Hamiltonian, one must take linear combinations of the wavefunctions given by Eq. (6) as follows:

$$\psi^{S,M_S}_{m'n'm''n''\nu'}(\underset{\sim}{K}) = \sum_{\underset{\sim}{\gamma},\underset{\sim}{\gamma}',\underset{\sim}{R}_0} G^{SM_S}_{m'n'm''n''\nu'}(\underset{\sim}{R}_0,\underset{\sim}{\gamma},\underset{\sim}{\gamma}',\underset{\sim}{K})\,\psi^{\omega\omega'\eta\eta'}_{m'n'm''n''}(\underset{\sim}{R}_0,\underset{\sim}{\gamma},\underset{\sim}{\gamma}',\underset{\sim}{K}) \tag{7}$$

where S is the total spin and M_S is the spin projection, both being functions of ω, ω', η and η'. No one has ever tried to diagonalize the Hamiltonian in order to solve for the G's in a general case. The case of two Frenkel excitons ($\underset{\sim}{\gamma} = \underset{\sim}{0}$ and $\underset{\sim}{\gamma}' = \underset{\sim}{R}_0$ or vice versa) has been treated.[10-13] Also the binding energy of two Wannier excitons to form a biexciton has also been extensively discussed in the literature but the form of Eq. (7) was restricted to a particular function having only a few parameters.[14-16]

What we wish to find out is into which two excitons (what form for G) a high-energy exciton of the form of Eq. (4) would fission with the highest probability. The part of the Hamiltonian which couples states of the form (7) with states of the form (4) is the electron-electron potential energy term $\sum_{i<j} e^2/r_{ij}$, where r_{ij} is the separation between the ith electron and the jth electron. Only states having the same $\underset{\frown}{K}$ will be coupled. One electron terms of the Hamiltonian cannot couple these states and still conserve energy. For simplicity, the initial state that will be considered here is a triplet exciton (S = 1) having $M_S = 1$, that is, having $\sigma = \sigma' = \alpha$ in Eq. (4). There are three possible final spin states having S = 1 and $M_S = 1$. One orthonormal set of spin states satisfying S = 1 and $M_S = 1$ is $\{2^{-\frac{1}{2}}\,\alpha\alpha(\alpha\beta - \beta\alpha),\ 2^{-\frac{1}{2}}(\alpha\beta - \beta\alpha)\alpha\alpha$, and $\frac{1}{2}(\alpha\alpha(\alpha\beta + \beta\alpha) - (\alpha\beta + \beta\alpha)\alpha\alpha)\}$. However, other linear combinations of these states can be found which are also orthonormal.

The matrix element of interest is

$$\langle \Psi^{S=1,M_S=1}_{m'n'm''n''\nu'}(\underset{\frown}{K}) \,|\, \sum_{i<j} \frac{e^2}{r_{ij}} \,|\, \psi^{\alpha\alpha}_{mn\nu}(\underset{\frown}{K})\rangle \quad . \tag{8}$$

This equals

$$\{N^{-1} \sum_{\underset{\frown}{T}} e^{-i\underset{\frown}{K}\cdot\underset{\frown}{T}} \sum_{\underset{\frown}{\gamma},\underset{\frown}{\gamma}',\underset{\frown}{R}_0} \sum_{\omega\omega'\eta\eta'}{}' \, G^{SM_S^*}_{m'n'm''n''\nu'}(\underset{\frown}{R}_0,\underset{\frown}{\gamma},\underset{\frown}{\gamma}',\underset{\frown}{K}) \sum_{\underset{\frown}{R}} e^{i\underset{\frown}{K}\cdot\underset{\frown}{R}}$$

$$\sum_{\underset{\frown}{B}} U_{mn\nu\underset{\frown}{K}}(\underset{\frown}{B})\} \int \mathcal{A}\, a^{*\alpha}_{m\underset{\frown}{R}_1} \cdots a^{*\omega}_{m'\underset{\frown}{T}}\; a^{*\omega'}_{n'\underset{\frown}{T}+\underset{\frown}{\gamma}} \cdots a^{*\eta}_{m''\underset{\frown}{T}+\underset{\frown}{R}_0}\; a^{*\eta'}_{n''\underset{\frown}{T}+\underset{\frown}{\gamma}'}$$

$$\cdots a^{*\beta}_{m\underset{\frown}{R}_N} \sum_{i<j} \frac{e^2}{r_{ij}} \;\mathcal{A}\, a^{\alpha}_{m\underset{\frown}{R}_1} \cdots a^{\alpha}_{m\underset{\frown}{R}}\; a^{\alpha}_{n\underset{\frown}{R}+\underset{\frown}{B}} \cdots a^{\beta}_{m\underset{\frown}{R}_N}\; d^3\underset{\frown}{r} \tag{9}$$

where $d^3\underset{\sim}{r}$ means integration over all the coordinates of all the electrons and the prime over the spin summation restricts the sum to states having $M_S = 1$ and $S = 1$. In order to conserve energy, one must change two electrons, as mentioned previously. Thus either $m \neq m'$ and $m \neq m''$ or $n \neq n'$ and $n \neq n''$. Using this and expanding Eq. (9) one gets

$$
\begin{aligned}
&A(\underset{\sim}{K})\{\langle a_{n'\underset{\sim}{T}+\underset{\sim}{\gamma}}\, a_{n''\underset{\sim}{T}+\underset{\sim}{\gamma}'} |g| a_{n\underset{\sim}{R}+\underset{\sim}{B}}\, a_{m''\underset{\sim}{T}+\underset{\sim}{R}_0}\rangle\, \delta_{mm'}\, \delta_{\underset{\sim}{R}\underset{\sim}{T}}\, \delta_{\omega\alpha}\, \delta_{\omega'\alpha}(\delta_{\eta\alpha}\delta_{\eta'\beta}-\delta_{\eta\beta}\delta_{\eta'\alpha})\\
&-\langle a_{n'\underset{\sim}{T}+\underset{\sim}{\gamma}}\, a_{n''\underset{\sim}{T}+\underset{\sim}{\gamma}'} |g| a_{m''\underset{\sim}{T}+\underset{\sim}{R}_0}\, a_{n\underset{\sim}{R}+\underset{\sim}{B}}\rangle\, \delta_{mn'}\, \delta_{\underset{\sim}{R}\underset{\sim}{T}}\, \delta_{\omega\alpha}\, \delta_{\eta'\alpha}(\delta_{\eta\alpha}\delta_{\omega'\beta}-\delta_{\eta\beta}\delta_{\omega'\alpha})\\
&+\langle a_{n'\underset{\sim}{T}+\underset{\sim}{\gamma}}\, a_{n''\underset{\sim}{T}+\underset{\sim}{\gamma}'} |g| a_{m'\underset{\sim}{T}}\, a_{n\underset{\sim}{R}+\underset{\sim}{B}}\rangle\, \delta_{mm''}\, \delta_{\underset{\sim}{R},\underset{\sim}{T}+\underset{\sim}{R}_0}\, \delta_{\eta\alpha}\, \delta_{\eta'\alpha}(\delta_{\omega\alpha}\delta_{\omega'\beta}-\delta_{\omega\beta}\delta_{\omega'\alpha})\\
&-\langle a_{n'\underset{\sim}{T}+\underset{\sim}{\gamma}}\, a_{n''\underset{\sim}{T}+\underset{\sim}{\gamma}'} |g| a_{n\underset{\sim}{R}+\underset{\sim}{B}}\, a_{m'\underset{\sim}{T}}\rangle\, \delta_{mm''}\, \delta_{\underset{\sim}{R},\underset{\sim}{T}+\underset{\sim}{R}_0}\, \delta_{\eta\alpha}\, \delta_{\omega'\alpha}(\delta_{\omega\alpha}\delta_{\eta'\beta}-\delta_{\omega\beta}\delta_{\eta'\alpha})\\
&+\langle a_{m\underset{\sim}{R}}\, a_{n''\underset{\sim}{T}+\underset{\sim}{\gamma}'} |g| a_{m'\underset{\sim}{T}}\, a_{m''\underset{\sim}{T}+\underset{\sim}{R}_0}\rangle\, \delta_{nn'}\, \delta_{\underset{\sim}{T}+\underset{\sim}{\gamma},\,\underset{\sim}{R}+\underset{\sim}{B}}\, \delta_{\omega'\alpha}\, \delta_{\omega\alpha}(\delta_{\eta\beta}\delta_{\eta'\alpha}-\delta_{\eta\alpha}\delta_{\eta'\beta})\\
&-\langle a_{m\underset{\sim}{R}}\, a_{n''\underset{\sim}{T}+\underset{\sim}{\gamma}'} |g| a_{m''\underset{\sim}{T}+\underset{\sim}{R}_0}\, a_{m'\underset{\sim}{T}}\rangle\, \delta_{nn'}\, \delta_{\underset{\sim}{T}+\underset{\sim}{\gamma},\,\underset{\sim}{R}+\underset{\sim}{B}}\, \delta_{\omega'\alpha}\, \delta_{\eta\alpha}(\delta_{\omega\beta}\delta_{\eta'\alpha}-\delta_{\omega\alpha}\delta_{\eta'\beta})\\
&+\langle a_{m\underset{\sim}{R}}\, a_{n'\underset{\sim}{T}+\underset{\sim}{\gamma}} |g| a_{m''\underset{\sim}{T}+\underset{\sim}{R}_0}\, a_{m'\underset{\sim}{T}}\rangle\, \delta_{nn''}\, \delta_{\underset{\sim}{T}+\underset{\sim}{\gamma}',\,\underset{\sim}{R}+\underset{\sim}{B}}\, \delta_{\eta'\alpha}\, \delta_{\eta\alpha}(\delta_{\omega\beta}\delta_{\omega'\alpha}-\delta_{\omega\alpha}\delta_{\omega'\beta})\\
&-\langle a_{m\underset{\sim}{R}}\, a_{n'\underset{\sim}{T}+\underset{\sim}{\gamma}} |g| a_{m'\underset{\sim}{T}}\, a_{m''\underset{\sim}{T}+\underset{\sim}{R}_0}\rangle\, \delta_{nn''}\, \delta_{\underset{\sim}{T}+\underset{\sim}{\gamma}',\,\underset{\sim}{R}+\underset{\sim}{B}}\, \delta_{\eta'\alpha}\, \delta_{\omega\alpha}(\delta_{\eta\beta}\delta_{\omega'\alpha}-\delta_{\eta\alpha}\delta_{\omega'\beta})\}
\end{aligned}
\tag{10}
$$

where $A(\underset{\sim}{K})$ is the expression in braces in Eq. (9) and $g = e^2/|\underset{\sim}{r}_1 - \underset{\sim}{r}_2|$.

Since Wannier functions are very localized ones,[3] some of the sums in Eq. (10) can be approximated by single terms. In particular since $\langle a_{JR}a_{KT}|g|a_{LU}a_{MV}\rangle$ represents the Coulomb interaction between $a^*_{JR}a_{LU}$ and $a^*_{KT}a_{MV}$, this term will be very small unless $R = U$ and $T = V$ (so that the charge clouds overlap). Thus

$$\langle a_{JR}a_{KT}|g|a_{LU}a_{MV}\rangle \approx \langle a_{JR}a_{KT}|g|a_{LR}a_{MT}\rangle\,\delta_{RU}\,\delta_{TV}\,. \qquad (11)$$

Using Eq. (11), Eq. (10) becomes

$$\begin{aligned}
&\sum_{\underset{\frown}{R}_0,\underset{\frown}{B}} G^{\alpha\alpha(\alpha\beta-\beta\alpha)*}_{mn'm''n''}(\underset{\frown}{R}_0,\underset{\frown}{B},\underset{\frown}{R}_0,\underset{\frown}{K})\,U_{mn\nu\underset{\frown}{K}}(\underset{\frown}{B})\langle a_{n'\underset{\frown}{B}}a_{n''\underset{\frown}{R}_0}|g|a_{n\underset{\frown}{B}}a_{m''\underset{\frown}{R}_0}\rangle\\
-&\sum_{\underset{\frown}{R}_0,\underset{\frown}{B}} G^{\alpha(\beta\alpha-\alpha\beta)\alpha*}_{mn'm''n''}(\underset{\frown}{R}_0,\underset{\frown}{R}_0,\underset{\frown}{B},\underset{\frown}{K})\,U_{mn\nu\underset{\frown}{K}}(\underset{\frown}{B})\langle a_{n'\underset{\frown}{R}_0}a_{n''\underset{\frown}{B}}|g|a_{m''\underset{\frown}{R}_0}a_{n\underset{\frown}{B}}\rangle\\
+&\sum_{\underset{\frown}{R}_0,\underset{\frown}{B}} e^{i\underset{\frown}{K}\cdot\underset{\frown}{R}_0}\,G^{(\alpha\beta-\beta\alpha)\alpha\alpha*}_{m'n'mn''}(\underset{\frown}{R}_0,\underset{\frown}{0},\underset{\frown}{R}_0+\underset{\frown}{B},\underset{\frown}{K})\,U_{mn\nu\underset{\frown}{K}}(\underset{\frown}{B})\langle a_{n'\underset{\frown}{0}}a_{n''\underset{\frown}{R}_0+\underset{\frown}{B}}|g|a_{m'\underset{\frown}{0}}a_{n\underset{\frown}{R}+\underset{\frown}{B}}\rangle\\
-&\sum_{\underset{\frown}{R}_0,\underset{\frown}{B}} e^{i\underset{\frown}{K}\cdot\underset{\frown}{R}_0}\,G^{\alpha\alpha\alpha\beta-\beta\alpha\alpha\alpha*}_{m'n'mn''}(\underset{\frown}{R}_0,\underset{\frown}{R}_0+\underset{\frown}{B},\underset{\frown}{0},\underset{\frown}{K})\,U_{mn\nu\underset{\frown}{K}}(\underset{\frown}{B})\langle a_{n'\underset{\frown}{R}_0+\underset{\frown}{B}}a_{n''\underset{\frown}{0}}|g|a_{n\underset{\frown}{R}_0+\underset{\frown}{B}}a_{m'\underset{\frown}{0}}\rangle\\
+&\sum_{\underset{\frown}{R}_0,\underset{\frown}{B}} G^{\alpha\alpha(\beta\alpha-\alpha\beta)*}_{m'nm''n''}(\underset{\frown}{R}_0,\underset{\frown}{B},\underset{\frown}{R}_0,\underset{\frown}{K})\,U_{mn\nu\underset{\frown}{K}}(\underset{\frown}{B})\langle a_{m\underset{\frown}{0}}a_{n''\underset{\frown}{R}_0}|g|a_{m'\underset{\frown}{0}}a_{m''\underset{\frown}{R}_0}\rangle\\
-&\sum_{\underset{\frown}{R}_0,\underset{\frown}{B}} e^{i\underset{\frown}{K}\cdot\underset{\frown}{R}_0}\,G^{\beta\alpha\alpha\alpha-\alpha\alpha\alpha\beta*}_{m'nm''n''}(\underset{\frown}{R}_0,\underset{\frown}{R}_0+\underset{\frown}{B},\underset{\frown}{0},\underset{\frown}{K})\,U_{mn\nu\underset{\frown}{K}}(\underset{\frown}{B})\langle a_{m\underset{\frown}{R}_0}a_{n''\underset{\frown}{0}}|g|a_{m''\underset{\frown}{R}_0}a_{m'\underset{\frown}{0}}\rangle\\
+&\sum_{\underset{\frown}{R}_0,\underset{\frown}{B}} e^{i\underset{\frown}{K}\cdot\underset{\frown}{R}_0}\,G^{(\beta\alpha-\alpha\beta)\alpha\alpha*}_{m'n'm''n}(\underset{\frown}{R}_0,\underset{\frown}{0},\underset{\frown}{R}_0+\underset{\frown}{B},\underset{\frown}{K})\,U_{mn\nu\underset{\frown}{K}}(\underset{\frown}{B})\langle a_{m\underset{\frown}{R}_0}a_{n'\underset{\frown}{0}}|g|a_{m''\underset{\frown}{R}_0}a_{m'\underset{\frown}{0}}\rangle\\
-&\sum_{\underset{\frown}{R}_0,\underset{\frown}{B}} G^{\alpha(\alpha\beta-\beta\alpha)\alpha*}_{m'n'm''n}(\underset{\frown}{R}_0,\underset{\frown}{R}_0,\underset{\frown}{B},\underset{\frown}{K})\,U_{mn\nu\underset{\frown}{K}}(\underset{\frown}{B})\langle a_{m\underset{\frown}{0}}a_{n'\underset{\frown}{R}_0}|g|a_{m'\underset{\frown}{0}}a_{m''\underset{\frown}{R}_0}\rangle
\end{aligned}$$

$$(12)$$

where $a_{m\underset{\frown}{0}}$, for instance, is the mth Wannier function at the site $\underset{\frown}{R} = \underset{\frown}{0}$ (the origin). Since the final wavefunction must be normalized, each term in Eq. (12) will have its greatest magnitude when the G's represent one "Frenkel-like" exciton (either $\underset{\wedge}{\gamma} = \underset{\wedge}{0}$, $\underset{\wedge}{\gamma}' = \underset{\wedge}{0}$, $\underset{\wedge}{\gamma} = \underset{\wedge}{R}_0$ or $\underset{\wedge}{\gamma}' = \underset{\wedge}{R}_0$) and a distribution for the other electron of roughly the same spatial extent as $U_{mn\nu\underset{\wedge}{K}}(\underset{\wedge}{B})$. This will maximize the terms because in this case the G's will not waste their amplitude in places that won't increase the values of the sums in Eq. (12). Thus the final state will have a "Frenkel-like" exciton and a general exciton of roughly the same spatial extent as the initial exciton. It would be an actual Frenkel exciton if the two excitations did not interact at all. Figure 1 in section A shows roughly what the process will look like if one of the last four terms dominates, that is, if the excited electron remains in the same orbital. The above equations demonstrate that the most efficient relaxation process for a general high-energy exciton in an insulator is to "fission" into a Frenkel exciton and an exciton of the same type as the initial one. Naturally energy must be conserved in this process. This final result rests almost entirely on the approximation given by Eq. (11). However, this approximation should be a very good one for any orthonormal set of functions which represent an insulator. It should be especially good for the holes, that is, for the charge clouds $a^*_{\ell R}\, a_{\ell' T}$ where ℓ and ℓ' equal m, m′ or m″.

In order to generalize this result to any insulating condensed material only a couple of changes would have to be made. (1) $\underset{\wedge}{K}$ would no longer be a valid wavevector so states of different $\underset{\wedge}{K}$ would have matrix elements connecting them. (2) Wannier functions could not be used but another set of localized orthonormal functions could be found by some kind of orthogonalization procedure (see for example Löwdin[17]). Thus the result obtained here does apply to any insulating condensed material and the conclusion that the most efficient relaxation process is an "exciton fission" or "energy fission" process leading to one localized excitation (in the Frenkel exciton sense) and one excitation which has roughly the same delocalization as the initial state is still valid.

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PART II

USE OF GREEN'S FUNCTIONS TO STUDY RADIATIONLESS TRANSITIONS, LIGHT SCATTERING AND FLUORESCENCE IN MODEL SYSTEMS

INTRODUCTION

A problem of major interest to spectroscopists within the last few years is the nature of resonance Raman and Rayleigh scattering and the difference between these scattering processes and fluorescence. This problem has arisen due to the change in experimental techniques of the last few years.

In a traditional off-resonance Raman scattering experiment, the experimentalist used to excite the system with a very narrow light source (mathematically a delta function in frequency). Then by observing the light coming out from the system at frequencies displaced from this original frequency, the experimentalist obtained information about the ground state of the molecule. No time information was obtained, however. On the other hand, in a traditional resonance fluorescence experiment a broad-banded light source that turned on and off very quickly (mathematically a delta function in time) was used to prepare the system in an excited state. Then by observing the fluorescence decay, the lifetime of the excited state was measured.

Now, however, with the advent of lasers that are relatively narrow in frequency (on the order of tens of wavenumbers or less) and <u>also</u> relatively narrow in time (as fast as 5 picoseconds), experiments can be done with excitation having a narrow frequency bandwidth and with time resolution as well. Also, by using pulsed tunable dye lasers, excitation over wide ranges in the visible and ultraviolet can be obtained.

In an experiment on I_2, Williams, Rousseau and Dworetsky[1] observed that when they excited exactly on resonance and looked at the time decay of the light displaced from their incoming light by a vibrational quantum of the ground state, they saw an exponential decay with a lifetime τ. This was exactly like previous fluorescence experiments. However, if they moved their exciting line slightly off resonance, they saw two different decay times--a fast one that looked like their light source and a slow one with the same lifetime τ. They did not, however, have a good explanation of their results.

To explain their results, a simple model of a primary state having all the oscillator strength and interacting with a continuum of states was used. The primary state represented the excited state of I_2 they were exciting and the continuum represented states having the molecule in any vibronic level of its ground electronic state and having a photon of any frequency present. The exciting light source was modelled as an uncertainty-limited pulse having width in both time and frequency. The solution of this problem using Green's functions is given in section A.

An extension of this work to include two vibronic levels of the excited electronic state is discussed in section B. Naturally, a model containing two primary states with oscillator strength was used.

However, a one-photon light source interacts with a molecule in its ground vibronic state to form not only the molecule in its excited state and no photons present but also the molecule in its excited state with two photons present. These so-called two-photon terms contribute to the Rayleigh and Raman cross sections, especially off-resonance. A model having many states with oscillator strength which do not interact with each other but do interact with the continuum of one-photon states was used in section C to discuss the contribution of these two-photon states. This same model was used to discuss excitation profiles for Rayleigh and Raman scattering from a diatomic molecule in section D.

The one-resonance model of section A can also be used to discuss radiationless transitions.[2] In this case the continuum states can be not only the states of the radiation field but can also be vibrational levels of other electronic states which carry no oscillator strength. If these latter states interact strongly with the primary state, then the peaks of the absorption spectrum in the neighborhood of the primary state will not occur at the positions of the zero-order states. A method was found, however, of extracting the positions of the zero-order states directly from the absorption spectrum. This method is given in section E and is shown to give good results for naphthalene.

The key formulae needed in this part of the thesis will be proven in the mathematical appendices.

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Section A

THEORY OF TIME-RESOLVED RESONANCE SCATTERING[*]

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[*] Chemical Physics Letters 29, 305 (1974).

[†] Contribution No. 4928

I. INTRODUCTION

Whole new classes of optical and spectroscopic experiments are being made possible with the development of narrow line tunable dye lasers,[1] and in the near future the availability of tunable "uncertainty-limited width" pulses is expected.[2] The latter will afford the experimentalist with the best combined frequency and temporal resolution consistent with the limitations imposed by the uncertainty principle. One question that naturally arises from these types of experiments concerns the temporal characteristics of excitation by a pulse as it is tuned through an atomic or molecular resonance. This question was specifically raised by Williams et al.[3] in a time-resolved scattering experiment on the I_2 molecule.

A theory to infinite order in perturbation theory describing the resonance or near resonance interaction of an excitation source of general shape with an atomic line of general shape has recently been developed. While the general problem requires numerical solution,[4] an analytical result is possible for uncertainty-limited excitation pulses which have Lorentzian frequency shapes providing the radiation field for spontaneous emission can be adequately approximated as a uniform continuum over the range of the resonance. This model is relevant to resonance or near resonance scattering and to absorption of white radiation followed by re-emission of light. We shall first outline a more general theory and then apply it to this special case. Afterwards, the case of two resonances will be considered, from which resonance Raman scattering formulas can be derived.

II. GENERAL SOLUTION FOR A SINGLE RESONANCE

The time evolution for $t \geq 0$ of a state φ_p prepared at $t = 0$ by a delta function pulse is

$$\theta(t) = U(t)\,\varphi_p, \tag{1}$$

where the time-evolution operator

$$U(t) = e^{-i\mathcal{H}t} \tag{2}$$

is expressed in terms of the exact hamiltonian,

$$\mathcal{H} = H_{atom} + H_{rad} + H_{int}, \tag{3}$$

for the atom interacting with the radiation continuum [ref. 5, ch. 3, section 13]. For a non-delta function pulse S(t) of intensity sufficiently weak that one may ignore the effects of stimulated emission and $n \neq 1$ photon transitions, the time-development of the state φ_p is

$$\psi(t) = \int_{-\infty}^{t} e^{-i\mathcal{H}(t-t')}\,S(t')\,\varphi_p\,dt'. \tag{4}$$

Note that $\psi(t)$ satisfies the time-dependent Schrödinger equation because the operators are retarded, giving no contribution beyond the observational time t. $S(t')$ can be thought of as an envelope of $\delta(t')$ pulses, each of which is supposed to prepare the state φ_p instantaneously. Though each pulse is infinitely broad in frequency space, interference among them gives rise to a pulse of finite bandwidth.

$\psi(t)$ is thus the coherent superposition of the decays of the prepared state at times t' over the range $-\infty \leqslant t' \leqslant t$. Eq. (4) is thus the generalization of eq. (1) for non-delta function excitation pulses. $S(t')$ has the transform

$$S(t') = (2\pi)^{-1} \int_{-\infty}^{+\infty} e^{-i\lambda t'} S(\lambda)\, d\lambda\,, \tag{5}$$

where $S(\lambda)$ describes the frequency shape of the excitation pulse.

From Cauchy's theorem,

$$\psi(t) = (2\pi i)^{-1} \int_{-\infty}^{t} dt'\, S(t') \oint \frac{e^{-i\lambda(t-t')} d\lambda}{\lambda - \mathcal{H}}\, \varphi_p \tag{6}$$

where the path of $\oint$ must enclose the poles of $\mathcal{H}$ (a branch cut along the real axis). A suitable contour runs from $+\infty$ to $-\infty$ just above the real axis and then into the lower half-plane around a semicircle of radius $R \to \infty$. The probability amplitude squared at time t is thus,

$$|\langle\varphi_p|\psi(t)\rangle|^2 = \left|\frac{i}{2\pi} \int_{-\infty}^{t} S(t')\, dt' \int_{-\infty}^{+\infty} d\lambda\, e^{-i\lambda(t-t')} G_{pp}(\lambda)\right|^2, \tag{7}$$

where $G = (\lambda - \mathcal{H})^{-1}$.

In the physically artificial, but illuminating, case[6] where there is but a single resonance, that is, where the state φ_p carries all the oscillator strength,

$$G_{pp}(\lambda) = [\lambda - \lambda_0 - \Gamma(\lambda)]^{-1} \tag{8}$$

with

$$\Gamma(\lambda) = \int_{-\infty}^{+\infty} \frac{|V_{pk}|^2 \rho(\epsilon_k)\, d\epsilon_k}{\lambda - \epsilon_k} \tag{9}$$

where for the present problem V_{pk} is the matrix element of H_{int} between the zero-order atomic level with frequency λ_0 and a radiation continuum level at frequency ϵ_k ; $\rho(\epsilon_k)$ is the density of such continuum levels.

In the neighborhood of the resonance, it is a good approximation to consider $|V_{pk}|^2 \rho(\epsilon_k)$ constant. Denote this constant by $\pi^{-1}\gamma$, in which case $\mathrm{Im}\Gamma(\lambda) = -\gamma$, and the Cauchy principal value of eq. (9) gives $\mathrm{Re}\Gamma(\lambda) = 0$. Thus,

$$G_{pp}(\lambda) = [(\lambda - \lambda_0) - i\gamma]/[(\lambda - \lambda_0)^2 + \gamma^2]. \tag{10}$$

This Green function, as is well-known, leads to a Lorentzian-shaped absorption line, which has half-width γ at half-height, centered at $\lambda = \lambda_0$.

The simple Lorentzian lineshape problem is described here only because it leads to an analytical expression for the time dependence. If $|V_{pk}|^2 \rho(\epsilon_k)$ is nonuniform, even of arbitrary shape containing maxima and minima, a dispersion relation from eqs. (8) and (9) allows $G_{pp}(\lambda)$ to be obtained for the near resonance problem by numerical methods from the absorption spectrum,[4] which is proportional to $\mathrm{Im}G_{pp}(\lambda)$. In such cases, $\mathrm{Re}\Gamma(\lambda)$, a frequency-dependent "level-shift" term, is nonzero and plays an important role.[7] The limit of narrow, "shapeless" resonances often used in the physics literature[8,9] is avoided.

Continuing now with eq. (10) and letting the excitation pulse $S(\lambda)$ also be a Lorentzian $a^2/(a^2 + \lambda^2)$ in the frequency variable λ, for convenience centered at $\lambda = 0$ with half-width a at half-height, one has,

$$S(t') = \tfrac{1}{2} a\, e^{-|at'|} \tag{11}$$

a cusp function. The intensity of the excitation pulse is $|S(\lambda)|^2$, a Lorentzian squared. The shape of $S(\lambda)$, and thus $S(t')$, was chosen for several reasons: (1) it yields an analytic solution; (2) neither $S(\lambda)$ nor $S(t')$ have physically unreasonable discontinuities such as arise for instantaneous turn-ons; and (3) both $S(\lambda)$ and $S(t')$ have only one maximum, consistent with the way pulses generally look. A gaussian $S(\lambda)$ yields a gaussian $S(t')$ but does not lead to analytical expressions as in eqs. (12) below. A pulse $S(\lambda) = 1/(\lambda + ia)$ (which yields a Lorentzian in intensity) has a Fourier transform $S(t')$ which is zero for $t' < 0$ and $-ie^{-at'}$ for $t' \geqslant 0$ and thus does not satisfy criterion (2); while square pulses, even with finite rise and fall times, do not meet criterion (3). The cusp function $S(t')$ in eq. (11) does resemble the subpicosecond pulses recently developed.[2]

Using eqs. (10) and (11) in (7) and evaluating the elementary integrals yields,

$$|\langle\varphi_p|\psi(t)\rangle|^2 = \{4[(\gamma + a)^2 + \lambda_0^2]\}^{-1} a^2 e^{2at}, \quad t \leqslant 0\,; \tag{12a}$$

$$|\langle\varphi_p|\psi(t)\rangle|^2 = \{[(\gamma - a)^2 + \lambda_0^2][(\gamma + a)^2 + \lambda_0^2]\}^{-1}$$

$$\times\ a^2\{a^2 e^{-2\gamma t} + \tfrac{1}{4}[(\gamma + a)^2 + \lambda_0^2]e^{-2at}$$

$$-\ a\,e^{-(\lambda+a)t}[(\gamma + a)\cos\lambda_0 t - \lambda_0 \sin\lambda_0 t]\}, \quad t \geqslant 0. \qquad (12b)$$

Eqs. (12a) and (12b) give the probability that the state p is occupied at time t; the total intensity of light emitted or scattered at time t is proportional to this probability. It should be stressed that these results are for uncertainty-limited excitation pulses, where $S(\lambda)$ and $S(t')$ are Fourier transforms of one another; all the ramifications of the uncertainty principle are built in automatically. Both $|\langle\varphi_p|\psi(t)\rangle|^2$ and its first derivative with respect to time are continuous at $t = 0$, although eq. (11) has a cusp there.

It is important to note that the decay is dependent only upon the half-widths γ and a, and is independent of the frequency separation between the atomic resonance and the excitation pulse. The frequency separation λ_0 occurs in an oscillatory part of the time evolution. This result is not in agreement with the statements of Williams et al.,[3] "As the incident frequency is moved only slightly away from resonance, the lifetime (Δt) for the re-emission is expected to be limited by the frequency difference ($\Delta\omega$) between the excited state and the incident frequency, and should be given approximately by an uncertainty relationship, $\Delta t = 1/\Delta\omega$", and "As the laser frequency is tuned away from resonance with a discrete transition, both the re-emission intensity and lifetime must continuously decrease". Eq. (12b) shows that as λ_0 increases, the term decaying as e^{-2at} (light-source decay) increases in intensity relative to the other terms, but there is no change in the two exponents. Thus as the light source moves off resonance one must look in the low intensity portion of the overall decay curve in order to pick out the temporal component characteristic of the resonance. This can be confirmed by looking at the experimental results of Williams et al.,[3] although their resonance was Doppler broadened. This would tend to cause an incoherent superposition of the oscillatory decays and average them out.

When the exciting light is purely monochromatic, a → 0, $S(t')$ is infinitely broad, and the time evolution reaches a steady state having the Breit-Wigner[10] form,

$$|\langle\varphi_p|\psi(t)\rangle|^2 = \tfrac{1}{4}a^2(\gamma^2 + \lambda_0^2)^{-1} . \tag{13}$$

This is equivalent to Heitler's formula [ref. 5, pp. 201-203] for the intensity of "resonance fluorescence" excited by a sharp line. It is also of course the same as near-resonance "Rayleigh scattering" formulas. Off resonance, the theory describes the interaction of the imposed exciting light pulse with the "tail" of an atomic resonance. The resonance and its tail in this case arise from the natural width for spontaneous emission, i.e., an atom interacting with the radiation field as in eq. (3). There is no need to bring in "virtual state" language, since the tail of the resonance corresponds to actual states of $\mathcal{H}$.

In the opposing limit where excitation is by white light, $S(t')$ is a single delta function, a → ∞, and eq. (12b) tends towards exponential decay proportional to $e^{-2\gamma t}$. This is the limit of absorption and reemission by the atomic system. It is important to note that to effect absorption and re-emission from an atomic state, one must excite the entire state, not just part of it. This requires broad-banded excitation. In this limit for a Lorentzian line, real and imaginary parts of G contribute equal exponentially decaying parts to the time evolution of the excited state. On the other hand, if the pulse used is narrow-banded, the process excites a mixture of the atomic state and radiation field states [Ref. 5, pp. 201-203]. Real and imaginary parts of G contribute unequally. The contribution from the real part is small in the vicinity of resonance but falls off less strongly than does the imaginary part as $(\lambda - \lambda_0)$ increases. Thus, narrow-line excitation, even for $(\lambda - \lambda_0)$ approaching zero, is physically different from absorption into and reemission from the atomic state. It perhaps is more properly called <u>scattering</u>, either of the resonance or nonresonance variety. However, if one wants to go to the trouble, it is perfectly possible for any type of excitation interacting with a Lorentzian resonance to extract out a component having equal contributions from real and imaginary G, which could be called the "absorptive part" of the process.

III. TWO RESONANCES

Exact Green function matrix elements are also known[11] for the case of two atomic levels interacting with the radiation continuum. With the level corresponding to φ_p placed at λ_0 and that corresponding to $\varphi_{p'}$ at λ_0',

$$G_{pp} = \frac{\lambda - \lambda_0' - \Gamma'}{(\lambda - \lambda_0 - \Gamma)(\lambda - \lambda_0' - \Gamma') - (V_{pp'} + \Delta')(V_{p'p} + \Delta)} \tag{14}$$

$$G_{p'p} = \frac{V_{p'p} + \Delta}{(\lambda - \lambda_0 - \Gamma)(\lambda - \lambda_0' - \Gamma') - (V_{pp'} + \Delta')(V_{p'p} + \Delta)} , \tag{15}$$

where Γ is as before and,

$$\Delta = \int \frac{V_{p'k} V_{kp} \rho(\epsilon_k)}{\lambda - \epsilon_k} d\epsilon_k . \tag{16}$$

Γ', Δ', $G_{p'p'}$, and $G_{pp'}$ can be obtained from the above by appropriately substituting p for p′, λ_0 for λ_0', and vice versa. If the uniform continuum approximation is again made, $|V_{pk}|^2 \rho(\epsilon_k) = \pi^{-1}\gamma$ and $|V_{p'k}|^2 = \pi^{-1}\gamma'$, then $\Gamma = -i\gamma$ and $\Gamma' = -i\gamma'$ in eqs. (14) and (15).

Now if one excites a state $\chi = (\varphi_p + f^{\frac{1}{2}} \varphi_{p'})/(1 + f)^{\frac{1}{2}}$ where f is the ratio of the squared matrix element of H_{int} between the ground state and $\varphi_{p'}$ divided by that of φ_p, then the time evolution of this state is given by eq. (6) with φ_p replaced by χ. Since G is retarded, the integral over $d\lambda$ in eq. (7) is zero if $t < t'$, and substitution of eq. (5) into eq. (6) then yields

$$\psi(t) = \frac{i}{2\pi} \int_{-\infty}^{+\infty} S(\lambda) e^{-i\lambda t} G(\lambda) \chi d\lambda . \tag{17}$$

To obtain the total scattering intensity in the time-independent regime, we suppose that $S(\lambda) = \delta(\lambda - \bar{\lambda})$, in which case

$$|\langle\chi|\psi(t)\rangle|^2 = [2\pi(1+f)]^{-2}\,|G_{pp}(\bar{\lambda}) + fG_{p'p'}(\bar{\lambda}) + f^{\frac{1}{2}}\,G_{pp'}(\bar{\lambda}) + f^{\frac{1}{2}}\,G_{p'p}(\bar{\lambda})|^2 \,. \tag{18}$$

Eq. (18) should be compared with the usual perturbation expression for Rayleigh and Raman scattering near a resonance.* If summations over multiple resonances and vibrational quantum numbers are not considered, the perturbation result can be obtained from eq. (18) by way of the following approximations: (1) neglect of $G_{p'p'}$; (2) neglect of $(V_{p'p} + \Delta)$ and $(V_{pp'} + \Delta')$ in the denominators of G_{pp}, $G_{p'p}$ and $G_{pp'}$; (3) neglect of Δ and Δ' in the numerators of $G_{p'p}$ and $G_{pp'}$; (4) setting $(\bar{\lambda} - \lambda_0' - \Gamma')$ equal to $(\lambda_0 - \lambda_0')$. Approximation (1) and the trivial approximation (4) are valid near the resonance $\bar{\lambda} \approx \lambda_0$. Approximation (3) is the neglect of indirect interaction of φ_p with $\varphi_{p'}$ through the radiation continuum in comparison with the direct interaction. Since natural linewidths are usually small compared with the magnitude of the direct (interelectronic or vibronic) coupling, approximation (3) is undoubtedly valid in most cases. Approximation (2), however, which neglects the effect of carrying the perturbation expansion to infinite order, is questionable when $\bar{\lambda} - \lambda_0$ is small compared with $V_{pp'}\,V_{p'p}/(\bar{\lambda} - \lambda_0')$. In fact, the neglected terms are dominant in the resonance region, but cause only a spectral shift.

To obtain the time dependence in the two-resonance problem for an "uncertainty-limited" excitation pulse of general shape, one may perform the integrations in eq. (7) or (17) numerically. This problem has not yet been investigated in detail.

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*See eqs. (15) in ref. 12.

ADDENDUM

After this paper was finished, a paper by Friedman and Hochstrasser was submitted for publication in Chemical Physics.[13] A major difference between the two papers is in the shape of the excitation pulse, but a number of minor differences exist as well. Both papers support the idea that the temporal behavior following the interaction of light sources with resonances depends crucially on the nature of the light source,* and furthermore that these results can be calculated quantitatively not only for limiting cases but for intermediate ones as well. It is these intermediate cases that may prove to be the most interesting. It should also be noted here that another paper entitled "Radiationless Transitions" by J. Jortner and S. Mukamel in preprint form was received by the authors more recently. A portion of this paper deals with similar subject matter as presented here and reaches similar conclusions. It is fair to say that there is apparently considerable activity in this area.

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*This idea was stressed in an early paper by Rhodes _et al._[14] See also a recent paper by Rhodes.[15]

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Section B

RAYLEIGH AND RAMAN SCATTERING FROM A TWO-LEVEL SYSTEM*

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*Condensed from a paper entitled "Lineshape-Lifetime Relationship and Emission and Scattering of Light by Polyatomic Molecules", Canadian Journal of Physics **53**, 2068 (1975). This paper was contribution no. 5081 from the Department of Chemistry, California Institute of Technology.

I. INTRODUCTION

In the usual theories of Raman and Rayleigh scattering,[1-4] the light source is considered to be a delta function in frequency. In a previous paper,[5] the interaction of a light source having widths in both time and frequency with a single resonance was discussed. In this paper the model will be extended to include two vibronic levels of an excited electronic state in order to be more realistic for near resonance Raman scattering.

II. MODEL AND FORMALISM

The total Hamiltonian of the system is

$$\mathcal{H} = H_0 + V \tag{1}$$

where H_0 contains the molecular Hamiltonian and the radiation field Hamiltonian and V contains the molecule-radiation field interaction. The model system used consisted of a ground (g) and a single excited electronic state (e) lying 20,000 cm^{-1} above the ground state. Each of these electronic states was given two vibrational levels $v = 0$ and $v = 1$ with vibrational spacing 1200 cm^{-1} and 1000 cm^{-1} for the ground and excited states respectively. The two vibrational levels of the upper state ($|p\rangle = |e\,0\rangle$ and $|p'\rangle = |e\,1\rangle$) were considered as discrete, and interactions between these two levels were neglected. The two vibrational levels of the ground state plus the radiation continuum were modeled as two continua ($|a\rangle + |b\rangle$) having zero-order energies $\epsilon_a = \epsilon_g + \hbar\omega$ and $\epsilon_b = \epsilon_g + \epsilon_{vg} + \hbar\omega$, respectively, where $\hbar\omega$ is a photon energy, ϵ_{vg} is the ground vibrational spacing and ϵ_g is the energy of the ground vibrational level of the g state. From now on ϵ_g will be set equal to zero; $V_{aa'}$, $V_{bb'}$, and V_{ab} were also neglected.

The light source excited $\chi = (|p\rangle + f^{\frac{1}{2}}|p'\rangle)\frac{1}{(1+f)^{\frac{1}{2}}}$ where $f^{\frac{1}{2}} = \frac{\langle g0|V|p'\rangle}{\langle g0|V|p\rangle}$ (this assumes that at $t = -\infty$ the molecule is in the ground state). Therefore the wavefunction of this system at time t is given by[5-8]

$$\psi(t) = \frac{i}{2\pi}\int_{-\infty}^{t} dt'\, S(t') \int_{-\infty}^{\infty} \frac{d\lambda\, e^{-i\lambda(t-t')}}{\lambda - \mathcal{H} + i\eta}\, \chi\,, \tag{2}$$

where the limit $\eta \to 0^+$ is taken after the integrations and $S(t')$ is the amplitude of an uncertainty-limited pulse at time t' whose frequency spectrum is $S(\omega)$, that is

$$S(t') = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} e^{-i\omega t'} S(\omega)\, d\omega\,. \tag{3}$$

To calculate the intensity of emitted/scattered light, one needs to know the probability that one ends up at $t = \infty$ in each $|a\rangle$ state and each $|b\rangle$ state. The total intensity $I(\omega)$ at a given photon frequency ω is proportional to

$$I(\omega) \propto \omega\rho(\omega)\{|\langle a|\psi(t=\infty)\rangle|^2 + |\langle b|\psi(t=\infty)\rangle|^2\} \tag{4}$$

where $\omega_a = \frac{\epsilon_a}{\hbar} = \omega$, $\omega_b = \frac{\epsilon_b}{\hbar} = \frac{\epsilon_{vg}}{\hbar} + \omega$ (same photon emitted) and $\rho(\omega)$ is the density of photon states at frequency ω. Now

$$|\langle a|\psi(t)\rangle|^2 = \left|\frac{i}{2\pi}\,\frac{1}{(1+f)^{\frac{1}{2}}}\int_{-\infty}^{t} dt'\,S(t')\int_{-\infty}^{\infty} d\lambda\, e^{-i\lambda(t-t')}\left(G_{ap}(\lambda)+f^{\frac{1}{2}}\,G_{ap'}(\lambda)\right)\right|^2 \tag{5}$$

from Eq. (2) where $G(\lambda) = (\lambda - \mathcal{H} + i\eta)^{-1}$. The matrix elements G_{ap} and $G_{ap'}$ can be easily calculated from Dyson's equation[9,10] to be

$$G_{ap}(\lambda) = \frac{V_{ap}}{(\lambda - \epsilon_a + i\eta)(\lambda - \epsilon_p + i\gamma)} \tag{6}$$

and similarly for $G_{ap'}(\lambda)$, where ϵ_p is the zero-order energy of the $|p\rangle$ state (20,000 cm^{-1}). The approximations made in Eq. (6) are the neglect of the coupling through the continuum of $|p\rangle$ to $|p'\rangle$ and the assumption that $|V_{ap}|^2\rho(\epsilon_a)$ and $|V_{bp}|^2\rho(\epsilon_b)$, where $\rho(\epsilon_a)$ is the density of "a" states at zero-order energy ϵ_a, are independent of ϵ_a and ϵ_b, respectively. This latter assumption leads to Lorentzian lineshapes for $|p\rangle$ and $|p'\rangle$.

If $S(\omega)$ is a Lorentzian[5]

$$S(\omega) = \frac{A^2}{A^2 + (\omega - \omega_0)^2} \tag{7}$$

with full width at half maximum of 2A and centered at $\omega = \omega_0$, then $S(t')$ from Eq. (3) becomes

$$S(t') = \left(\frac{\pi}{2}\right)^{\frac{1}{2}} A\, e^{-|At'|}\, e^{-i\omega_0 t'}, \tag{8}$$

a cusp function. This assumes that the pulse is transform-limited.

Now if one evaluates the integrals in Eq. (5) using Eqs. (6) and (8) following the method of Srivastava and Fontana,[10] one gets

$$|\langle \psi(t=\infty) \rangle|^2 = \frac{1}{1+f} \, \frac{2}{A^2+(\omega_i-\omega_0)^2} \left[1 + \frac{A^2-(\omega_i-\omega_0)^2}{A^2+(\omega_i-\omega_0)^2} \right]$$

$$\times \left\{ \frac{|V_{ip}|^2}{(\omega_i-\omega_p)^2+\gamma^2} + \frac{f|V_{ip'}|^2}{(\omega_i-\omega_{p'})^2+\gamma^2} + \frac{2f^{\frac{1}{2}} V_{ip} V_{ip'}[(\omega_i-\omega_p)(\omega_i-\omega_{p'})+\gamma^2]}{[(\omega_i-\omega_p)^2+\gamma^2][(\omega_i-\omega_{p'})^2+\gamma^2]} \right\} \tag{9}$$

where i is a or b and γ was set equal to γ' for convenience.

To calculate actual spectra from Eqs. (4) and (9), the usual dipole approximation for the matrix elements V_{ip} was used and the electronic transition dipole was assumed independent of vibrational coordinates. That is,

$$\langle g0|\mu|ej\rangle \approx \langle g|\mu|e\rangle\langle g0|ej\rangle, \tag{10}$$

where $\langle g0|ej\rangle$ is a Franck-Condon factor, and μ is the dipole moment operator. The following values for the Franck-Condon integrals were assumed,

$$\langle g0|e0\rangle = \frac{\sqrt{3}}{2} \qquad \langle g0|e1\rangle = -\tfrac{1}{2}$$

$$\langle g1|e0\rangle = \tfrac{1}{2} \qquad \langle g1|e1\rangle = +\frac{\sqrt{3}}{2}$$

such that the usual conditions of completeness and orthogonality

$$\sum_i \langle gj|ei\rangle\langle ei|gk\rangle = \delta_{jk} \tag{11}$$

are obeyed.

III. RESULTS

A representative spectrum calculated from Eq. (4) is shown in Fig. 1. The values of the parameters chosen for Fig. 1 are $A = 20\ \mathrm{cm}^{-1}$, $\gamma = 10\ \mathrm{cm}^{-1}$, and $\omega_0 = 15{,}000\ \mathrm{cm}^{-1}$. The ordinate is the relative intensity (since no value was assigned to $\langle g|\mu|e\rangle$). The dominant peak in Fig. 1 occurs at ω_0, the peak of the exciting light, and is thus what is normally called the Rayleigh peak. The second largest peak occurs at $\omega_0 - \epsilon_{vg}/\hbar$ and thus is the Raman peak. The four small peaks at higher energy correspond to the "off-resonance fluorescence" peaks. Energy conservation has not been violated because of the presence of the high-energy wing of the light source.

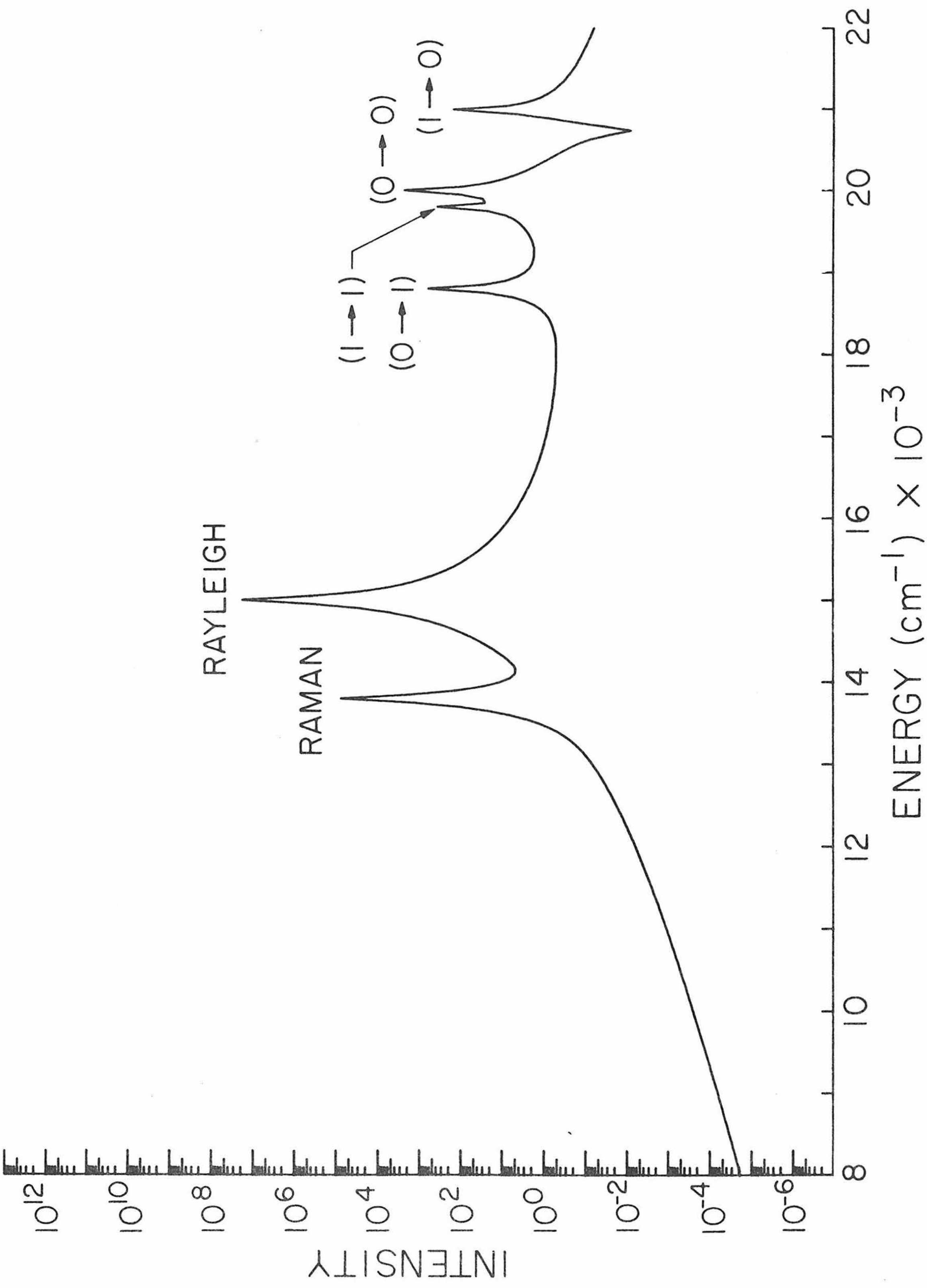
The relative heights of the "Rayleigh" vs. the "fluorescence" peaks are governed by the relative intensities of the wings of the light source and resonance. The widths and shapes of the Rayleigh and Raman peaks are almost exactly those of the light source (the wings of the resonances only distort them slightly). Similarly the fluorescence peaks have approximately the shapes of the resonances. On-resonance the shape of the emission peak is the product of the light source shape and the resonance shape.

IV. DISCUSSION

The right-hand side of Eq. (10) is the first term in a Herzberg-Teller expansion (see, for instance, Albrecht[1])

$$\mu(Q) = \mu_0 + \left(\frac{\partial \mu}{\partial Q}\right)_0 Q + \cdots \tag{12}$$

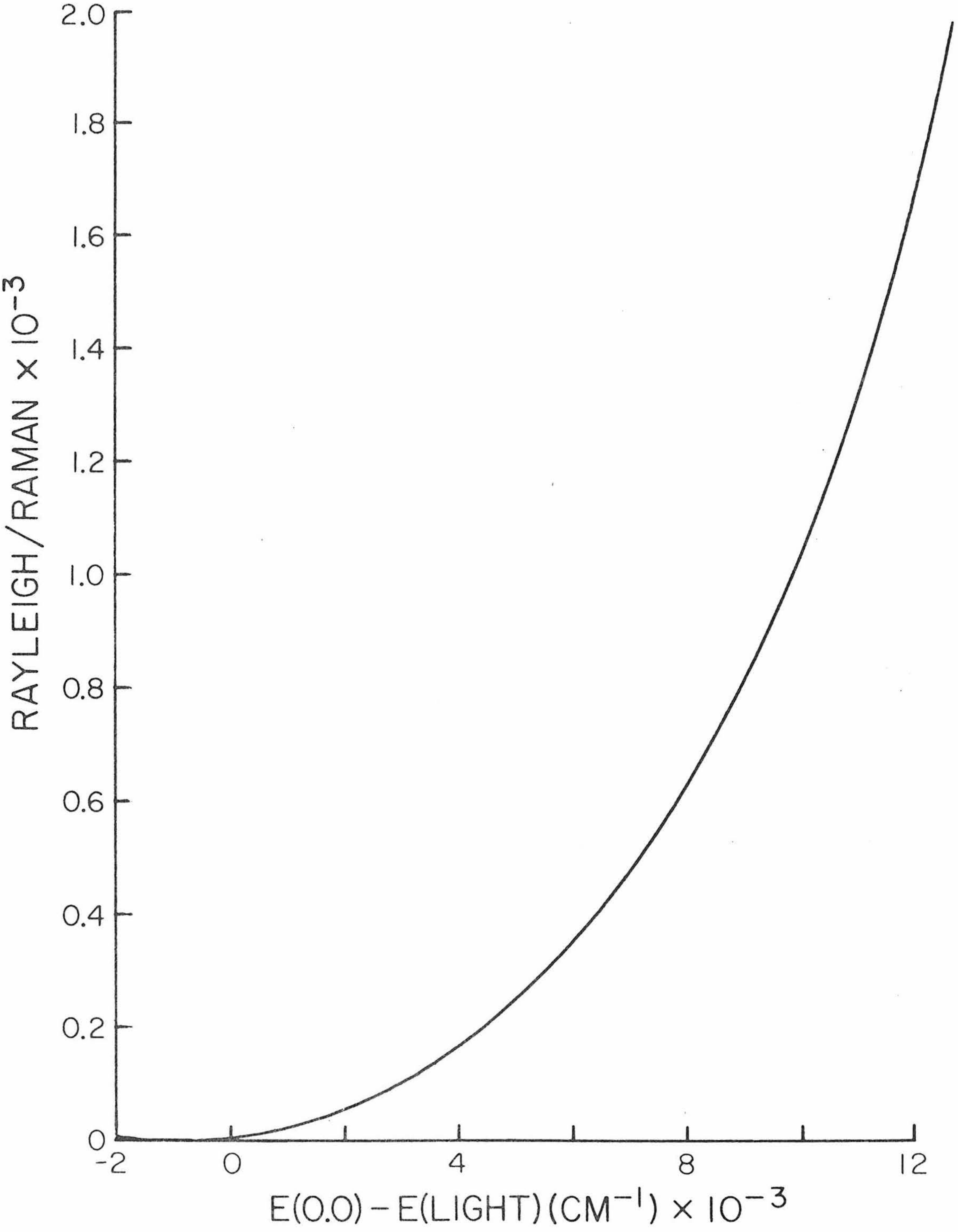
Figure 1. A semilog plot of the relative emission intensity calculated from Eq. (4) when the excitation frequency (ω_0) is at 15,000 cm^{-1}.


INTENSITY
10^12
10^10
10^8
10^6
10^4
10^2
10^0
10^-2
10^-4
10^-6
ENERGY (cm^-1) × 10^-3
8
10
12
14
16
18
20
22
RAMAN
RAYLEIGH
(1 → 1)
(0 → 1)
(0 → 0)
(1 → 0)

where Q is a normal coordinate. The second term (the vibronic coupling term) of this expansion is responsible for the usual $\Delta v = \pm 1$ selection rule for the Raman effect.[1] However, Fig. 1 shows that Raman-like intensity occurs even in the absence of the vibronic coupling term. The reason for this is that the electronic energy spacing relative to the exciting line is not so large that vibrational spacings can be ignored in Eq. (9). Because of Eq. (11), only Rayleigh scattering can occur in the limit of excitation very far from the vibronic levels without the vibronic coupling term. However, as the energy of the exciting line approaches that of the electronic resonance, an imbalance in favor of the lower vibrational levels of the upper electronic state occurs, and the scattering becomes modified by Franck-Condon factors. In fact, in a real case where there are many vibrational levels, an entire Franck-Condon envelope of lines will begin to emerge as resonance is approached. This fact has been confirmed experimentally.[11-13]

The spectroscopist would ordinarily think of a line displaced from the exciting line by a vibrational frequency of the ground state as a Raman line. However, since this line occurs without the vibronic coupling term, it may better be thought of as a Franck-Condon addition to Rayleigh scattering. The intensity ratio of the Rayleigh-like line to the Raman-like line as a function of off-resonance energy for the above simple model [Eqs. (4), (9) and (10)] is shown in Fig. 2. Again $A = 20\ \text{cm}^{-1}$ and $\gamma = 10\ \text{cm}^{-1}$. Unfortunately, little experimental data is available to check this. The only system for which we could find Rayleigh/Raman cross sections was benzene,[14] and their

Figure 2. The ratio of the Rayleigh to Raman peak intensities as a function of the energy displacement of the excitation frequency (ω_0) from the $0 \rightarrow 0$ transition frequency.


RAYLEIGH/RAMAN × 10⁻³
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
-2
0
4
8
12
E(0.0) − E(LIGHT) (CM⁻¹) × 10⁻³

excitation was so far from resonance that the contributions from many excited states would be nearly equal; thus our simple model would not hold.

The relative intensities of the contributions of the first two terms in Eq. (12) to Rayleigh-Raman scattering depend upon the nearness to resonance, the magnitudes of the dipole derivatives $(\partial\mu/\partial Q)_0$ for various normal coordinates, the Franck-Condon factors, and the manner by which the wings of the resonance and light source decrease with frequency. All this information is contained in the absorption spectrum and/or the emission spectrum of the molecule, and in fact the formalism given in Eq. (2) allows one to calculate scattering intensities directly from an absorption spectrum in a way previously outlined for another problem.[15] A word of warning, which is fairly obvious, is that in a real molecular problem, not only is there an entire set of vibrational levels associated with each electronic state, but many electronic states may contribute to the scattering. This presents a particularly troublesome problem when the exciting line is far away from any one resonance, and the wings of all the various resonances are contributing in a complicated way, with weight often being in favor of intense, but distant, ones. Such overlapping of contributions will tend to smear out to some extent the effects discussed here. Inclusion of distant resonances is possible using the methods of Mower[16] and of Hong.[17]

Time dependence associated with the scattering process can be obtained from Eq. (2) and, as mentioned in a previous paper,[5] consists of more than a single component. In general there is expected to be a decay term (not necessarily exponential) associated with each isolated peak of a resonance,* a decay term associated with the light source, and beat terms among them. For very complicated multipeaked resonances the decay is complicated with its own maxima and minima, and no simple statements can be made about it. See, however, Delory and Tric,[18] where a simplified approach is used to obtain some interesting properties of multipeaked resonances. In general, however, one must simply solve Eq. (2) in all its glory from a knowledge of S(t) and G(ω).

V. CONCLUSION

Raman scattering, Rayleigh scattering, and the absorption and reemission of light on-, near-, or off-resonance are all one and the same phenomenon from a theoretical point of view. This paper outlines ideas and methods unifying the theory of such effects.

The major point of the paper is that molecular or atomic resonances are considered in a higher order of approximation than in the conventional theories of the interaction of radiation and matter,

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*This part and the molecular beat terms are the "most important" parts if one is interested primarily in the molecule. The approximate approach of Delory and Tric[18] utilizes this fact, but the neglect of the light source and the treatment of the compound resonance as a superposition of simple resonances are not expected to provide an adequate theoretical description for the response to transform-limited light sources in the subnanosecond region.

the radiative continuum for spontaneous emission together with non-radiative continua being included to infinite order in perturbation theory at the outset. The resulting "resonances" have widths and shapes depending upon the density of states in these continua and the strength of the interactions with them.

The exciting light source is looked upon as an added perturbation to which the system instantaneously responds. While further theoretical elaboration is possible, in the present paper the light source is considered only as a means of "preparing" states belonging to the resonance. In this context the scattering of light from a narrow-banded source interacting far out on the wings of a resonance can be loosely thought of as an absorption and reemission process from these wings. The "virtual state" language of the traditional perturbation theory is unnecessary. The absorption intensity as a function of frequency over the entire resonance, including the fantastically weak wings, is therefore a quantity of importance. In polyatomic molecules, where smooth and structured continua from many sources may play a role, conventional theories of light scattering, which in effect assume a particular type of simplified lineshape, will undoubtedly be found wanting when compared with measured scattering amplitudes over a wide range of light-source frequencies.

In the near-resonance region the conventional theories also fail, requiring higher- and higher-order perturbation theory on the one extreme, or the inclusion of an artificial damping term on the other. The present theory smoothly bridges the gap from far off-resonance right into the resonance region, with the added advantage of flexibility in the light source function and the resonance shapes. The theory applies equally well to narrow-banded excitation, traditionally thought by the experimentalist to constitute a scattering experiment, right through to broad-banded excitation, the traditional absorption and reemission experiment.

The time dependence of these scattering problems also reveals itself in a transparent way, being composed of, besides quantum beat terms, light source parts and molecular parts whose relative intensities vary, among other things, with the off-resonance energy $(\omega_a - \omega_0)$. The off-resonance energy also affects the Franck-Condon factors in the scattering process. Very far off-resonance, the vibrational levels in a given electronic state can, to a good approximation, be treated as equienergetic, giving rise to the traditional selection rules $\Delta v = 0$ in the absence of vibronic coupling or $\Delta v = 0, \pm 1$ in the presence of first-order vibronic coupling. Nearer resonance, the vibrational energy levels closest to the light source frequency have greater weight, and Franck-Condon factors begin to evolve. As resonance with a single vibrational level is reached, this level strongly dominates all the others giving rise to the familiar Franck-Condon envelope in absorption and re-emission processes.

ACKNOWLEDGMENT

This work has been supported jointly by the National Science Foundation (Grant No. GP-42286X), the U.S. Army Research Office, Durham, North Carolina (Contract No. DAHC 04-74-C-0010), and by a grant from the Australian Research Grants Committee. J.O.B. acknowledges support from a National Science Foundation predoctoral fellowship. The work could not have been accomplished without this support, and it is gratefully acknowledged. Both authors also wish to acknowledge many hours of discussion with Dr. Graham Fleming, which led to many improvements in the paper, G.W.R. wishes to thank Dr. Colin Barraclough for bringing to his attention some recent work on the resonance Raman effect and for clarifying discussions of this effect, and J.O.B. thanks Dr. Charles Langhoff for many helpful discussions.

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Section C

CONTRIBUTION OF TWO-PHOTON STATES TO THE TIME-DEPENDENT THEORY OF LIGHT SCATTERING

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I. INTRODUCTION

In previous papers,[1-3] a time-dependent theory of near-resonance scattering/fluorescence was outlined. In this theory the effect of interactions[†] of the discrete molecular energy levels with neighboring continua are, in principle, carried to infinite order of perturbation theory. The continuum due to the decay photon field[4] is particularly important, but continua, say, from the vibrational density of states in a sufficiently complex molecule may also have to be included.[5,6] The scattering process is then viewed as the interaction of another field, the externally imposed exciting light source field, with the resulting resonance profiles, near a maximum for near-resonance scattering or far out on the "wings" of a resonance for off-resonance scattering. The time dependence is described by the time evolution of system states in the resonance profiles "prepared" by the exciting light source.

To describe accurately light scattering excited fairly far from an intensity maximum of a resonance profile, it is necessary to include the effects of two-photon components in the composition of the system states. These components yield the so-called antiresonance terms in second-order perturbation theory. Contributions of these components to the resonance profile and participation of them in the time evolution process are essential for a complete theory of

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[†] We used the word interaction here in the spectroscopist's context. The interactions occur, of course, between the particles comprising the system, not the states.

scattering/fluorescence. Our earlier papers[2,3] dealt mainly with near-resonance excitation, where the two-photon contributions are unimportant. The present paper shows how two-photon terms can be included, if coupling between them is not allowed, in this resonance profile theory. Three and more photon contributions and relativistic effects will not be included. Formulas will be derived for time-dependent scattering/fluorescence for a weak exciting light, of arbitrary frequency composition and having variable position from far off-resonance into the resonance region. This formalism thus unifies the perturbation theory results for time-independent off-resonance scattering with the recent time-dependent theories for near-resonance scattering.[1-3, 7-9] In addition it yields the time-dependencies of the antiresonance terms, which have not been given before.

II. INTERACTION SCHEME

The total Hamiltonian of the system is given by

$$H = H_{mol} + H_{field} + H_{int} \cdot \tag{1}$$

The radiation-matter-interaction Hamiltonian in the non-relativistic approximation is[10†]

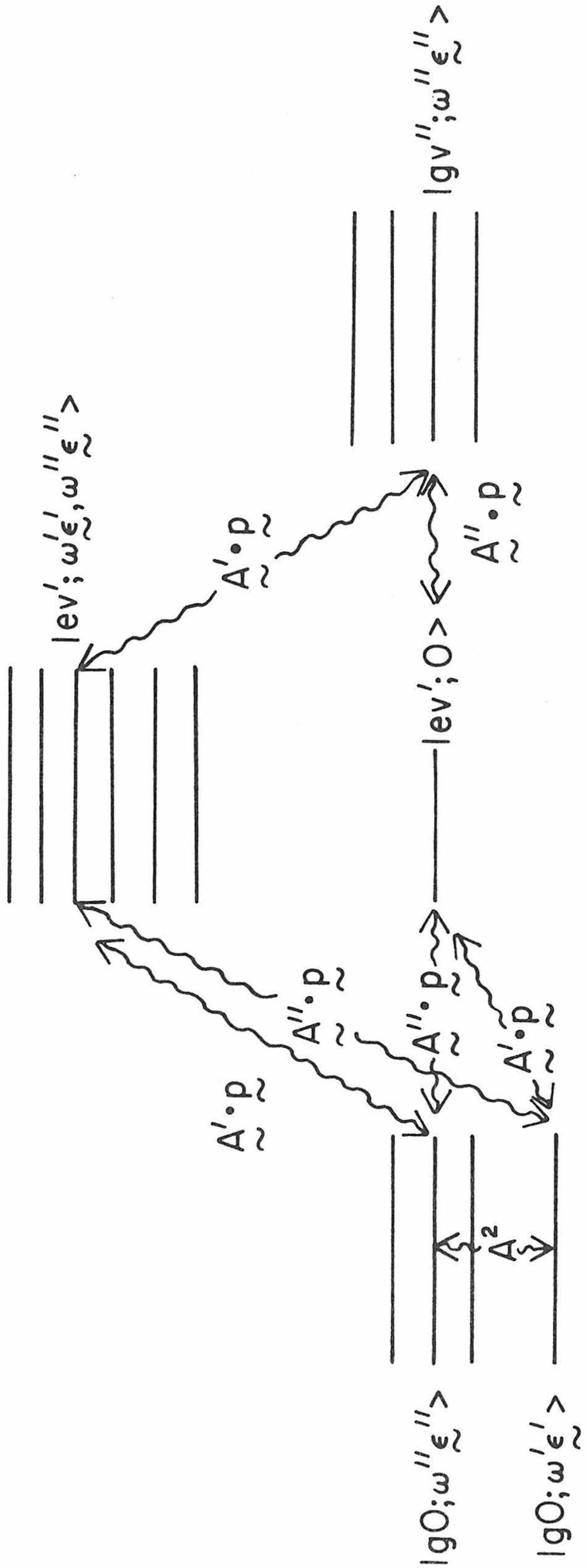
$$H_{int} = \sum_{i} \{ - \frac{e}{mc} [\underset{\wedge}{A}(x_i, t) \cdot \underset{\wedge}{p}_i] + \frac{e^2}{2mc^2} \underset{\wedge}{A}(x_i, t) \cdot \underset{\wedge}{A}(x_i, t) \} \tag{2}$$

[†] We shall use Gaussian unrationalized units throughout.

where the summation is over the molecular electrons, $\underset{\sim}{p}_i$ is the linear momentum of the i^{th} electron, and $\underset{\wedge}{A}(x_i,t)$ is the vector potential of the field at the position of the i^{th} electron. In (2) the term $\underset{\sim}{p}_i \cdot \underset{\wedge}{A}(x_i,t)$ has been set equal to $\underset{\wedge}{A}(x_i,t) \cdot \underset{\sim}{p}_i$, since the field is transverse. The field operators $\underset{\wedge}{A}(x_i,t)$ in (2) are linear combinations of creation and annihilation operators.[11] Thus the $\underset{\wedge}{A}(x_i,t) \cdot \underset{\sim}{p}_i$ term changes the photon occupation number by ±1 and at the same time gives rise to off-diagonal matrix elements between molecular zero-order components. The $\underset{\wedge}{A}(x_i,t) \cdot \underset{\wedge}{A}(x_i,t)$ term in (2) changes the photon occupation number by $0, \pm 2$. Fig. 1 shows the interaction scheme in terms of the eigenstates of $H_{mol} + H_{field}$, which, as in the conventional approach, form a convenient zero-order basis for the problem.

To illustrate the method, the ground vibronic level (g0), an excited vibrational level (gv″) in the molecular ground electronic state, and an excited vibronic level (ev′) of the molecule need be considered. To reproduce a resonance profile theory that contains as a special case the conventional second-order perturbation result, one need retain (Fig. 1) the zero-order zero-photon state $|ev';0\rangle$ and those of the type $|g0;\omega'\underset{\wedge}{\epsilon}'\rangle$, $|gv'';\omega''\underset{\wedge}{\epsilon}''\rangle$ and $|ev';\omega'\underset{\wedge}{\epsilon}',\omega''\underset{\wedge}{\epsilon}''\rangle$. The molecule is assumed to be initially in its vibronic ground state and a one-photon wavepacket $\int d\omega\, S(\omega)\, |\omega\underset{\wedge}{\epsilon}\rangle$ (in the interaction representation) is assumed to be present, where $S(\omega)$ is the amplitude of the packet at frequency ω and $\underset{\wedge}{\epsilon}$ is the polarization vector of the packet. All zero-order states except $|ev';0\rangle$ are continuous. For later comparison, the conventional second-order perturbation results will now be given,

Figure 1. The eigenstates of $H_{mol} + H_{field}$. Also shown are the interactions between some of the states due to H_{int}. For clarity some interactions were omitted, but all the various types of interactions considered in this paper are shown.


$|gv'';\omega''\underset{\sim}{\epsilon}''\rangle$
$|ev';\omega'\underset{\sim}{\epsilon}',\omega''\underset{\sim}{\epsilon}''\rangle$
$\underset{\sim}{A}'\cdot\underset{\sim}{p}$
$\underset{\sim}{A}''\cdot\underset{\sim}{p}$
$|ev';0\rangle$
$\underset{\sim}{A}'\cdot\underset{\sim}{p}$
$\underset{\sim}{A}''\cdot\underset{\sim}{p}$
$\underset{\sim}{A}''\cdot\underset{\sim}{p}$
$\underset{\sim}{A}'\cdot\underset{\sim}{p}$
$\underset{\sim}{A}^2$
$|g0;\omega''\underset{\sim}{\epsilon}''\rangle$
$|g0;\omega'\underset{\sim}{\epsilon}'\rangle$

III. CONVENTIONAL SECOND-ORDER PERTURBATION THEORY

In conventional second-order perturbation theory the incoming photon is considered to be monochromatic. The differential scattering cross section (using the dipole approximation in the conventional Kramers-Heisenberg theory) from an initial state $|g0;\omega'\hat{\epsilon}'\rangle$ to a final state $|gv'';\omega''\hat{\epsilon}''\rangle$ is given by[12*]

$$\frac{d\sigma}{d\Omega} = \left(\frac{e^2}{mc^2}\right)^2 \left(\frac{\omega''}{\omega'}\right) \Bigg| \delta_{0v''}(\hat{\epsilon}'\cdot\hat{\epsilon}'') - \frac{1}{m}\sum_{v'}$$

$$\times \left[\frac{\langle gv''|\hat{p}\cdot\hat{\epsilon}''|ev'\rangle\langle ev'|\hat{p}\cdot\hat{\epsilon}'|g0\rangle}{E(ev') - E(g0) - \hbar\omega'} + \frac{\langle gv''|\hat{p}\cdot\hat{\epsilon}'|ev'\rangle\langle ev'|\hat{p}\cdot\hat{\epsilon}''|g0\rangle}{E(ev') - E(g0) + \hbar\omega''} \right] \Bigg|^2 , \tag{3}$$

where the factor $\delta_{0v''}$ means that the first term in Eq. (3) can lead only to Rayleigh scattering. The summations involving the other sets of terms (the so-called resonance and anti-resonance terms) are only over the vibronic components ev' since we have considered just a single excited state of the molecule.

In this formula, the two-photon states give rise to the third set of terms, the <u>antiresonance</u> terms. Note that the energy denominator for the antiresonance terms is $(\hbar\omega_0 + \hbar\omega'')$, where $\hbar\omega_0 = E(ev') - E(g0)$, while for the resonance terms it is $(\hbar\omega_0 - \hbar\omega')$. The only other difference in the resonance and antiresonance contributions are an

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*Sakurai's formula has been multiplied by the factor 4π to convert his Heavyside-Lorentz rationalized units to the Gaussian units used in this paper.

interchange of $\underset{\frown}{\epsilon}'$ and $\underset{\frown}{\epsilon}''$, the summations being over an identical set of molecular excited levels.

An important point to be learned from these well-known facts is that a two-photon component $|ev';\omega'\underset{\frown}{\epsilon}',\omega''\underset{\frown}{\epsilon}''\rangle$ with energy $[E(ev') - E(g0) + \hbar\omega' + \hbar\omega'']$ behaves as if it were a distant resonance interacting with a single decay photon "state" $|gv'';\omega''\underset{\frown}{\epsilon}''\rangle$ through the annihilation operator for $(\omega'\underset{\frown}{\epsilon}')$ photons. This two-photon component is thus totally analogous with that part of the zero-photon component $|ev';0\rangle$ destined to decay into a particular $|gv'';\omega''\underset{\frown}{\epsilon}''\rangle$.

Eq. (3) clearly fails to give reasonable results on resonance since the first term in brackets blows up. It also does not apply for time-dependent scattering, since its derivation depends on the light source being turned on at $t = 0$ and left on forever. A more general theory, which encompasses these results and corrects their defects, will now be given.

IV. TIME-DEPENDENT THEORY

The cross section $\sigma_{b\leftarrow a}$ for a transition from a state $|a\rangle$ to a state $|b\rangle$ is defined as the transition probability per unit time $(W_{b\leftarrow a})$ divided by the flux,[13,14] which is c/V for a one-photon wavepacket, where V is the volume of the system. That is,

$$\sigma_{b\leftarrow a}(t) = \frac{V}{c} W_{b\leftarrow a}(t) . \tag{4}$$

The transition probability per unit time (for one molecule) is given by[15]

$$W_{b\leftarrow a}(t) = \frac{d}{dt}\,|\langle b|\psi(t)\rangle|^2 \tag{5a}$$

$$= (\langle b|\psi(t)\rangle)^*\,\frac{d}{dt}\langle b|\psi(t)\rangle + \mathrm{C.\,C.} \tag{5b}$$

where $\psi(t)$ is the wavefunction of the system at time t, C. C. means complex conjugate and at $t = -\infty$ the system was in the state $|a\rangle$. The case of interest here is where $|a\rangle = \int S(\omega)\,d\omega\,|g0;\omega\underset{\wedge}{\epsilon}\rangle$ (in the interaction representation), as mentioned in section II, and $\langle b| = \langle gv'';\omega''\underset{\wedge}{\epsilon}''|$.

For transform-limited light source output,[3] the amplitude function S(t) in the time regime is related to $S(\omega)$ in the frequency regime through the Fourier transform,

$$S(t) = (2\pi)^{-\frac{1}{2}} \int_{-\infty}^{+\infty} e^{-i\omega t}\,S(\omega)\,d\omega\;. \tag{6}$$

Using the time development operator $U(t,-\infty)$ in the interaction representation[16,7] one gets

$$\langle b|\psi(t)\rangle = \langle gv'';\omega''\,\underset{\wedge}{\epsilon}''|\int d\omega\, e^{iH_0 t/\hbar}\, e^{-iHt/\hbar}\, S(\omega)$$
$$\times\,[1 + H_{int}\,G(\hbar\omega)]\,|g0;\omega\underset{\wedge}{\epsilon}\rangle \tag{7}$$

where the zero-order Hamiltonian H_0 is the sum of the first two terms on the right-hand side of Eq. (1). Then[14]

$$\frac{d}{dt}\langle b|\psi(t)\rangle = -i/\hbar\,\langle gv'';\omega''\underset{\wedge}{\epsilon}''|\int d\omega\, e^{i(E_{v''}/\hbar+\omega'')t}\, e^{-i\omega t}\, S(\omega)$$
$$T\,|g0;\omega\underset{\wedge}{\epsilon}\rangle \tag{8}$$

where $E_{v''} + \hbar\omega''$ and $\hbar\omega$ are the zero-order energies of the states $|gv'';\omega''\hat{\epsilon}''\rangle$ and $|g0;\omega\hat{\epsilon}\rangle$, respectively and T is the transition matrix which is defined as[13,14,17]

$$T|g0;\omega\hat{\epsilon}\rangle = (H_{int} + H_{int}\, G(\hbar\omega)\, H_{int})|g0;\omega\hat{\epsilon}\rangle \tag{9}$$

where $G(\hbar\omega)$ is the Green's function $(\hbar\omega - H)^{-1}$. Similarly[14]

$$\langle b|\psi(t)\rangle =$$

$$\langle gv'';\omega''\hat{\epsilon}''|\int d\omega \frac{e^{i(E_{v''}/\hbar + \omega'')t}\, e^{-i\omega t} S(\omega) T}{\hbar\omega - E_{v''} - \hbar\omega'' + i\eta}|g0;\omega\hat{\epsilon}\rangle \tag{10}$$

if one does not look head-on at one's light beam.

In a Rayleigh or Raman experiment, one counts all photons which come out in a range of frequencies at least as broad as one's light source. So if one puts Eqs. (8), (10) and (5b) into Eq. (4) and integrates over ω'' one gets

$$\sigma_{b \leftarrow a}(t) = \frac{2\pi V}{\hbar c}|\langle gv'';\omega''\hat{\epsilon}''|\int d\omega\, S(\omega)\, e^{-i\omega t}\, T|g0;\omega\hat{\epsilon}\rangle|^2 \rho_{\omega''} d\Omega \tag{11}$$

where $d\Omega$ signifies a solid angle and the density of photon states at at energy $\hbar\omega''$ is given by[18]

$$\rho_{\omega''}\, d\Omega = V \frac{\omega''^2\, d\Omega}{(2\pi c)^3 \hbar} \tag{12}$$

Equation (11) depends upon a knowledge of the experimental excitation function $S(\omega)$ in addition to $G(\hbar\omega)$. $G(\hbar\omega)$ may be obtained semi-empirically from the absorption spectrum and a dispersion relation.[1,5,19] It may also be calculated analytically for certain models. The integration must usually be carried out numerically. One can see from Eq. (11) that the greatest relative contribution to the cross section for the transition comes from that part of the frequency spectrum where there is good overlap between $S(\omega)$ and $G(\hbar\omega)$. $G(\hbar\omega)$ of course is large near the center of a resonance but small on the wings of a resonance. Naturally, if one excites more than one resonance, there will be interferences between them.

V. TWO-PHOTON STATES IN THE TIME-DEPENDENT THEORY

The results of the previous section are exact. Now in order to apply the formalism to the problem at hand, several approximations will have to be made: (1) neglect all matrix elements of $H_{\text{int}}^{(2)}$ [the second term in Eq. (2)] except the ones directly coupling the initial and final states, (2) keep only the two photon states $|ev';\omega\hat{\epsilon},\omega''\hat{\epsilon}''\rangle$, and (3) neglect all couplings amongst the two-photon states or between the two-photon states and the zero-photon state. With these approximations Eq. (11) becomes [using Eq. (9)]

$$\frac{d\sigma_{b\leftarrow a}}{d\Omega}(t) = \frac{2\pi}{\hbar}\frac{V}{c}\rho_{\omega''}\left|\langle gv'';\omega''\hat{\epsilon}''\right|\int d\omega e^{-i\omega t}S(\omega)$$

$$[H_{int}^{(2)}|g0;\omega\hat{\epsilon}\rangle + H_{int}^{(1)}|ev';0\rangle\frac{1}{\hbar(\omega-\omega_0)-\Gamma_0}\langle ev';0|H_{int}^{(1)}|g0;\omega\hat{\epsilon}\rangle$$

$$-H_{int}^{(1)}|ev';\omega\hat{\epsilon},\omega''\hat{\epsilon}''\rangle\frac{1}{\hbar(\omega''+\omega_0)+\Gamma_{\omega''\omega}}\langle ev';\omega\hat{\epsilon},\omega''\hat{\epsilon}''|H_{int}^{(1)}|g0;\omega\hat{\epsilon}\rangle]|^2 \tag{13}$$

where $H_{int}^{(1)}$ is the first term in Eq. (2). In Eq. (13) the matrix elements of G were derived from the two-resonance model.[2,13,20] These matrix elements are

$$\langle ev';0|G(\hbar\omega)|ev';0\rangle = \frac{1}{\hbar(\omega-\omega_0)-\Gamma_0} \tag{14a}$$

$$\langle ev';\omega\hat{\epsilon},\omega''\hat{\epsilon}''|G(\hbar\omega)|ev';\omega\hat{\epsilon},\omega''\hat{\epsilon}''\rangle = -\frac{1}{\hbar(\omega''+\omega_0)+\Gamma_{\omega''\omega}} \tag{14b}$$

where $\hbar\omega_0$ is the zero-order energy of the $|ev';0\rangle$ state and the Γ's are the level shift operators

$$\Gamma_i(\lambda) = \int_{-\infty}^{+\infty}\frac{V_i(\epsilon)^2\rho(\epsilon)}{\lambda-\epsilon}d\epsilon\ , \tag{15}$$

where λ is now a complex energy variable, $\rho(\epsilon)$ is the density of continuum states as a function of the (real) energy ϵ; and $V_i(\epsilon)$, assumed real, is the energy-dependent interaction matrix element between the zero- or the two-photon state with states in the decay photon continuum at energy ϵ. Thus the light source prepares $|ev';0\rangle$ and states of the form $|ev';\omega\underset{\wedge}{\epsilon},\omega''\underset{\wedge}{\epsilon}''\rangle$ for all ω. If the frequency dependence of the matrix elements of H_{int} can be ignored, Eq. (13) becomes

$$\begin{aligned}\frac{d\sigma_{b\leftarrow a}}{d\Omega}(t) = \frac{V\omega''^2}{(2\pi)^2c^4\hbar^2}\Big|&\langle gv'';\omega''\underset{\wedge}{\epsilon}''|H_{int}^{(2)}|g0;\overline{\omega}\underset{\wedge}{\epsilon}\rangle S(t)\sqrt{2\pi}\,\delta_{v''0}\\ &+\langle gv'';\omega''\underset{\wedge}{\epsilon}''|H_{int}^{(1)}|ev';0\rangle\int\frac{d\omega e^{-i\omega t}S(\omega)}{\hbar(\omega-\omega_0)-\Gamma_0}\langle ev';0|H_{int}^{(1)}|g0;\overline{\omega}\underset{\wedge}{\epsilon}\rangle\\ &-\langle gv'';\omega''\underset{\wedge}{\epsilon}''|H_{int}^{(1)}|ev';\overline{\omega}\underset{\wedge}{\epsilon}\,\omega''\underset{\wedge}{\epsilon}''\rangle\langle ev';\overline{\omega}\underset{\wedge}{\epsilon}\,\omega''\underset{\wedge}{\epsilon}''|H_{int}^{(1)}|g0;\overline{\omega}\underset{\wedge}{\epsilon}\rangle\\ &\left(\frac{1}{\hbar(\omega_0+\omega'')+\Gamma_{\omega''\overline{\omega}}}S(t)\sqrt{2\pi}\right)\Big|^2\end{aligned}\tag{16}$$

where $\overline{\omega}$ signifies an average frequency of $S(\omega)$, and $S(t)$ is given by Eq. (6). Thus, within the approximations made, the first and third terms have time dependencies exactly following the light source, while the term involving the zero-photon resonance will yield three types of terms--ones following the light source, ones decaying as $\exp[\mathrm{Im}\Gamma_0 t]$, where $\mathrm{Im}\Gamma_0$ is the imaginary part of Γ_0 and is negative, and beat terms between them--as has been previously discussed in theories of near-resonance light scattering.[2,3,7-9] The two-photon states show no intrinsic time dependence of their own even if they have structure and width from $\Gamma_{\omega''\overline{\omega}}$. The reason for this is that the part of the light source having a frequency ω interacts with the resonance that is $\hbar\omega'' + \hbar\omega_0$ higher in energy. Thus, the light source can never get close enough to the resonance in order to "see" its structure.

If one neglects $H_{int}^{(2)}$ and the two-photon terms in Eq. (16), then Eq. (16) reduces to the same results as the recent theories of near-resonance light scattering.[2,3,7-9] For near-resonance light scattering the second set of terms in Eq. (16) is much larger than the third set (the antiresonance terms) due to the denominators. However, the contribution of the first term to Rayleigh scattering can be comparable to that of the second set of terms.[21] Off-resonance, in a calculation on a model diatomic molecule,[21] the antiresonance terms accounted for nearly half the scattering cross section for excitations below resonance with the 0-0 transition by more than 7000 cm^{-1}.

VI. REDUCTION TO THE RESULTS OF SECOND-ORDER PERTURBATION THEORY

The conventional second-order perturbation results [Eq. (3)] for light scattering uses a very narrow-banded exciting line. For comparison with that result we can assume in Eq. (16) a delta function form for $S(\omega)$,

$$S(\omega) = \delta(\omega - \omega') \tag{17}$$

centered at frequency ω'. This yields a time-independent cross section since Eqs. (6) and (17) imply constant $|S(t)|^2$. If one now neglects the level shift operators Γ in Eq. (16) and uses the matrix elements of H_{int} given by Heitler,[22] then Eq. (16) reduces to Eq. (3).

Eq. (3) can also be derived from a second-order perturbation expansion of T in the equation for monochromatic excitation[13,23]

$$\sigma_{b\leftarrow a} = \frac{2\pi}{\hbar}\,\frac{V}{c}\,\left|\langle gv'';\omega''\underset{\wedge}{\epsilon}''\,|\,T\,|\,g0;\omega'\underset{\wedge}{\epsilon}'\rangle\right|^2\,\delta(E_{v''} + \hbar\omega'' - \hbar\omega') \tag{18}$$

as has been done by Bandrauk.[24]

The level shift terms, Γ_0 and $\Gamma_{\omega''\overline{\omega}}$, are generally small for off-resonance scattering. Near resonance, however, the imaginary part of Γ_0 forms the damping term and must be included. It is generally introduced in an ad hoc fashion in theories of resonance scattering and line breadth,[25] but such a procedure may not adequately take into account the effects of detailed lineshape on the scattering cross section. The real part of Γ_0 is also not small for a state interacting with a bumpy molecular continuum.[5,19,26]

VII. CONCLUSION

Inclusion of the two-photon states in the resonance profile theory shows that they always behave as a distant resonance, exhibiting no intrinsic time dependence of their own, but always building up and decaying with the light source. The two-photon states have been included under the assumption that they do not interact with each other nor with the zero-photon state--that is, that all these states behave as isolated resonances interacting only with the one-photon states of the decay photon continuum. For time-independent scattering from a monochromatic light source, the resonance profile theory yields both the resonance and antiresonance terms found in conventional second-order perturbation theory results. Eq. (16) is thus a generalization of previous theories of near-resonance, time-dependent light scattering to include the "antiresonance terms" which are very important off resonance. Therefore it can be used for time-dependent (or time-independent) light scattering regardless of whether the excitation is on, near, or far from resonance.

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Section D

RAYLEIGH AND RAMAN SCATTERING FOR A DIATOMIC MOLECULE

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I. INTRODUCTION

There has been a lot of interest lately, both experimentally and theoretically, in the excitation frequency dependence of resonant and near-resonant light scattering.[1] Most experimental papers[2-7] have tried to fit their excitation profiles with a few parameters to the theories of either Albrecht[8, 9] or Peticolas et al.,[10] thereby neglecting the vibrational structure in the excited state. A few experimental excitation profiles have been fitted to either a two-vibrational-level model[11] or a displaced harmonic oscillator model[12-14] to include this vibrational structure. However, the interference effects between the resonances have been blurred out in these papers due to the large widths assigned to the states. This was also true in the theoretical paper of Shorygin,[15] who used the displaced harmonic oscillator model but applied it to a model system where again the widths were too broad. The only papers to discuss interference effects between resonances have been ones which used models with only two states.[16-18]

This paper combines the resolution of the two-state model with the on resonance interference effects due to many levels in the displaced harmonic oscillator model and discusses Rayleigh and Raman scattering from a diatomic molecule. In contrast to the use of harmonic oscillator models in these previous papers, data for an actual molecule will be used as the basis of the discussion here. However, rotational levels will not be included. In addition, a formula for the scattering cross section other than that usually used by Raman spectroscopists, is shown to be more accurate if a truncated basis set is used.

The only other paper to carry out a detailed theoretical examination of resonance Raman scattering from a diatomic is the very recent paper by Rousseau and Williams.[19] However, they did not calculate excitation profiles but instead calculated what Raman spectra they should expect to see upon excitation into the dissociative continuum for I_2.

The assumptions and simplifications used in this paper will be discussed in section II. In section III a comparison of our formalism and the usual perturbation formalism will be given. Sections IV and V will give the results, a discussion of the interference effects and the effect of relaxing some of the assumptions.

II. MODEL AND ASSUMPTIONS

The model to be used in this paper is a generalization of the model used in our last paper,[20] which allows the inclusion of more than one excited level. The molecule will be assumed to have two electronic states, a ground and excited state, each having a full set of vibrational levels. Rotational levels will be neglected. Thus the model could apply to a dilute matrix of the molecule in a rare gas at low temperature. Alternatively, the rotational effects could be added in later, as has been done by Rousseau and Williams.[19] Each of the zero-photon excited state vibronic levels $|ev';0\rangle$, where the 0 stands for the vacuum level of the radiation field, will be allowed to interact with all states of the form $|gv'';\omega''\hat{\epsilon}''\rangle$, where gv″ is the v″ level of the ground electronic state and $\omega''\hat{\epsilon}''$ stands for a one-photon state having frequency ω'' and polarization vector $\hat{\epsilon}''$. In addition, the two-photon excited state levels $|ev';\omega'\underset{\wedge}{\epsilon}',\omega''\underset{\wedge}{\epsilon}''\rangle$ will also be included and allowed to interact with the one-photon ground state levels having one of the same photons present.

III. FORMALISM

The initial state considered here is $a \equiv |g0;\omega'\underset{\wedge}{\epsilon}'\rangle$, which assumes that the light source is a delta function in frequency. The complications arising from relaxing this restriction have been previously discussed.[20] The cross section for scattering from this state to a state $b \equiv |gv'';\omega''\underset{\wedge}{\epsilon}''\rangle$ is given by[20]

$$\frac{d\sigma_{b\leftarrow a}}{d\Omega} = \frac{e^4}{\hbar^2 c^4}\,\frac{\omega''}{\omega'}\,\Bigg|\,\frac{\hbar}{m}\,\delta_{v'',0}\,\underset{\wedge}{\epsilon}'\cdot\underset{\wedge}{\epsilon}''$$

$$+\sum_{v'}\frac{\hbar}{m^2}\{\langle gv''|\underset{\wedge}{p}\cdot\underset{\wedge}{\epsilon}''|ev'\rangle\langle ev';0|G(\hbar\omega')|ev';0\rangle\langle ev'|\underset{\wedge}{p}\cdot\underset{\wedge}{\epsilon}'|g0\rangle$$

$$+\langle gv''|\underset{\wedge}{p}\cdot\underset{\wedge}{\epsilon}'|ev'\rangle\langle ev';\omega'\underset{\wedge}{\epsilon}',\omega''\underset{\wedge}{\epsilon}''|G(\hbar\omega')|ev';\omega'\underset{\wedge}{\epsilon}',\omega''\epsilon''\rangle\langle ev'|\underset{\wedge}{p}\cdot\underset{\wedge}{\epsilon}''|g0\rangle\}\Bigg|^2 \tag{1}$$

where Ω denotes a solid angle, $\underset{\wedge}{p}$ is the momentum operator and $G(\hbar\omega')$ is the Green's function operator given by $(\hbar\omega' - H)^{-1}$, where H is the total Hamiltonian of the system. The approximations in Eq. (1) are (1) the inclusion of only two-photon states having both the initial and final photons present, (2) the neglect of interactions amongst the excited state levels and (3) a neglect of interactions due to the A^2 term in the photon-molecule interaction Hamiltonian except for the term which directly couples the initial and final states and leads to the first term in Eq. (1). As mentioned in a previous paper,[20] these assumptions are equivalent to those made in second-order perturbation theory.

With the assumptions given above, the problem reduces to that of a set of isolated levels interacting separately with a series of continua (the $|gv'';\omega\underset{\wedge}{\epsilon}\rangle$ continua). In a manner analogous to one state interacting with several continua the matrix elements of the Green's function are then given by[21, 22]

$$\langle ev';0|G(\hbar\omega')|ev';0\rangle = \frac{1}{\hbar\omega' - (E_{ev'} - E_{g0}) - \Gamma_{v'}(\hbar\omega')} \tag{2a}$$

$$\langle ev';\omega'\underset{\wedge}{\epsilon}',\omega''\underset{\wedge}{\epsilon}''|G(\hbar\omega')|ev';\omega'\underset{\wedge}{\epsilon}',\omega''\underset{\wedge}{\epsilon}''\rangle$$

$$= \frac{-1}{\hbar\omega'' + (E_{ev'} - E_{g0}) + \Gamma_{v'\omega'\omega''}(\hbar\omega')} \tag{2b}$$

where $E_{ev'}$ is the zero-order energy of the $|ev';0\rangle$ state

$$\Gamma_{v'}(\hbar\omega') = \int_{-\infty}^{\infty} \frac{H_{int}^{v'2}(\epsilon)\,\rho(\epsilon)\,d\epsilon}{\hbar\omega' - \epsilon} \tag{2c}$$

and similarly for $\Gamma_{v'\omega'\omega''}(\hbar\omega')$ where $H_{int}^{v'}$ is the interaction matrix element of the $|ev', 0\rangle$ state with the continuum states having zero-order energy ϵ and $\rho(\epsilon)$ is the density of these continuum states. For a large molecule one would have to include molecular continua due to other electronic states, as has been done previously.[23, 24]

However, for a diatomic molecule, the only continua that need to be included are those of the one-photon ground-state levels. If one then assumes that $H_{\text{int}}^{v'2}(\epsilon)\rho(\epsilon)$ is independent of ϵ, one gets

$$\Gamma_{v'}(\hbar\omega') = -ia \qquad (3)$$

where a is a positive constant. This last approximation thus results in a neglect of the real part of the level shift operator Γ and assumes that the imaginary part is a constant. $\Gamma_{v',\omega',\omega''}$ will be neglected entirely since the denominator is so large already that it will not make a difference.

With these last approximations the cross section from Eq. (1) reduces to the usual Kramers-Heisenberg formula[20,25] with a "damping" coefficient inserted.

$$\frac{d\sigma_{b\leftarrow a}}{d\Omega} = \frac{e^4}{\hbar^2 c^4}\,\frac{\omega''}{\omega'}\,\Big|\,\frac{\hbar}{m}\,\delta_{v'',0}\,\underset{\wedge}{\epsilon}'\cdot\underset{\wedge}{\epsilon}''$$

$$+\sum_{v'}\frac{\hbar}{m^2}\left\{\frac{\langle gv''|\underset{\wedge}{p}\cdot\underset{\wedge}{\epsilon}''\,|ev'\rangle\langle ev'|\underset{\wedge}{p}\cdot\underset{\wedge}{\epsilon}'\,|g0\rangle}{\hbar\omega' - (E_{ev'} - E_{g0}) + ia}\right.$$

$$\left.-\,\frac{\langle gv''|\underset{\wedge}{p}\cdot\underset{\wedge}{\epsilon}'\,|ev'\rangle\langle ev'|\underset{\wedge}{p}\cdot\underset{\wedge}{\epsilon}''\,|g0\rangle}{\hbar\omega'' + (E_{ev'} - E_{g0})}\right\}\Big|^2 \; . \qquad (4)$$

If one now uses the well-known relationship

$$\underset{\wedge}{p} = \frac{m}{i\hbar}\,[\underset{\wedge}{r}H - H\underset{\wedge}{r}] \qquad (5)$$

one gets

$$\frac{d\sigma_{b \leftarrow a}}{d\Omega} = \frac{e^4}{\hbar^2 c^4}\,\frac{\omega''}{\omega'}\,\Big|\,\frac{\hbar}{m}\,\delta_{v'',0}\,\underset{\wedge}{\epsilon}'\cdot\underset{\wedge}{\epsilon}''$$

$$+\sum_{v'}\frac{(E_{ev'}-E_{gv''})(E_{ev'}-E_{g0})}{\hbar}\Big\{\frac{\langle gv''|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}''|ev'\rangle\langle ev'|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}'|g0\rangle}{\hbar\omega'-(E_{ev'}-E_{g0})+ia}$$

$$-\frac{\langle gv''|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}'|ev'\rangle\langle ev'|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}''|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}''|g0\rangle}{\hbar\omega''+(E_{ev'}-E_{g0})}\Big\}\Big|^2 . \qquad (6)$$

The formula usually used by Raman spectroscopists[1, 8] is

$$\frac{d\sigma_{b \leftarrow a}}{d\Omega} = \frac{e^4}{\hbar^2 c^4}\,\omega''^3\omega'\,\Big|\sum_{\alpha''}\hbar\Big\{\frac{\langle gv''|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}''|\alpha''\rangle\langle\alpha''|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}'|g0\rangle}{\hbar\omega'-(E_{\alpha''}-E_{g0})+ia}$$

$$-\frac{\langle gv''|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}'|\alpha''\rangle\langle\alpha''|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}''|g0\rangle}{\hbar\omega''+(E_{\alpha''}-E_{g0})}\Big\}\Big|^2 \qquad (7)$$

where the sum over α'' is over a complete set of states (electronic and vibrational). Resonance Raman spectroscopists generally truncate the sum in Eq. (7) to include only one or two electronic states.[1, 8] Equation (7) can be derived from Eq. (6)[26] if one extends the sum in Eq. (6) to a complete set of states, uses the commutation relations between $\underset{\wedge}{r}$ and $\underset{\wedge}{p}$, and neglects a small term coming from the ia in the denominator. However, Eq. (7) cannot be as accurate as Eq. (6) if one does not use a complete set of states since its derivation depends crucially on having a complete set. A comparison of the results obtained from Eq. (7) and Eq. (8) will be given in section IV.

Since for a diatomic molecule the vibration is totally symmetric, one can make the approximation of Eq. (8b)

$$\langle gv'' | \underset{\sim}{r} \cdot \underset{\sim}{\epsilon}' | ev' \rangle = \langle gv'' \langle g | \underset{\sim}{r} \cdot \underset{\sim}{\epsilon}' | e \rangle \, ev' \rangle \tag{8a}$$

$$\approx \langle gv'' | ev' \rangle \langle g | \underset{\sim}{r} \cdot \underset{\sim}{\epsilon}' | e \rangle \tag{8b}$$

where the first factor in Eq. (8b) is a Franck-Condon overlap and the second factor is the purely electronic dipole matrix element. This approximation leads to the terms generally referred to as the Albrecht A terms.[8] For a more accurate calculation the true dependence of the inner matrix element on the right-hand side of Eq. (8a) (which is integrated only over electronic coordinates) as a function of internuclear distance over a wide range of internuclear distance would be given. This leads to the Albrecht B terms.[8] However, very few of these calculations have been done over a wide enough range of internuclear distance[27] so the approximation of Eq. (8b) had to be made here.

If one substitutes Eq. (8b) into Eq. (6) and assumes the wavefunctions are real, one gets

$$\frac{d\sigma_{b\leftarrow a}}{d\Omega} = \frac{e^4}{\hbar^2 c^4} (\langle g|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}'|e\rangle)^2 (\langle g|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}''|e\rangle)^2$$

$$\times \frac{\omega''}{\omega'} \left| \frac{\hbar}{m} \frac{\delta_{v'',0}\underset{\wedge}{\epsilon}'\cdot\underset{\wedge}{\epsilon}''}{\langle g|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}'|e\rangle\langle g|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}''|e\rangle} \right.$$

$$+ \sum_{v'} \frac{1}{\hbar} (E_{ev'} - E_{gv''}) (E_{ev'} - E_{g0}) \langle gv''|ev'\rangle\langle ev'|g0\rangle$$

$$\left. \times \left\{ \frac{1}{\hbar\omega' - (E_{ev'} - E_{g0}) + ia} - \frac{1}{\hbar\omega'' + (E_{ev'} - E_{g0})} \right\} \right|^2 . \qquad (9)$$

IV. RESULTS

Our calculations were performed for the diatomic molecule BaO using as the state e its $A^1\Sigma$ excited state. This molecule is one of a list of awkward choices of diatomic molecules having relatively discrete absorption bands in the visible region. Literature values for the constants ω_e, $\omega_e x_e$, $\omega_e y_e$ and $\omega_e z_e$[28, 29] for this state and the ground state were inputted into the RKR procedure of Demtröder, McClintock and Zare[30] which was used to calculate turning points for each vibrational level. Wavefunctions for each level were then obtained by integrating the splined turning point data by the finite difference method.[31] The average value for the electronic transition moment, $|\langle g|\underset{\wedge}{r}\cdot\underset{\wedge}{\epsilon}'|e\rangle|^2$, is one-third of R_e^2, the value of the transition moment in the molecular frame. This latter value was taken as

1.39×10^{-17} cm^2.[32] The 0-0 energy was taken as 16,722.3 cm^{-1}.[28,29]

For all the calculations the a's for each state were assumed to be 10 cm^{-1}. This was done for plotting convenience only; in actuality the lifetime widths in a solid would be much less than this and the linewidths would be governed by inhomogeneous broadening. Setting the widths equal to 10 cm^{-1} affects only the peak heights on resonance and of course the state widths. It does not affect the interference effects that will be discussed later.

Twenty upper vibrational levels were included in the v' sum. Although the energies and the Franck-Condon overlaps for the higher states will not be as accurate as the ones for the lower levels due to inaccuracies in the potential, truncating the sum at eleven or twelve states led to significant errors off resonance for the Raman overtones.

Figure 1 shows the absorption cross section as a function of frequency in wavenumbers. This was calculated in two different ways. One way is from[17]

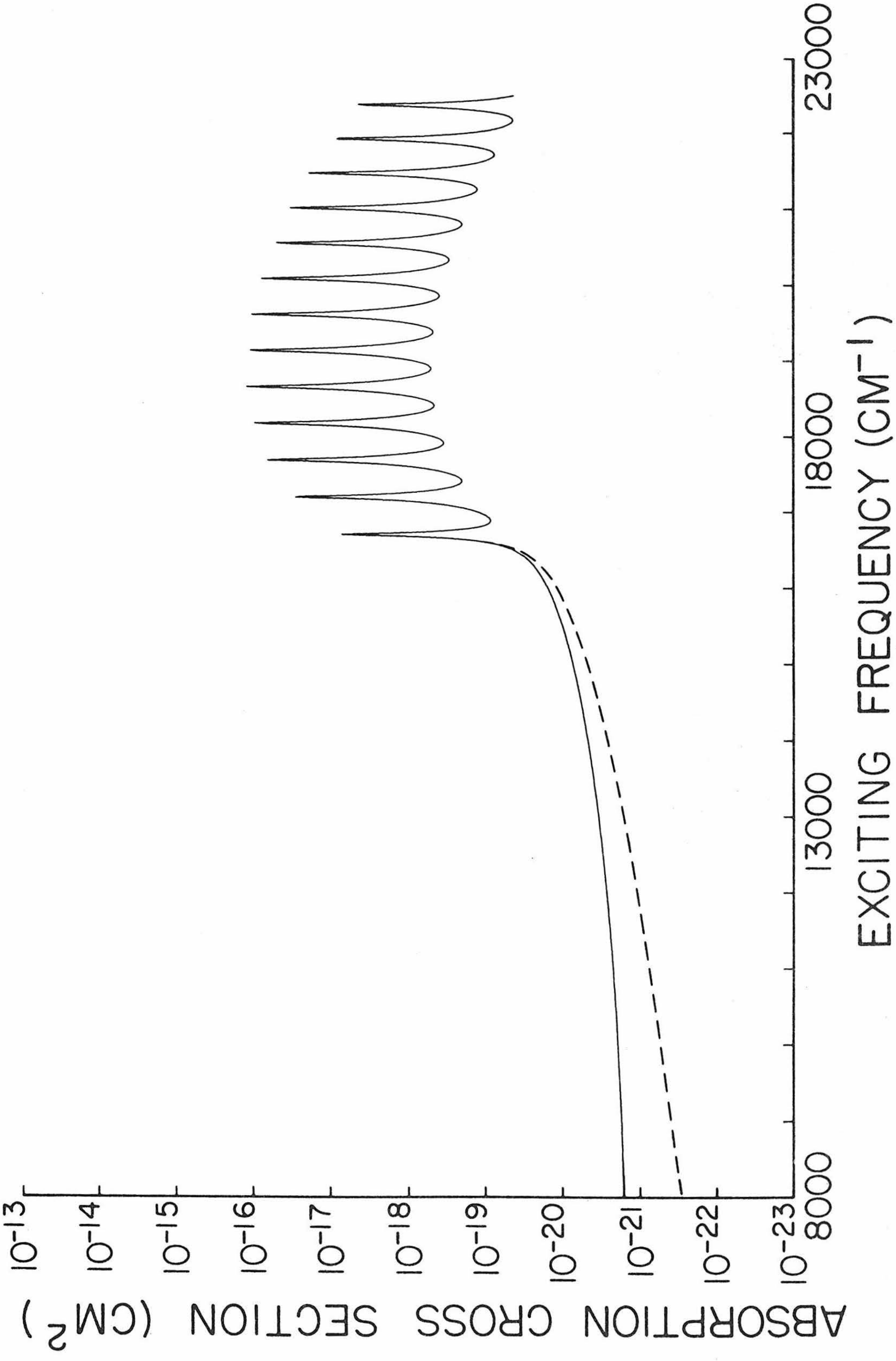
$$\sigma_{abs}(\omega) = -\frac{2V}{\hbar c}\, \mathrm{Im}\langle g0;\omega\hat{\epsilon}\,|\,T\,|\,g0;\omega\hat{\epsilon}\rangle \qquad (10)$$

where Im signifies the imaginary part, $T = H_{int} + H_{int}\,G\,H_{int}$, H_{int} is the photon-molecule interaction, and V is the volume of the system. Using the matrix elements of H_{int}[20,33] and G[20] one gets

$$\sigma_{abs}(\omega) = \frac{4\pi e^2}{c}\, |\langle g|\hat{r}\cdot\hat{\epsilon}|e\rangle|^2\, \frac{1}{\hbar^2\omega} \sum_{v'} \frac{(E_{ev'} - E_{g0})^2\, |\langle g0|ev'\rangle|^2\, a}{[\hbar\omega - (E_{ev'} - E_{g0})]^2 + a^2}$$

(11)

Figure 1. The absorption cross section in cm^2 is plotted on a log scale versus the exciting frequency in wavenumbers. The solid line is the calculation from Eq. (11) and the dashed line shows the calculation from Eq. (12) where it differs from the solid line.


ABSORPTION CROSS SECTION (CM^2)
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
10^{-18}
10^{-19}
10^{-20}
10^{-21}
10^{-22}
10^{-23}
8000
13000
18000
23000
EXCITING FREQUENCY (CM^{-1})

The other formula for the absorption cross section is given by Harris[34]

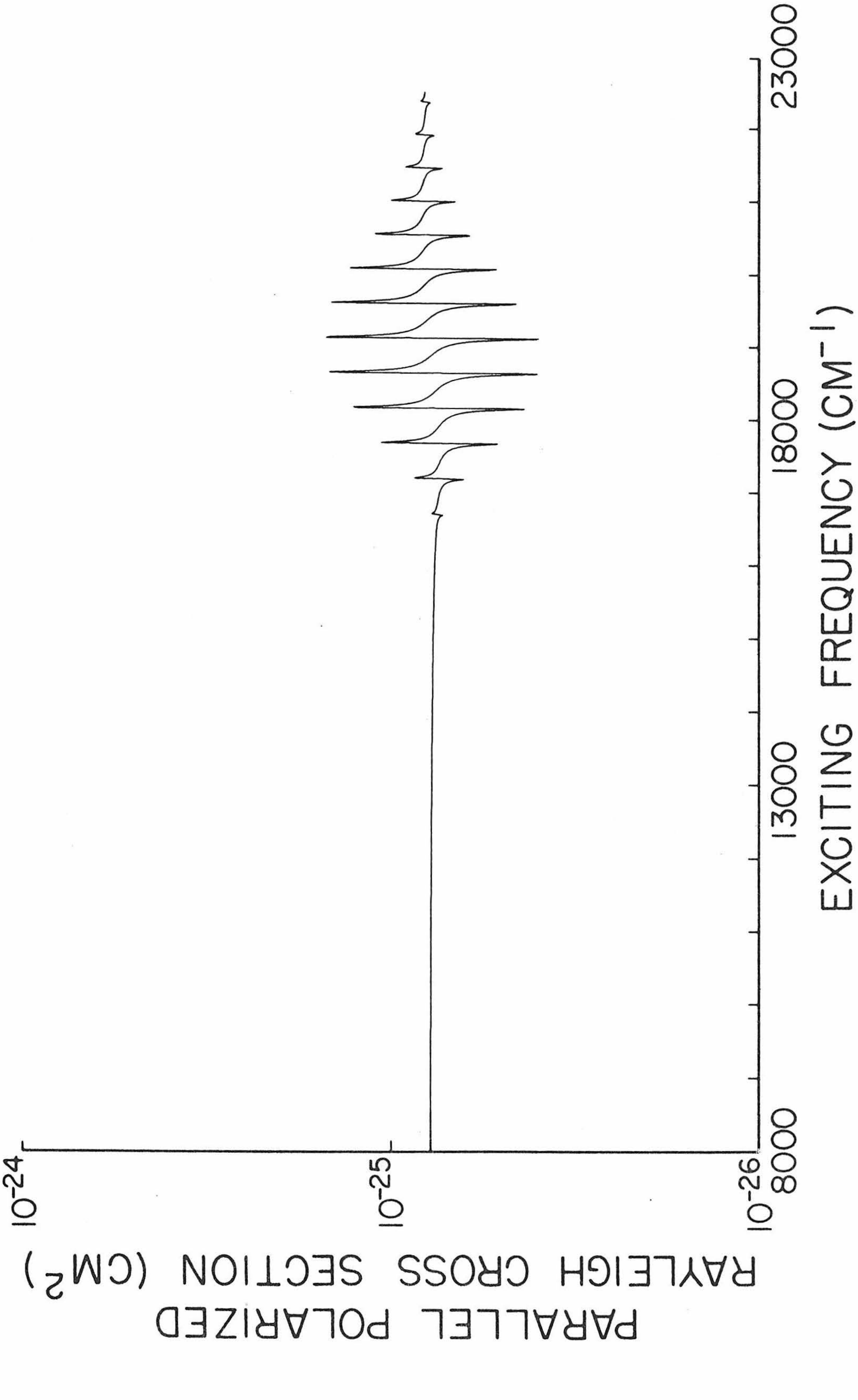
$$\sigma_{abs}(\omega) = \frac{4\pi e^2}{c} |\langle g | \underset{\frown}{r} \cdot \underset{\frown}{\epsilon} | e \rangle|^2 \, \omega \sum_{v'} \frac{|\langle g0 | ev' \rangle|^2 a}{[\hbar\omega - (E_{ev'} - E_{g0})]^2 + a^2} , \qquad (12)$$

where Harris' formula has been divided by two to give agreement with Eq. (11) for on resonance excitation with an isolated resonance. Since Harris derived his formula using the semiclassical $H_{int} = -\underset{\frown}{\mu} \cdot \underset{\frown}{E}$, where $\underset{\frown}{\mu}$ is the dipole moment and $\underset{\frown}{E}$ is the electric field, rather than the quantum mechanical H_{int}, one expects Eq. (11) to be more accurate than Eq. (12). The semiclassical H_{int} cannot take spontaneous emission into account and thus cannot treat properly the loss of photons from a beam due to scattering processes.

From Fig. 1, one can see that on resonance and between the resonances, the cross section calculated from Eq. (11) and that calculated from Eq. (12) are superposable. However, off-resonance the two formulae lead to different results -- Eq. (11) leads to a greater cross section than Eq. (12) below resonance.

The parallel polarized $(\underset{\frown}{\epsilon}' \cdot \underset{\frown}{\epsilon}'' = 1)$ Rayleigh cross section is shown as a function of incoming photon frequency in Fig. 2. It was calculated from Eq. (9). Note that the cross section is essentially constant, only varying right near a resonance. This is due to the fact that the first term in Eq. (9), which does not vary with frequency, dominates except near a resonance.

Figure 2. The parallel polarized ($\underset{\wedge}{\epsilon}' \cdot \underset{\wedge}{\epsilon}'' = 1$) Rayleigh cross section calculated from Eq. (9) is plotted on a log scale in units of cm^2 versus the exciting frequency in wavenumbers.


PARALLEL POLARIZED
RAYLEIGH CROSS SECTION (CM^2)
10^{-24}
10^{-25}
10^{-26}
8000
13000
18000
23000
EXCITING FREQUENCY (CM^{-1})

The perpendicularly polarized ($\underset{\wedge}{\epsilon}' \cdot \underset{\wedge}{\epsilon}'' = 0$) Rayleigh cross section calculated in three different ways is shown in Fig. 3. These calculations are from (1) Eq. (9), (2) Eq. (7), and (3) Eq. (9) without the antiresonance term (the second term in braces). On resonance and between the resonances calculations (1) and (3) are almost identical, with calculation (3) differing only slightly from it (not enough to see in the figure). However, far off resonance (7000-8000 cm^{-1}) the antiresonance terms account for nearly half of the perpendicularly polarized Rayleigh intensity. Also off resonance the calculated cross section using the normal ω^4 dependent formula [Eq. (7)] and the truncated basis set leads to more than an order of magnitude error for excitations off resonance by more than 6000 cm^{-1}.

The excitation profile for the normal Raman process ($v = 0 \rightarrow v = 1$) calculated in the same three ways as the perpendicularly polarized Rayleigh scattering is shown in Fig. 4. The three calculations lead to very different results off resonance--Eq. (7) is unable to predict the off-resonance interference effect, which will be discussed in the next section, and omitting the antiresonance terms shifts its position by over 1000 cm^{-1}. Note that the Raman cross section even 8000 cm^{-1} off resonance is only three orders of magnitude less intense than the perpendicularly polarized Rayleigh intensity. It is also important to stress[35] again that one can get Raman intensity reasonably far off resonance even with the approximation made in Eq. (8b). Thus the Albrecht A term can lead to appreciable Raman intensity off resonance.

Figure 3. The perpendicularly polarized $(\underset{\wedge}{\epsilon}' \cdot \underset{\wedge}{\epsilon}'' = 0)$ Rayleigh cross section calculated in three ways is plotted on a log scale in units of cm^2 versus the exciting frequency in wavenumbers. The solid line is the calculation using Eq. (9), the dashed line is the calculation from Eq. (7) and the dotted line is the calculation from Eq. (9) without the antiresonance term (the second term in braces).

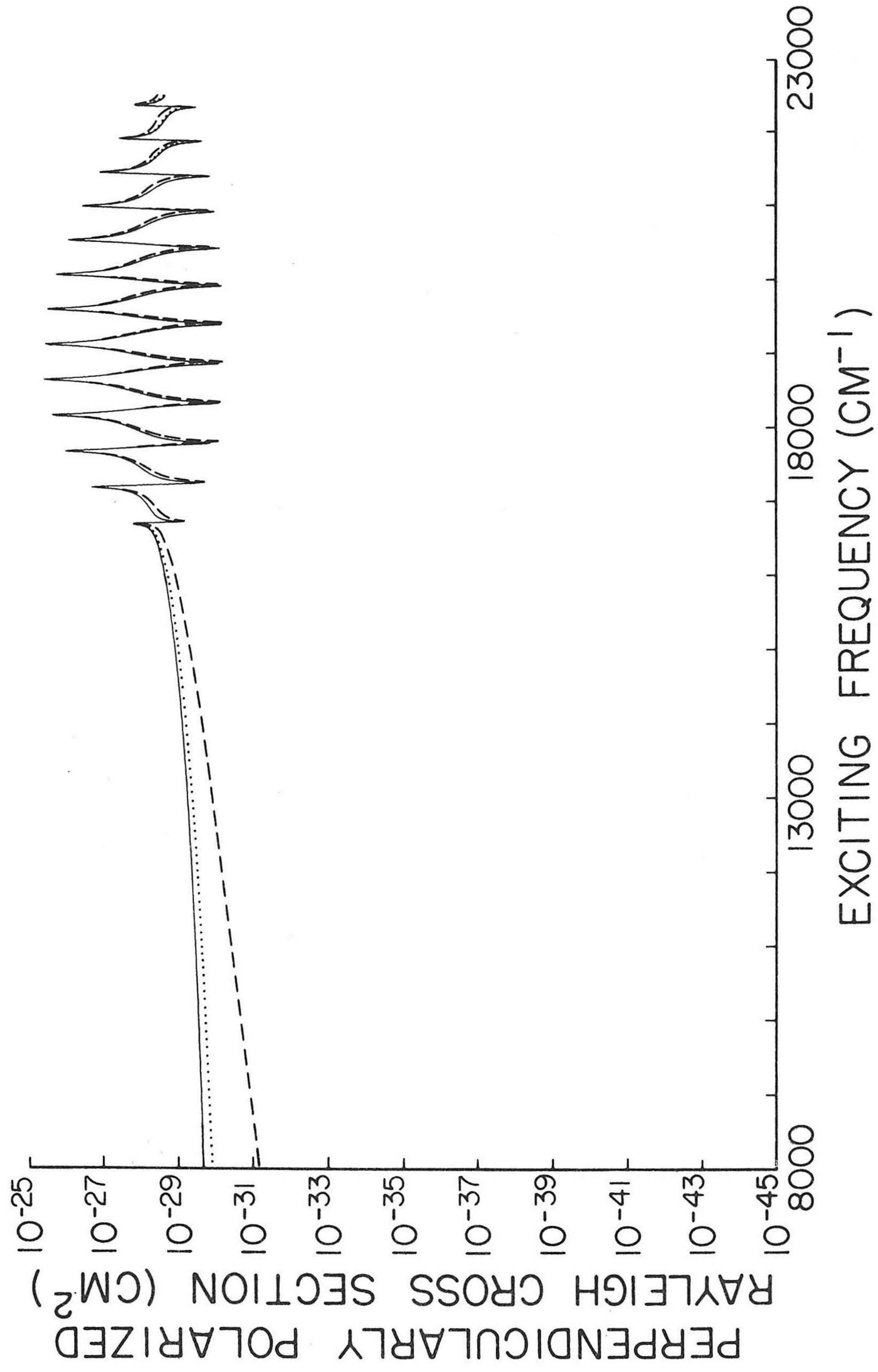
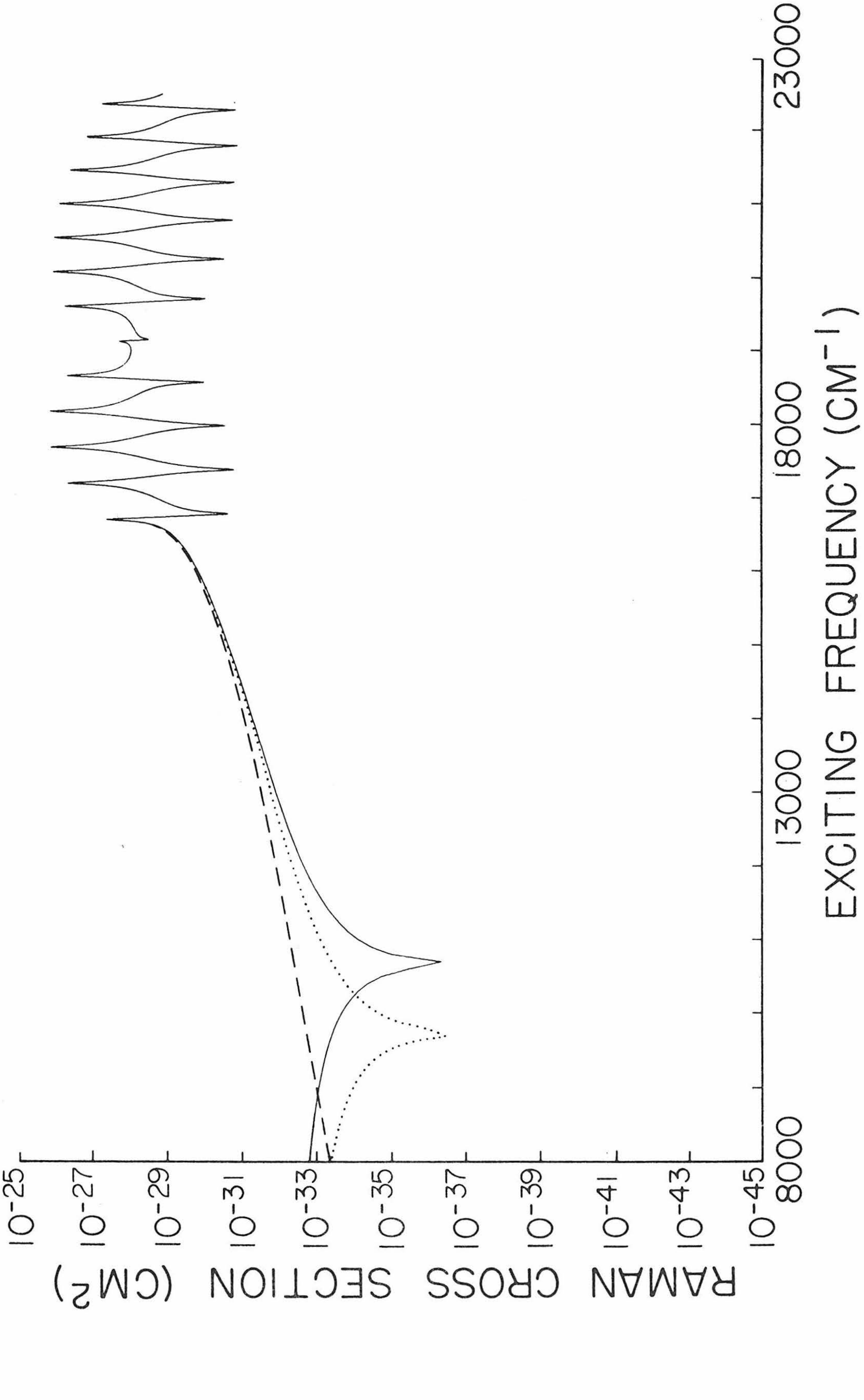

PERPENDICULARLY POLARIZED
RAYLEIGH CROSS SECTION (CM^2)
10^{-25}
10^{-27}
10^{-29}
10^{-31}
10^{-33}
10^{-35}
10^{-37}
10^{-39}
10^{-41}
10^{-43}
10^{-45}
8000
13000
18000
23000
EXCITING FREQUENCY (CM^{-1})

Figure 4. The calculated Raman cross section in cm^2 is plotted on a log scale versus the exciting frequency in wavenumbers. The solid line is the calculation using Eq. (9), the dashed line is the calculation from Eq. (7) and the dotted line is the calculation from Eq. (9) without the antiresonance term (the second term in braces).


RAMAN CROSS SECTION (CM^2)
10^{-25}
10^{-27}
10^{-29}
10^{-31}
10^{-33}
10^{-35}
10^{-37}
10^{-39}
10^{-41}
10^{-43}
10^{-45}
8000
13000
18000
23000
EXCITING FREQUENCY (CM^{-1})

Excitation profiles for the first through fourth overtones of the Raman spectrum are shown in Figs. 5-8. Note that the cross sections for the Raman overtones 8000 cm^{-1} off resonance are more than two orders of magnitude lower than the Raman fundamental. This is in agreement with off resonance experiments where Raman overtones are not observed.[19] For the second, third and fourth overtones, the antiresonance terms account for nearly half the cross section 8000 cm^{-1} off resonance and the calculation using Eq. (7) differs from that using Eq. (9) by more than an order of magnitude for excitations that far off resonance. For the first Raman overtone the errors are small due to a mutual cancellation in each of the sum terms.

V. DISCUSSION

There are three kinds of interferences shown in Figs. 2-7. The first kind is the destructive interference between each of the resonances in Fig. 3. This kind of interference is also shown between most of the resonances in Figs. 4-8. This vibrational level interference is caused by a partial cancellation of the two largest terms (the ones coming from the two resonances on each side) due to their opposite signs between the resonances. These destructive interferences occur only between resonances whose products of Franck-Condon overlaps in Eq. (9) have the same sign. If these overlaps have opposite signs one gets constructive interference between them as, for example, between the fifth and sixth resonances in Fig. 4, and between the second and third and between the sixth and seventh resonances in Fig. 6. These interference effects have been discussed

Figure 5. The cross section for the first overtone of Raman in cm^2 is plotted on a log scale versus the exciting frequency in wavenumbers. The solid line is the calculation using Eq. (9), the dashed line is the calculation from Eq. (7) and the dotted line is the calculation from Eq. (9) without the antiresonance term (the second term in braces).

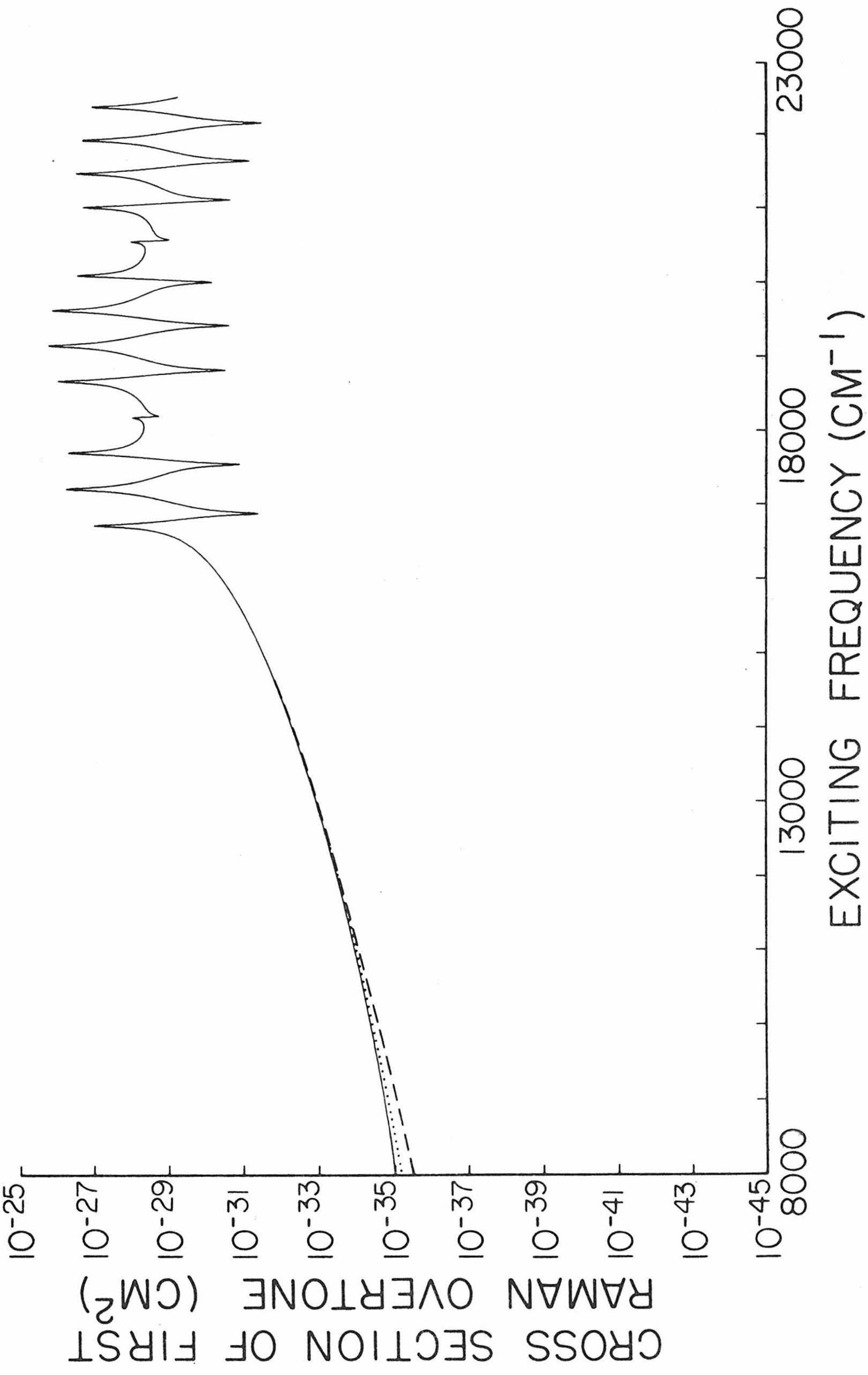

CROSS SECTION OF FIRST
RAMAN OVERTONE (CM^2)
10^{-25}
10^{-27}
10^{-29}
10^{-31}
10^{-33}
10^{-35}
10^{-37}
10^{-39}
10^{-41}
10^{-43}
10^{-45}
8000
13000
18000
23000
EXCITING FREQUENCY (CM^{-1})

Figure 6. The cross section for the second overtone of Raman in cm^2 is plotted on a log scale versus the exciting frequency in wavenumbers. The solid line is the calculation using Eq. (9), the dashed line is the calculation from Eq. (7) and the dotted line is the calculation from Eq. (9) without the antiresonance term (the second term in braces).

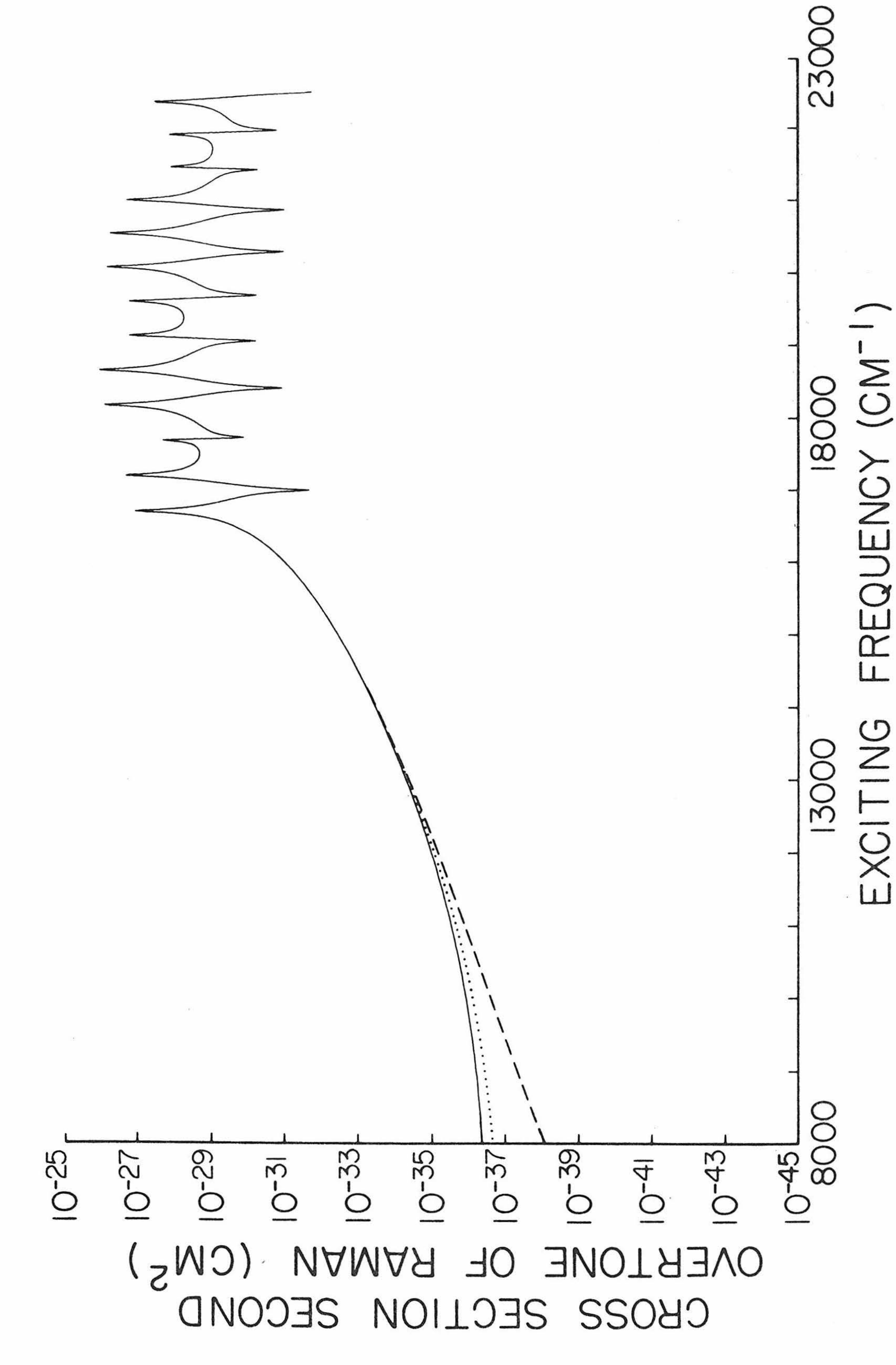

CROSS SECTION SECOND OVERTONE OF RAMAN (CM^2)
10^{-25}
10^{-27}
10^{-29}
10^{-31}
10^{-33}
10^{-35}
10^{-37}
10^{-39}
10^{-41}
10^{-43}
10^{-45}
8000
13000
18000
23000
EXCITING FREQUENCY (CM^{-1})

Figure 7. The cross section for the third overtone of Raman in cm^2 is plotted on a log scale versus the exciting frequency in wavenumbers. The solid line is the calculation using Eq. (9), the dashed line is the calculation from Eq. (7) and the dotted line is the calculation from Eq. (9) without the antiresonance term (the second term in braces).

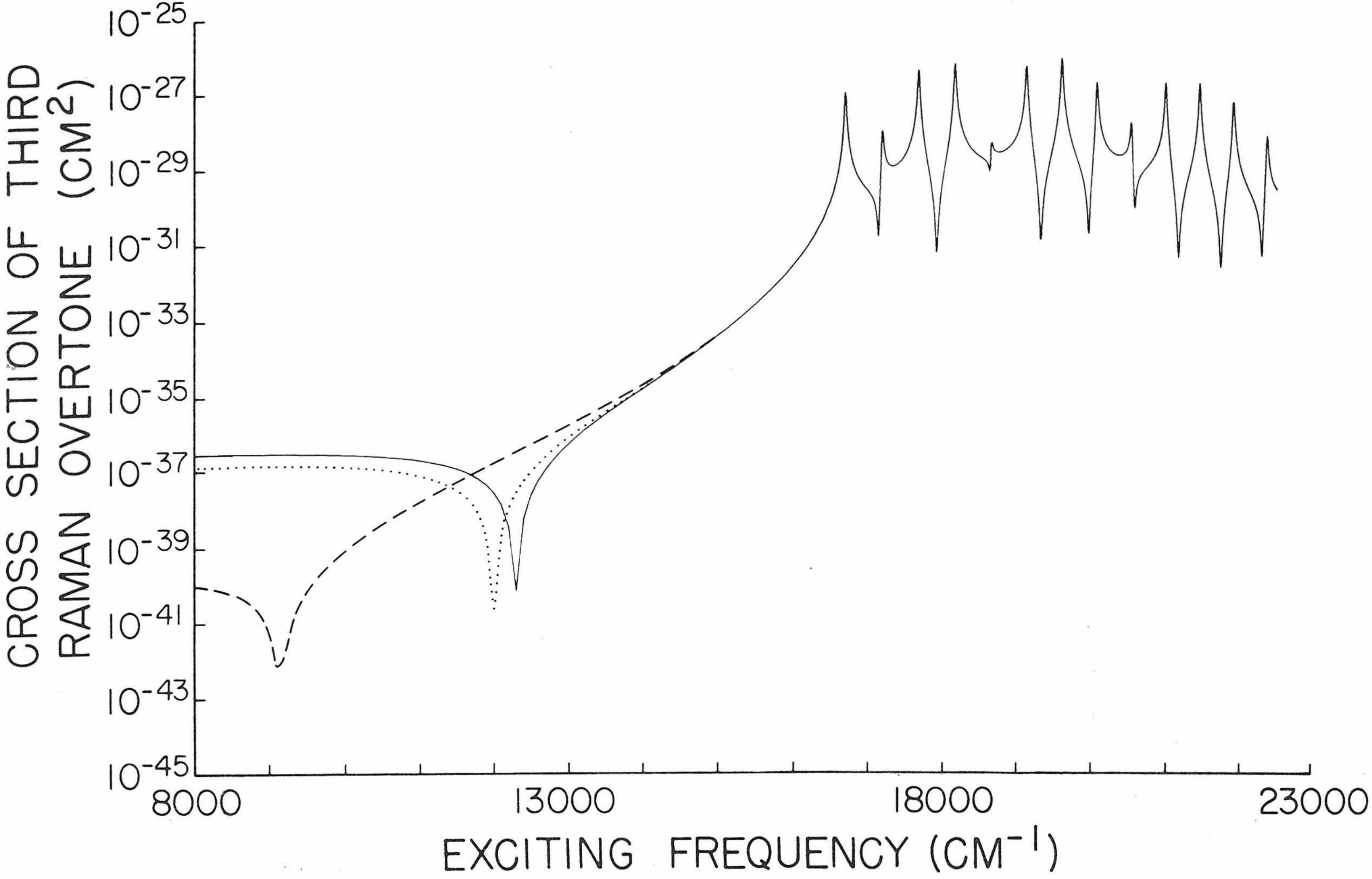
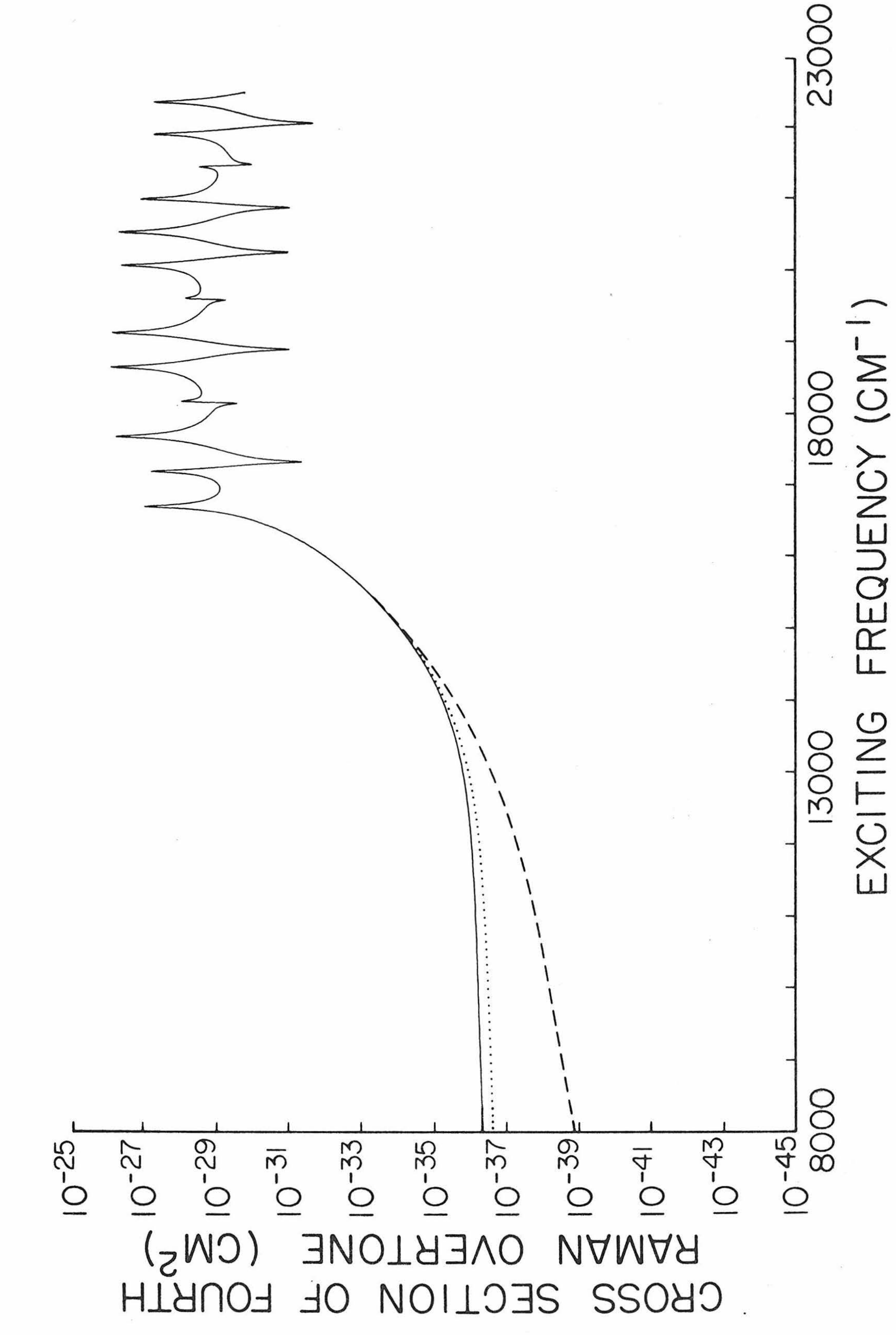

CROSS SECTION OF THIRD RAMAN OVERTONE (CM^2)
10^{-25}
10^{-27}
10^{-29}
10^{-31}
10^{-33}
10^{-35}
10^{-37}
10^{-39}
10^{-41}
10^{-43}
10^{-45}
8000
13000
18000
23000
EXCITING FREQUENCY (CM^{-1})

Figure 8. The cross section for the fourth overtone of Raman in cm^2 is plotted on a log scale versus the exciting frequency in wavenumbers. The solid line is the calculation using Eq. (9), the dashed line is the calculation from Eq. (7) and the dotted line is the calculation from Eq. (9) without the antiresonance term (the second term in braces).


CROSS SECTION OF FOURTH RAMAN OVERTONE (CM^2)
10^{-25}
10^{-27}
10^{-29}
10^{-31}
10^{-33}
10^{-35}
10^{-37}
10^{-39}
10^{-41}
10^{-43}
10^{-45}
8000
13000
18000
23000
EXCITING FREQUENCY (CM^{-1})

in the two-state model in references 16 and 18.

The second type of interference effect is on resonance resulting in a peak that is not nearly as high as the surrounding ones, as for instance in Fig. 4 at the sixth resonance. This is caused by the small Franck-Condon overlaps $\langle ev' | gv'' \rangle$ in Eq. (9) for certain vibrational levels.[12,15]

The third type of interference is the off resonance interference, as in Figs. 4 and 7. This interference effect is caused by a near complete cancellation of the summation. Due to the near equal participation of all of the terms, this type of interference effect is extremely sensitive to the number of terms included in the summation. Even if a complete set of states were included in Eq. (9) or Eq. (7) (which would then be equivalent to each other), such a cancellation could occur. The exact position of such an interference effect is impossible to predict from such a limited calculation.

The resonances in the scattering cross sections sometimes occur a few wavenumbers from the position of the excited state level, but still within the linewidth (2a) of the level. This happens because exactly on the excited state position the real part of the dominant term goes to zero and so the cross terms in the absolute value squared are small since the other terms have much larger real parts than imaginary parts. Thus, even within a few wavenumbers of resonance, the cross terms still make a large contribution, not individually, but because of their number. This effect was also noticed by O. S. Mortensen for a two-state model.[16]

Including other electronic states in the sums in Eq. (9) and Eq. (7) would cause a general increase in the background level, especially since the $X^1\Sigma \rightarrow A^1\Sigma$ transition is fairly weak. This would cause the interference effects between the levels and possibly the resonances themselves not to be as noticeable. Off resonance it would still be possible to get some interference effects in fortuitous cases.

Throughout this paper it has been assumed that all the molecules are originally in their lowest vibrational level which implies a low temperature. At higher temperature one would have more excitation profiles, for example, for the Raman process from $v = 1$ to $v = 2$, and also the anti-Stokes line, from $v = 1$ to $v = 0$. However, everything mentioned above would still hold.

The inclusion of rotations would make the actual Raman spectra more complicated and one would have to add up many nearly degenerate contributions to Raman intensity having a particular outgoing photon.

VI. CONCLUSION

This paper has discussed Raman and Rayleigh scattering from a diatomic molecule. Several interference effects occur even in this simple case. The formulae for the scattering cross sections from our previous paper[20] reduce to the Kramers-Heisenberg second-order perturbation theory results with a damping term included. If resonances having shapes other than the simple Lorentzians assumed here occur, one would have to go back to Eq. (1) and put in a correct Γ. The usual formula used by most resonance Raman spectroscopists leads to errors of several orders of magnitude, more than 6000 cm^{-1} off resonance for BaO, due to the truncated basis set. The anti-resonance terms also contribute nearly 50% of the intensity that far off resonance.

Acknowledgment

The authors wish to thank R. H. Reiner for the use of his programs and assistance in calculating the Franck-Condon overlaps.

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Section E

EXTRACTION OF VIBRONIC INFORMATION FROM TANGLED SPECTRA[*]

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[†] Contribution No. 5301

I. INTRODUCTION

Recently Langhoff and Robinson[1] used a trial-and-error method to obtain a zero-order density function for the origin region of naphthalene's second excited singlet state. Much of the structure in the zero-order density function could be assigned to vibrational levels of the lowest excited singlet state of naphthalene. There were, however, several problems in the procedure they used to get the zero-order density function. First, their procedure was a tedious trial-and-error one where they first guessed a density function, then computed an absorption spectrum from it. They then compared this absorption spectrum to the experimental one given by Wessel,[2] readjusted the density function and so forth until they obtained reasonable agreement between the observed spectrum and the calculated one (40 or more iterations). Second, there was no systematic way to change the peak heights, widths and interactions to converge on a solution. Finally, nothing in their procedure showed that the zero-order density function they had found was unique.

More recently, Hong[3] found a systematic way of finding the zero-order density function. However, this method is as time-consuming as Langhoff and Robinson's trial-and-error procedure.

A new, very simple method of calculating the zero-order density function directly from the absorption spectrum has been discovered which shortens both Hong's and Langhoff and Robinson's procedure. The method also demonstrates that the density function is unique. The purpose of this paper is to describe this method. The results for the density function of naphthalene in the origin region of its second excited singlet state will be given and shown to be in close agreement with those of Langhoff and Robinson.[1]

II. METHOD FOR OBTAINING THE DENSITY FUNCTION

The model that Langhoff and Robinson[1,4] used, and the one that will be used here, consists of a primary state p which carries all the oscillator strength and which interacts with a continuum of states K carrying no oscillator strength.* The above states are eigenstates of some zero-order Hamiltonian $\mathcal{H}_0$ having zero-order eigenvalues ϵ_p and ϵ_K, respectively. The total Hamiltonian $\mathcal{H}$ is given by

$$\mathcal{H} = \mathcal{H}_0 + V \tag{1}$$

where V contains the interactions between the zero-order states. It is furthermore assumed that

$$V_{pp} = V_{KK'} = 0 ; \qquad V_{pK} = V_{Kp} = f_K \quad (f_K , \text{real}). \tag{2}$$

The Green's function at energy λ is defined as

$$G(\lambda) = (\lambda - \mathcal{H})^{-1} . \tag{3}$$

For this model, the real and imaginary parts of the matrix element G_{pp} have been given by Zumino[5] as

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*Hong[3] used a multiple resonance model so his results are not directly comparable.

$$\mathrm{ReG}_{pp}(\lambda) = \frac{\lambda - \epsilon_p - \mathrm{Re}\Gamma(\lambda)}{[\lambda - \epsilon_p - \mathrm{Re}\Gamma(\lambda)]^2 + [\pi f^2(\lambda)\rho(\lambda)]^2} \tag{4a}$$

$$\mathrm{ImG}_{pp}(\lambda) = \frac{-\pi f^2(\lambda)\rho(\lambda)}{[\lambda - \epsilon_p - \mathrm{Re}\Gamma(\lambda)]^2 + [\pi f^2(\lambda)\rho(\lambda)]^2} \tag{4b}$$

$$\Gamma(\lambda) = \int_{-\infty}^{\infty} \frac{f^2(\epsilon_K)\rho(\epsilon_K)\,d\epsilon_K}{\lambda - \epsilon_K} \tag{4c}$$

where $\rho(\epsilon_K)$ is the density of K states at energy ϵ_K. Thus the zero-order weighted density of states is obtained by simply combining eqs. (4a) and (4b),

$$\pi f^2(\lambda)\rho(\lambda) = - \frac{\mathrm{ImG}_{pp}(\lambda)}{[\mathrm{ImG}_{pp}(\lambda)]^2 + [\mathrm{ReG}_{pp}(\lambda)]^2} . \tag{5}$$

Equation (5) shows that the density function for a given G_{pp} is unique.

The absorption cross section $\sigma(\omega)$ at frequency ω for this model is given by[6]

$$\sigma(\omega) = - \frac{4\pi\omega}{c} |\langle 0|\vec{\mu}\cdot\vec{e}|p\rangle|^2 \,\mathrm{ImG}_{pp} \tag{6}$$

where $\langle 0|\vec{\mu}\cdot\vec{e}|p\rangle$ is the transition dipole matrix element from the ground state to the p state and c is the speed of light. There exists a dispersion relationship between the real and imaginary parts of the matrix elements of $G(\lambda)$[7]

$$\mathrm{Re}G_{pp}(\lambda) = \frac{P}{\pi} \int_{-\infty}^{\infty} \frac{\mathrm{Im}G(\lambda')d\lambda'}{\lambda' - \lambda} \tag{7}$$

where P signifies the principal value.

Thus the procedure to calculate the zero-order density function from the absorption cross section has just three steps. First, obtain $\mathrm{Im}G_{pp}$ from $\sigma(\omega)$ using eq. (6). Second, calculate $\mathrm{Re}G_{pp}$ from eq. (7). Finally calculate $\pi f^2(\lambda)\rho(\lambda)$ from eq. (5). Since we care only about the relative value of the density function as a function of energy and we don't know the value of $|\langle 0|\vec{\mu}\cdot\vec{e}|p\rangle|^2$, we can neglect the constants in eq. (6) and obtain $\mathrm{Im}G_{pp}(\lambda)$ by dividing the absorption cross section by ω. One can then calculate $\mathrm{Re}\Gamma$ from eq. (4c) and ϵ_p from

$$\lambda - \epsilon_p = \mathrm{Re}\Gamma(\lambda) + \frac{\mathrm{Re}G_{pp}(\lambda)}{[\mathrm{Re}G_{pp}(\lambda)]^2 + [\mathrm{Im}G_{pp}(\lambda)]^2} \tag{8}$$

keeping in mind that the whole right side of eq. (8) has been multiplied by $(\frac{4\pi}{c}|\langle 0|\vec{\mu}\cdot\vec{e}|p\rangle|^2)^{-1}$ from eq. (6). Thus ratios of $(\lambda - \epsilon_p)$ at different λ's yield ϵ_p and $|\langle 0|\vec{\mu}\cdot\vec{e}|p\rangle|^2$. Using this method the results for naphthalene's second excited singlet state are given in the next section.

III. RESULTS

The model described in the last section applies very well to naphthalene for a short axis polarized absorption spectrum in the origin region of its second excited singlet state ($^1B_{2u}$).[1,2] For this polarization only the origin of $^1B_{2u}$ has any oscillator strength in this region. The states of the lower excited singlet ($^1B_{3u}$) having one quantum of a b_{1g} vibration plus quanta of a_g vibrations borrow oscillator strength from the $^1B_{2u}$ state. Note in general that the results of Langhoff and Robinson[1] have conclusively shown that symmetry selection rules apply to mixing of vibronic states, even in large molecules in a crystalline environment. Thus the zero-order weighted density function should have peaks where these "allowed" states occur. Other peaks in the density function could correspond to phonon additions of the proper symmetry to the $^1B_{3u}$ state.

The zero-order density function for the S_2 origin region of naphthalene-h_8 in p-xylene is given in fig. 1. Also given are Langhoff and Robinson's density function[1] and Wessel's absorption spectrum[2] for the same region.* Our density function was calculated from Wessel's spectrum after subtracting out his linearly increasing baseline (see fig. 1a). If one instead assumes a flat baseline, the density function peak positions do not change by more than 1 cm^{-1},

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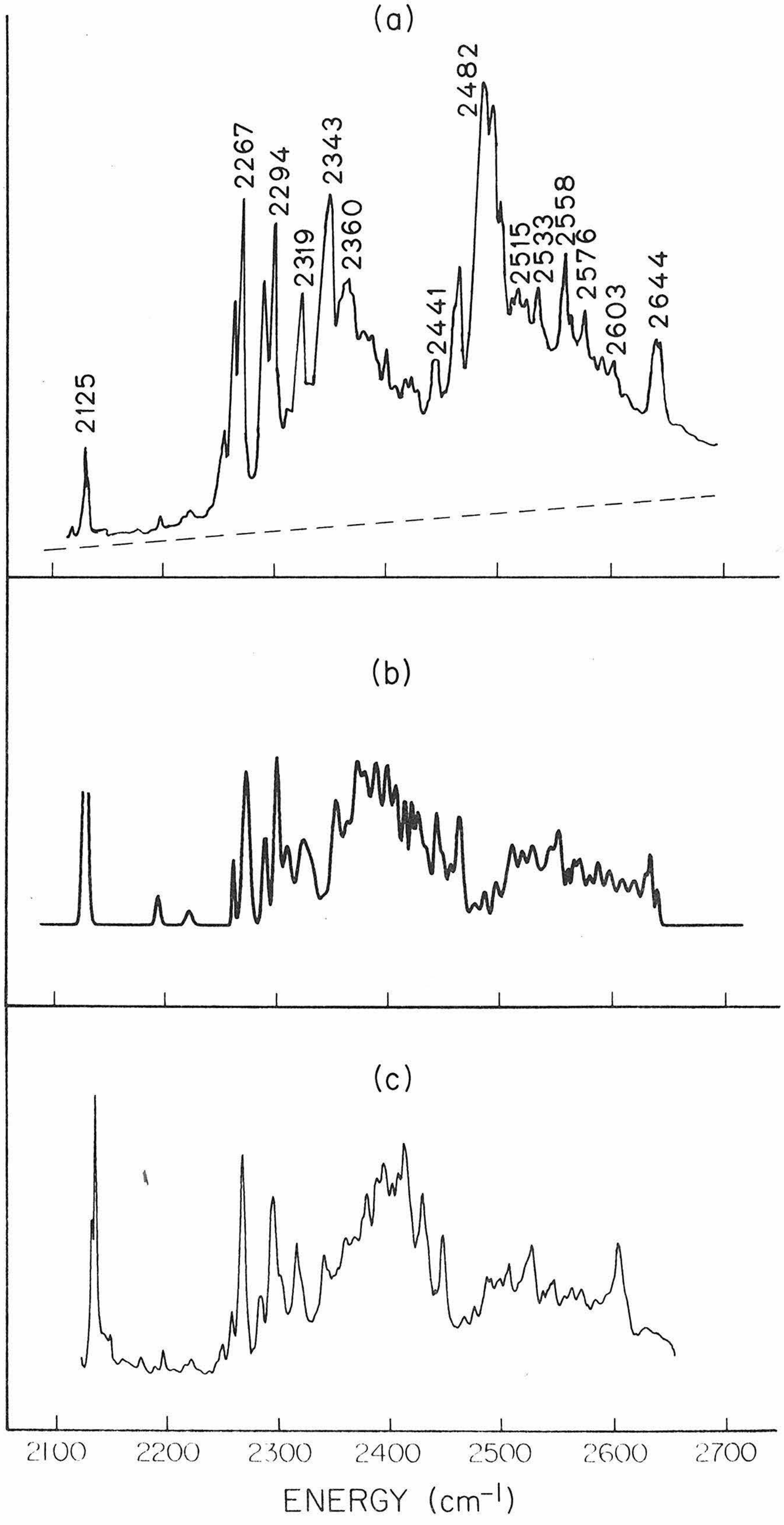
*Hong's density function[3] was not reproduced since he did not try to maximize his fit of the absorption spectrum but only used Langhoff and Robinson's parameters.

Figure 1. (a) The observed absorption spectrum from Wessel's thesis[2] plotted versus the energy in cm^{-1} above the first singlet excited state. The dashed line is his linearly increasing baseline. (b) Langhoff and Robinson's weighted density function.[1] (c) Our weighted density function calculated from eqs. (5), (6), and (7) and Wessel's spectrum. The y-axis is scaled in arbitrary units for all three curves.


(a)
2125
2267
2294
2319
2343
2360
2441
2482
2515
2533
2558
2576
2603
2644
(b)
(c)
2100
2200
2300
2400
2500
2600
2700
ENERGY (cm⁻¹)

but the relative peak heights do change. It is apparent from fig. 1 that, as noticed by Langhoff and Robinson,[1] the peaks in the density function in the perturbed region correspond to valleys in the absorption spectrum and vice versa.

Table 1 gives the values of the frequencies of the b_{1g} and a_g modes of naphthalene-h_8 in p-xylene. Slight adjustments were made in the frequencies from the values given in ref. (1) in order to fit the data better. Table 2 lists the values and assignments (if possible) of most peaks and shoulders in the density function and compares them to the calculated values using Table 1 and to Langhoff and Robinson's peak values. It is apparent from Table 2 that the results of the method described here are in reasonable agreement with the Langhoff and Robinson results. Peaks and shoulders were assigned if they agreed to within ± 3 cm^{-1} with the calculated values. Fifty-nine percent of the peaks and shoulders could be assigned. More importantly, out of the possible 45 peaks (with one quantum of a b_{1g} mode plus quanta of a_g modes) that could appear in this region, 36 occurred. An additional three of the possible peaks would have appeared within eight cm^{-1} of the edges, where, as discussed below, our density function is less accurate. Most of the other possible peak positions fall near visible asymmetries in the density function peaks. These were not assigned as shoulders due to the imprecision involved in establishing the position of the underlying peak. The ${}^1B_{2u}$ origin (ϵ_p) was calculated from eq. (8) to be at 2430 cm^{-1}, while Langhoff and Robinson put it at 2433 cm^{-1}. $|\langle 0|\vec{\mu}\cdot\vec{e}|p\rangle|^2$ could not be calculated since Wessel did not give $\sigma(\omega)$ in any absolute units.

Table 1

Frequencies of the a_g and b_{1g} modes of the lowest excited singlet state of naphthalene-h_8 in p-xylene

	a_g (cm^{-1})	b_{1g} (cm^{-1})
1	- -	- -
2	- -	- -
3	1495 (0)	1624 (0)
4	1424 (+2)	- -
5	1397 (0)	1236 (+1)
6	1142 (-2)	1053 (+1)
7	996 (-1)	903 (0)
8	707 (0)	424 (0)
9	502 (0)	- -

Numbers in parentheses are our values minus the values given by (1).

Table 2

Positions and assignments of peaks in our zero-order density function for naphthalene-h_8 in p-xylene in the origin region of its second singlet excited state

Position$^{(a)}$	Assignment$^{(b)}$ b_{1g}, a_g	Calculated$^{(c)}$ freq. (cm^{-1})	Langhoff-Robinson$^{(d)}$ peak^1
2135	8, 8 + 2×9	2135	- -
2138			- -
2144 (sh)	- -	- -	- -
2151	- -	- -	- -
2162 (br)	- -	- -	- -
2178	- -	- -	- -
2191	- -	- -	- -
2198	6, 6	2195	2194
2208 (w, br)	- -	- -	- -
2218 (w)	- -	- -	- -
2223	- -	- -	2222
2231 (sh)	5, 7	2232	- -
2240	5, 2×9	2240	- -
2252	- -	- -	- -
2260	6, 8 + 9	2261	2262
2270	8, 6 + 8	2273	2273
2286	- -	- -	- -
2297	7, 5	2300	2301
2303 (sh)			
2318	7, 2×8	2317	- -

Table 2 (continued)

Position[(a)]	Assignment[(b)] b_{1g}, a_g	Calculated[(c)] freq. (cm^{-1})	Langhoff-Robinson[(d)] peak[1]
2342	8, 2×8+9	2340	2343
2347 (sh)	- -	- -	- -
2351 (w)	8, 4+9	2350	2353
2355 (sh)	- -	- -	
2362	- -	- -	2364
2370	- -	- -	2372
2378 (sh)			
2381	5, 6	2378	2379
2390	- -	- -	2389
2396	7, 3	2398	2399
2404	7, 7+9	2401	
2409	7, 3+9	2409	2407
2414	8, 2×7	2416	2415
2431	8, 4× 9	2432	2434
2442	5, 8+9	2445	2444
2449	6, 5	2450	2449
2468	6, 2×8	2467	2464
2477	6, 4	2477	2477
2488	- -	- -	2486
2492	- -	- -	- -
2500	- -	- -	- -
2508	- -	- -	2505 2511

Table 2 (continued)

Position[(a)]	Assignment[(b)] b_{1g}, a_g	Calculated[(c)] freq. (cm^{-1})	Langhoff-Robinson[(d)] peak[1]
2516 (sh)	- -	- -	2519
2528	8, 5+8	2528	2528
2538	- -	- -	2538
2543 (sh)	8, 3×8	2545	2545
2545	7, 6+9	2547	
	6, 3	2548	
2548			
	6 7+9	2551	2552
2557	6 3×9	2559	2560
2564	8, 6+7	2562	2565
2572	8, 6+2×9	2570	2571
2578	- -	- -	2580
2585	- -	- -	2587
2595 (sh)	- -	- -	2597
2605	7, 7+8	2606	2608
2621 (w)	3, 7	2620	2619
2629-31 (br)	8, 3+8	2626	2629
	3, 2×9	2628	
	8, 7+8+9	2629	2634
	5, 5	2633	
2640 (sh, br)	8, 8+3×9	2637	2640

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[a] In cm^{-1} above the origin of the first excited singlet state ($^1B_{3u}$). sh = shoulder, br = broad, w = weak.

Table 2 (foonotes continued)

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[b] Assigned within ± 3 cm^{-1}, 59% of our peaks could be assigned.

[c] Calculated from table 1.

[d] Peaks given if assigned same way as our peak; if not assigned then if within ± 3 cm^{-1} of ours.

Errors in the results come mainly from two sources. First, the spectrum of Wessel's[2] used in eq. (6) was a copy from his thesis. The pen lines were 1-2 cm^{-1} wide. Thus digitization of this spectrum was accurate to only 2 cm^{-1} or so. Second, instead of integrating from $-\infty$ to $+\infty$ in eq. (7), integration was only over the region of the absorption spectrum. The true spectrum could not be used beyond this region since a_g additions to the S_2 origin start absorbing and the model breaks down. It was felt unknown errors would be introduced by trying to extrapolate the spectrum for the model as a Gaussian or Lorentzian outside this region. Integration only over a finite interval leads to an underestimate of the density function near the end points but gives very good results away from the edges. This was ascertained by applying the method to a Lorentzian $\text{Im}G_{pp}$ which should lead to a completely constant density function.

IV. CONCLUSION

A procedure for obtaining the zero-order density function directly from an absorption spectrum has been found. This method should greatly aid experimentalists in untangling complicated vibronic spectra and should further help to simplify and illuminate the relationship between spectral shape and radiationless transitions in complex polyatomic molecules.

ACKNOWLEDGMENTS

The author thanks Professor G. W. Robinson for encouragement and for valuable comments on the manuscript, Professor C. A. Langhoff for helpful discussions and Dr. J. E. Wessel for providing a copy of his Ph.D. thesis and for permission to use the data and reproduce one of his spectra.

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MATHEMATICAL APPENDICES

The key formulae and equations needed in sections A through E are (1) the formula for the cross section for a transition in terms of the T matrix, which is used in sections C and D, (2) the formula for the absorption cross section in terms of the T matrix, which is used in section D, (3) the dispersion relation between the real and imaginary parts of G, used in section E, (4) Dyson's equation, which is used to derive the matrix elements of G in all five sections, and (5) the formula for the probability of being in the excited state as a function of time when a light source having width in time and frequency is used to excite the system, which is used in sections A and B. The proofs of these formulae will be given in appendices one through five respectively.

APPENDIX 1 (condensed from reference 1)

Define S_{fi}, which is the transition amplitude for the system which is in state i at $t = -\infty$ to make a transition to state f at $t = \infty$, as

$$S_{fi} = \langle \psi_f^- | \psi_i^+ \rangle \tag{1-1}$$

where $\psi_a^\pm$ satisfy the Lippmann-Schwinger equations

$$\psi_a^\pm = \Phi_a + \lim_{\eta \to 0^+} \frac{1}{E_a - H_0 \pm i\eta} H_{int} \psi_a^\pm \, . \tag{1-2}$$

The total Hamiltonian is

$$H = H_0 + H_{int} \, , \tag{1-3}$$

and Φ_a and $\psi_a^\pm$ are eigenfunctions respectively of H_0 and H with the same eigenvalue E_a. That is,

$$H_0 \Phi_a = E_a \Phi_a \tag{1-4}$$

and

$$H \psi_a^\pm = E_a \psi_a^\pm \, . \tag{1-5}$$

The Lippmann-Schwinger equations can be proven using Eqs. (1-3) to (1-5). $\psi_a^\pm$ can also be shown to satisfy

$$\psi_a^\pm = \Phi_a + \lim_{\eta \to 0^+} \frac{1}{E_a - H \pm i\eta} H_{int} \Phi_a \, . \tag{1-6}$$

The T matrix or transition matrix is defined by

$$S_{fi} = \delta_{fi} - 2\pi i \delta (E_i - E_f) T_{fi} \, . \tag{1-7}$$

Now if one defines

$$S_{fi}^{\tau} = -T_{fi} \; i/\hbar \int_{-\tau/2}^{\tau/2} e^{i(E_i - E_f)t/\hbar} dt \tag{1-8}$$

one can show that

$$S_{fi} = \lim_{\tau \to \infty} S_{fi}^{\tau} \tag{1-9}$$

using

$$\pi \, \delta(x) = \lim_{\tau \to \infty} \frac{\sin x\tau}{x} \tag{1-10}$$

and

$$\delta(ax) = a^{-1} \delta(x) \, . \tag{1-11}$$

The transition amplitude per unit time ($W_{f \leftarrow i}$) can be defined as

$$W_{f \leftarrow i} = \lim_{\tau \to \infty} \frac{|S_{fi}^{\tau}|^2}{\tau} \, . \tag{1-12}$$

Then one can show

$$W_{f \leftarrow i} = \frac{2\pi}{\hbar} |T_{fi}|^2 \, \delta(E_i - E_f) \tag{1-13}$$

using

$$\pi \, \delta(x) = \lim_{\tau \to \infty} \frac{\sin^2 \tau x}{\tau x^2} \, . \tag{1-14}$$

The cross section is given by

$$\sigma_{f \leftarrow i} = \frac{W_{f \leftarrow i}}{F} \tag{1-15}$$

where F is the flux in units of particles (or photons) per cross sectional area per unit time. For a one-photon wavepacket this flux is c/V, where c is the speed of light and V is the volume of the system.

Now if one uses Eqs. (1-1) and (1-6) one can show

$$S_{fi} = \langle \Phi_f | \psi_i^+ \rangle + \frac{1}{E_f - E_i + i\eta} \langle \Phi_f | H_{int} | \psi_i^+ \rangle . \tag{1-16}$$

If one then uses Eq. (1-2) and the further definition

$$\pi \delta (x) = \lim_{\eta \to 0} \frac{\eta}{\eta^2 + x^2} \tag{1-17}$$

one gets

$$S_{fi} = \delta_{fi} - 2\pi i \delta(E_i - E_f) \langle \Phi_f | H_{int} | \psi_i^+ \rangle . \tag{1-18}$$

Comparing this formula with Eq. (1-7) shows

$$T_{fi} = \langle \Phi_f | H_{int} | \psi_i^+ \rangle . \tag{1-19}$$

Using Eq. (1-6) again one gets

$$T = H_{int} + H_{int} G H_{int} \tag{1-20}$$

where the Green's function G is defined as

$$G = (E - H + i\eta)^{-1} , \tag{1-21}$$

and it is understood that T must be evaluated between eigenstates of H_0 and that the E in Eq. (1-21) is the zero-order energy of the eigenstate on which it acts.

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APPENDIX 2 (condensed from reference 1)

The absorption cross section from a state a is given by

$$\sigma_{\text{abs}}^{a} = \sum_{b} \sigma_{b \leftarrow a} \, . \tag{2-1}$$

Using Eqs. (1-13) and (1-15) one gets

$$\sigma_{\text{abs}}^{a} = \frac{2\pi V}{\hbar c} \sum_{b} \left| T_{ab} \right|^{2} \delta(E_a - E_b) \, . \tag{2-2}$$

Since the states ψ_a^- form an orthonormal set (this can be proven using Eq. (1-2) and the orthonormality of the states Φ_a) one can show that

$$(S S^{\ddagger})_{ab} = \delta_{ab} \tag{2-3}$$

where $S_{ab}^{\ddagger}$ is the Hermitian conjugate of S_{ab}, that is

$$S_{ab}^{\ddagger} = S_{ba}^{*} \, . \tag{2-4}$$

Equation (2-3) proves that S is unitary. Now one can show using Eqs. (2-3) and (1-7)

$$i \delta (E_a - E_b)(T_{ab} - T_{ab}^{\ddagger}) = 2\pi \sum_{c} \delta(E_a - E_c) \, \delta(E_c - E_b) \, T_{ac} T_{cb}^{\ddagger} \, . \tag{2-5}$$

By the properties of the delta function this is equivalent to

$$i \delta (E_a - E_b)(T_{ab} - T_{ab}^{\ddagger}) = 2\pi \delta (E_a - E_b) \sum_{c} \delta(E_c - E_b) \, T_{ac} T_{cb}^{\ddagger} \, . \tag{2-6}$$

Canceling the equivalent delta functions on both sides and letting a = b, one gets

$$\text{Im } T_{aa} = -\pi \sum_{c} |T_{ac}|^2 \, \delta(E_c - E_b) \qquad (2\text{-}7)$$

where Im means the imaginary part. Therefore from Eq. (2-2)

$$\sigma^{a}_{abs} = -\frac{2V}{c\hbar} \text{ Im } T_{aa} \, . \qquad (2\text{-}8)$$

REFERENCE

1. P. Roman, Advanced Quantum Theory (Addison-Wesley, Reading, Mass., 1965) pp. 334-336.

APPENDIX 3 (basic steps taken from reference 1)

From the well-known formula[1,2]

$$\frac{1}{\omega \pm i\eta} = P\frac{1}{\omega} \mp i\pi\,\delta(\omega) \tag{3-1}$$

where P stands for the principal value, η is a small positive number and the limit $\eta \to 0$ is understood, one can show

$$\oint \frac{G(\omega')d\omega'}{\omega - \omega' - i\eta} = P\int_{-\infty}^{\infty} \frac{d\omega' G(\omega')}{\omega - \omega'} + i\pi G(\omega) \ , \tag{3-2}$$

where $G(\omega)$ is defined by Eq. (1-21). In Eq. (3-2) the Cauchy integral goes along the real axis and closes in the upper half plane. However by Cauchy's theorem this contour integral is zero since the integrand has no poles in the upper half plane. Therefore

$$i\pi \operatorname{Re} G(\omega) - \pi \operatorname{Im} G(\omega) = -P\int_{-\infty}^{\infty} \frac{d\omega' \operatorname{Re} G(\omega')}{\omega - \omega'} - i\,P\int_{-\infty}^{\infty} \frac{d\omega' \operatorname{Im} G(\omega')}{\omega - \omega'} \tag{3-3}$$

where Re and Im stand for the real and imaginary parts. Equating imaginary parts of Eq. (3-3) one gets

$$\operatorname{Re} G(\omega) = \frac{P}{\pi}\int_{-\infty}^{\infty} \frac{d\omega' \operatorname{Im} G(\omega')}{\omega' - \omega} \ . \tag{3-4}$$

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APPENDIX 4

From the definition of H (1-3), one can write

$$\lambda - H + i\eta = \lambda - H_0 + i\eta - H_{int} . \qquad (4-1)$$

Multiplying on the left by $(\lambda - H_0 + i\eta)^{-1} \equiv G_0$, one gets

$$G_0(\lambda - H + i\eta) = 1 - G_0 H_{int} . \qquad (4-2)$$

Now multiplying on the right by $(\lambda - H + i\eta)^{-1} \equiv G$, and rearranging one gets Dyson's equation

$$G = G_0 + G_0 H_{int} G . \qquad (4-3)$$

APPENDIX 5 (from references 1, 2 and 3)

The time evolution operator in the interaction representation is given by[1,2]

$$U(t,t') = e^{i/\hbar H_0 t}\, e^{-i/\hbar H(t-t')}\, e^{-i/\hbar H_0 t'} , \tag{5-1}$$

One can define[2]

$$U(t,-\infty) = \lim_{\epsilon \to 0^+} \epsilon \int_{-\infty}^{0} e^{\epsilon t'}\, U(t,t')\, dt' . \tag{5-2}$$

Putting (5-1) into (5-2) and using (1-4), one gets

$$U(t,-\infty)|\Phi_a\rangle = e^{i/\hbar H_0 t}\, e^{-i/\hbar Ht} \lim_{\epsilon \to 0^+} \epsilon \int_{-\infty}^{0} e^{\epsilon t'}\, e^{i/\hbar Ht'}\, e^{-i/\hbar E_a t'}\, dt' |\Phi_a\rangle \tag{5-3}$$

Now, performing the integral, Eq. (5-3) becomes

$$U(t,-\infty)|\Phi_a\rangle = e^{i/\hbar H_0 t}\, e^{-i/\hbar Ht} \lim_{\eta \to 0^+} \frac{i\eta}{E_a - H + i\eta} |\Phi_a\rangle \tag{5-4}$$

where $\eta = \hbar\epsilon$. Rearranging this equation one gets

$$U(t,-\infty)|\Phi_a\rangle = e^{i/\hbar H_0 t}\, e^{-i/\hbar Ht} [1 - \lim_{\eta \to 0^+} \frac{E_a - H}{E_a - H + i\eta}] |\Phi_a\rangle . \tag{5-5}$$

Now if one uses Eqs. (1-3) and (1-4), Eq. (5-5) becomes

$$U(t,-\infty)|\Phi_a\rangle = e^{i/\hbar H_0 t}\, e^{-i/\hbar Ht} [1 + \lim_{\eta \to 0^+} \frac{1}{E_a - H + i\eta} H_{int}] |\Phi_a\rangle . \tag{5-6}$$

But from Eq. (1-6)

$$[1 + \frac{H_{int}}{E_a - H + i\eta}]\,|\Phi_a\rangle = |\psi_a^+\rangle \tag{5-7}$$

so

$$U(t,-\infty)|\Phi_a\rangle = e^{i/\hbar H_0 t}\, e^{-i/\hbar E_a t}[1 + \lim_{\eta\to 0^+} \frac{1}{E_a - H + i\eta} H_{int}]|\Phi_a\rangle . \tag{5-8}$$

This is essentially the equation given in reference 1.

If the initial state at $t = -\infty$ is given by a one-photon wavepacket with amplitude $S(\omega)$ at frequency ω and the molecule in its ground state (g0), then

$$|\Phi_a\rangle = \int d\omega\, S(\omega)\,|g0,\omega\rangle . \tag{5-9}$$

So the wavefunction of this system at time t is

$$\begin{aligned}\psi(t) &= U(t,-\infty)|\Phi_a\rangle = \\ &= \sum_j e^{i/\hbar H_0 t} \int d\omega\, e^{-i\omega t}\, S(\omega)\ (|g0,\omega\rangle + G|j\rangle\langle j|H_{int}|g0,\omega\rangle)\end{aligned} \tag{5-10}$$

where the sum over j is over a complete set of states. For the model used in section A of this thesis, only the state p has oscillator strength. So the probability of being in state $|p,0\rangle$, where 0 signifies the vacuum state of the field, is

$$|\langle p,0|\psi(t)\rangle|^2 = |\int_{-\infty}^{\infty} d\omega\, e^{-i\omega t} S(\omega)\, G_{pp}(\omega)\langle p,0|H_{int}|g0,\omega\rangle|^2 . \tag{5-11}$$

Using the definition

$$S(\omega) = \int_{-\infty}^{\infty} e^{i\omega t'}\, S(t')\, dt' \tag{5-12}$$

Eq. (5-11) becomes

$$|\langle p,0|\psi(t)\rangle|^2 = |\int_{-\infty}^{\infty} dt' S(t') \int_{-\infty}^{\infty} d\omega\, e^{-i\omega(t-t')} G_{pp}(\omega)\langle p,0|H_{int}|g0,\omega\rangle|^2. \tag{5-13}$$

But since the poles of $G_{pp}(\omega)$ are only in the lower half plane the ω integral is zero unless $t > t'$. Therefore

$$|\langle p,0|\psi(t)\rangle|^2 = |\int_{-\infty}^{t} dt' S(t') \int_{-\infty}^{\infty} d\omega\, e^{-i\omega(t-t')} G_{pp}(\omega)\langle p,0|H_{int}|g0,\omega\rangle|^2. \tag{5-14}$$

This equation is exactly equal to Eq. (7) of section A except for factors of 2π and the presence of the H_{int} matrix element. If this matrix element does not depend on ω (as is usually assumed[1]), then the time-dependences from the two equations are equal.

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PROPOSITIONS

Proposition 1

MOLECULAR DYNAMICS STUDY OF THE INFINITE DILUTION CONDUCTANCE OF AN ION IN WATER

There is as of now no accurate theory predicting the infinite dilution conductances of small ions in water.[1,2] The best attempt so far is Zwanzig's[3] theory of dielectric friction which seems to show the right trends but gives conductances that are too low. One effect which has not yet been considered[1,2,4] is the effect of dielectric saturation on the force of the ion, but no one has been able to say what the true force should be. The above theories all use a continuum or hydrodynamic approach.

On the other hand, various groups have done molecular dynamics studies on pure water,[5-7] on water with an ion present[8] and on a diatomic polar liquid with an ion present.[9] In these studies, various potentials for the interactions between two water molecules and between a water molecule (or other polar molecule) and an ion have been used. The Ben-Naim-Stillinger[10] potential seems to give fairly accurate diffusion constants and other properties for water, which implies that the potential is reasonably good.

It is proposed therefore to use molecular dynamics and the Ben-Naim-Stillinger[10] model for water to study the conductances of ions in water at infinite dilution. In particular one would hope to gain insight into the environment of the ion and the real force acting on it, as well as the effects of the ion's charge and size.

Most theories on ionic conductances at infinite dilution start with Stokes'[11] law for the force on a spherical particle moving through a viscous medium

$$F = 6\pi\eta va \tag{1}$$

where F is the viscous drag force on the particle, η is the viscosity coefficient, v is the velocity of the particle and a is its radius. One assumption that Stokes used in deriving Eq. (1) was that the particle was much larger than the molecules of the medium and hence there was no relative motion at the surface of the particle with respect to the medium (a "stick" boundary condition). Clearly this assumption is not valid for the motion of an ion in water. Basset[12] recomputed Stokes' law for a "slip" boundary condition. For total slip at the surface of the particle the "6π" in Eq. (1) would be changed to a "4π".

Boyd[13] and Zwanzig[3,14] derived the additional force on the ion due to dielectric friction from the rotating dipoles in the vicinity of the ion. Zwanzig's[3] final result was

$$F = \text{"}4\pi\text{"}\,\eta v a + (B/a^3)\,v \tag{2}$$

where

$$B = 3\,Z^2 e^2 [(\epsilon_0 - \epsilon_{00})/(4\epsilon_0 (2\epsilon_0 + 1))]\tau \tag{3}$$

for the slip boundary condition where ϵ_0 is the static dielectric constant of the medium, ϵ_{00} is the high frequency dielectric constant, Ze is the charge on the ion, and τ is the dielectric relaxation time. The 4π is in quotation marks because it could be as high as 6π depending on the slip at the surface of the ion.

Now the equivalent conductance is defined[15] to be

$$\Lambda = I\,\ell\,\tilde{V}/(\Delta\Phi)(A) \tag{4}$$

where I is the current of ions, ℓ is the length of the cell, $\tilde{V}$ is the volume per equivalent of charge of the ion, $\Delta\Phi$ is the difference in electric potential between the terminals and A is the cross-sectional area of the plates. Now

$$A\ell = \tilde{V} \tag{5}$$

if the cell contains one equivalent of the ion. Also

$$I = \tilde{\mathfrak{F}} v/\ell \tag{6}$$

where $\tilde{\mathfrak{F}}$ is the Faraday (the charge on a mole of electrons). Putting Eqs. (5) and (6) into Eq. (4) one gets

$$\Lambda = \tilde{\mathfrak{F}} v\ell/(\Delta\Phi) \ . \tag{7}$$

But the force on the ion at infinite dilution is traditionally given as $Ze\,\Delta\Phi/\ell$. At equilibrium this force must be equal to the viscous drag as given by Eq. (2) giving

$$Ze\,\Delta\Phi/\ell = Ze\,\tilde{\mathfrak{F}} v/\Lambda_0 = \text{"}4\pi\text{"}\,\eta va + (B/a^3)\,v \tag{8}$$

where Λ_0 is the equivalent conductance at infinite dilution. Finally solving for Λ_0 one gets

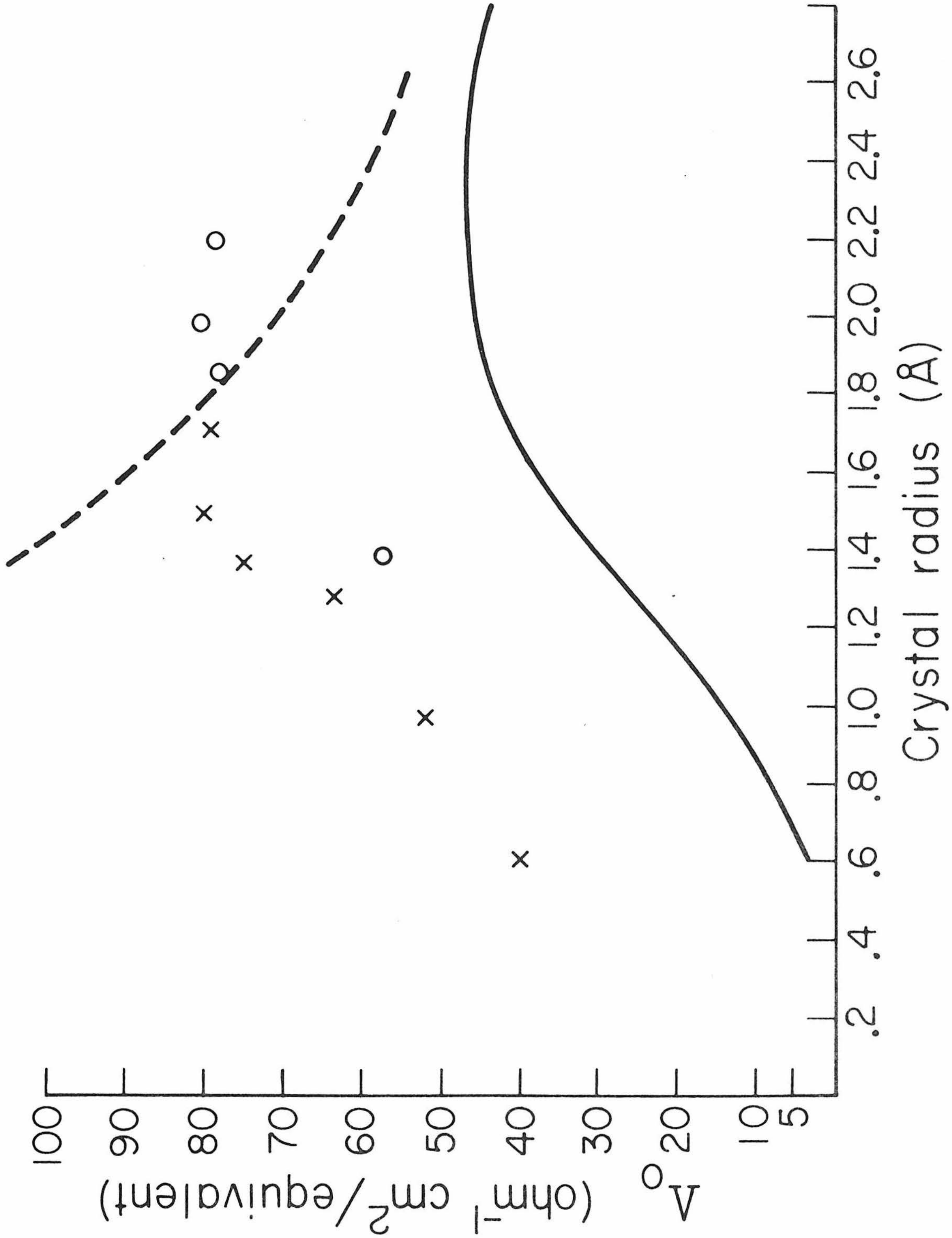
$$\Lambda_0 = Ze\,\tilde{\mathfrak{F}}/(\text{"}4\pi\text{"}\,\eta a + B/a^3). \tag{9}$$

If one uses Zwanzig's[3] value for B and Basset's[12] "4π" slip factor the maximum conductance predicted by Eq. (9) is still only 46 cm^2/ohm-equivalent for $Z = 1$. For comparison Table 1 gives the crystal radii, experimental Λ_0's, computed Λ_0's from Eq. (9) and the computed Λ_0's for $B = 0$ (just Stokes' law). Figure 1 plots Λ_0 versus ion size for the

Table 1

Ion	a (in Å)	Λ_0 (ohm^{-1} cm^2/equivalent) at 25° C		
	crystal[16]	experimental[17]	from (9) Zwanzig[3]	B =0
Li^+	0.60	38.6	3.6	227
Na^+	0.95	50.1	13	144
Ag^+	1.26	61.9	25	108
K^+	1.33	73.5	28	103
Rb^+	1.48	77.8	34	93
Cs^+	1.69	77.2	40	81
F^-	1.36	55.4	29	101
Cl^-	1.81	76.4	43	76
Br^-	1.95	78.1	44	70
I^-	2.16	76.8	46	63
Mg^{+2}	0.65	53.0	2.1	420
Ca^{+2}	0.99	59.5	7.5	276
Sr^{+2}	1.13	59.4	11	243
Ba^{+2}	1.35	63.6	18	203

Figure 1. The infinite dilution conductances of ions in ohm^{-1} cm^2/equivalent are plotted as a function of ion crystal radius in Å. The crosses and circles are the experimental points for Z = 1 and Z = -1, respectively. The dotted line is the calculation from Eq. (9) with B = 0 and Z = 1. The full line is the calculation from Eq. (9) with B = 8.43[3] and Z = 1. All values are for a temperature of 25° C.


Λo (ohm⁻¹ cm²/equivalent)
100
90
80
70
60
50
40
30
20
10
5
.2
.4
.6
.8
1.0
1.2
1.4
1.6
1.8
2.0
2.2
2.4
2.6
Crystal radius (Å)

experimental values, for Eq. (9) with Zwanzig's[3] value for B and for B = 0. Clearly the B = 0 curve shows the wrong trend for small ions--Λ_0 decreasing with increasing ion size. The curve for Eq. (9) with Zwanzig's[3] value for B shows the right trend but the values are all too low.

One explanation for the discrepancies is that the moving units are not the bare ions, but rather hydrated ions and are therefore larger, at least for the small positive ions.[18] This would tend to increase the agreement between the calculated and experimental values for both the B = 0 and Zwanzig's[3] B value curves for the small positive ions. However for the large negative ions (Br^- and I^-) to get agreement with the B = 0 curve, a smaller radius than the actual crystal radius would be needed. Also the Zwanzig[3] B value curve never gets above 46 cm^2/ohm-equivalent, so no size change would help for these larger ions.

Another reason for the discrepancies in Fig. 1 is that the field on the ion is not the average potential gradient, but rather is greater. This is due to the decrease in the dielectric constant in the vicinity of the ion caused by the field of the ion.[1,2,4] This would have the effect of increasing the left and center parts of Eq. (8) and thus increasing the Λ_0's calculated by Eq. (9).

One possible way to determine the field on the ion and the size of the moving unit is to use molecular dynamics. Molecular dynamics is a method of simulating a molecular system. One assumes a potential or force between particles, gives oneself an initial condition for the positions and velocities of the particles and then uses the force or potential to determine the motions of the particles with time. Adjustments may have to be made to get the system to the correct temperature if the initial condition did not do this.[5,6,8] Various properties of the system can be calculated by molecular dynamics. These include pair correlation functions, average interaction energies and diffusion coefficients.[5-9] These can then be compared to experimentally determined values to give a check on the assumed force or potential.

Rahman and Stillinger[5,6] have done this for pure liquid water using the effective potential given by Ben-Naim and Stillinger[10] and have gotten reasonably good agreement for various properties. Thus the effective potential Rahman and Stillinger[5,6] used gives a reasonable description of pure liquid water and possibly will give a good description of the forces between two water molecules even in a solution with other particles.

The Ben-Naim-Stillinger[10] potential for water is the sum of a Lennard-Jones type potential and a potential based on a four-point charge model for water, where the point charges are tetrahedrally located. Two are positive to simulate the protons and the other two are negative to simulate the lone pairs of electrons on the oxygen atom. The potential between the point charges is Coulombic with a cut-off to avoid any two point charges from being at the same point.

To study the conductance of an ion in water is a slightly harder problem and several new forces will have to be considered. First of all, an applied field (D) would have to be given to get a conductance [see Eq. (4)]. This applied field would act on all the particles. Second, one would need to decide what ion-water molecule potential to use. One obvious choice would be a Coulomb potential between the point charges given by the Ben-Naim-Stillinger model and the ion in question, with a cut-off at the crystal radius of the ion, plus a repulsive potential possibly of the Lennard-Jones type between the oxygen nucleus (or center of mass of the water molecule) and the ion.[8] The main problem with this kind of potential is the lack of consideration of the ion-water polarizability term. This would add a term $-\alpha Z^2 e^2/(2R^4)$[19] to the potential, where α is the polarizability of the water molecule and R is the ion-water molecule separation.

The problems with the above choice are that it is for an orientationally averaged interaction and it considers the water molecule to be a point particle. Nevertheless, it could be used as a starting approximation for the interaction. Another possibility to use for the potential between the ion and the water molecule is the energy surfaces calculated by Kistenmacher et al.[20] for a water molecule in the field of an ion. The problem is that they did energy surfaces for only certain relative orientations, and one would really need a continuous set of orientations. Possibly their results could be used to correct and modify the potential given above.

To do the actual molecular dynamics calculation one would want a cubical box of water molecules with the ion at the center and periodic boundary conditions for the water molecules (to keep the density in the box constant). One would compute the force on the ion due to all the water molecules in the box and the external field, while the force on each water molecule would be computed from the ion, the external field and the water molecules within a given radius (Rahman and

Stillinger[5] used 9.2 Å). Possibly a cut-off radius smaller than the size of the box could be used for the ion as well. (Those water molecules within a certain distance would be used to calculated the force on the ion, the ones outside would not be.) One could consider more water molecules than Rahman and Stillinger[5,6] did due to a recently developed computational method.[21]

The box would have to be moved to keep the ion at the center of the box to avoid having the periodic boundary conditions introduce another ion close to the edge of the box--there should be no other ion in the system. To measure the ion's velocity a master reference system would be used. The average velocity would be used in Eq. (7) to calculate the conductance and the average field would be calculated from

$$\Delta\Phi/\ell = E = D/\epsilon_0 \qquad (10)$$

where ϵ_0 is the dielectric constant of water, E is the average field and D is the applied field (of say 100 volts/cm). (A preliminary calculation should be made with the Ben-Naim-Stillinger[10] model for water and an applied D field to see that the average field inside is really D/ϵ_0.[7,22,23] If not, it may require a modification of their model.) Then Eq. (7) can be used to calculate the conductance.

If this conductance for a given ion (given crystal radius and Z) does not agree with experiment, the potential will have to be adjusted. If the conductance is too low, the magnitude of the water molecule-ion interaction was probably overstated and vice versa if the conductance is too high. Once the conductance agrees with experiment, other ions could be used. Hopefully, all this will help one to see what the environment of the ion is, what the size of the moving unit is, and what the average force on the ion is and how all these vary with Z and a. This will certainly help to increase our knowledge of electrolyte solutions.

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Proposition 2

CLUSTERING OF THYMINE DIMERS IN UV IRRADIATED POLY(dA)-POLY(dT)

It is well known that pyrimidine dimers are a major photoproduct of UV irradiated DNA and that their presence correlates with biological inactivation.[1,2] It has also been suggested[3-5] that pyrimidine dimers should form more easily near other pyrimidine dimers or other photoproducts. The reason given for this is that the structure of DNA in the neighborhood of the dimer is probably locally denatured making it easier for another dimer to form nearby.[3,5] Pyrimidine dimers form between adjacent pyrimidines in the same strand of DNA.[6] Two adjacent pyrimidines on the same strand of DNA are separated by a vertical distance of 3.4 Å and a rotation of 36°.[7] Thus, when a dimer forms, it must distort the structure of DNA in its immediate vicinity.

Experiments on denatured (single-stranded) DNA show about a factor of two greater dimer formation over native DNA.[8,9] Similarly, experiments on poly dU show a factor of two to three greater dimer formation over poly dU-poly dA.[5] These experiments suggest that dimer formation in the vicinity of another dimer in double-stranded polynucleotides should be enhanced if the polynucleotide is locally denatured. If, in addition to enhanced formation of dimers in these areas, long-range energy migration also took place in the polynucleotides, then one would see clustering of dimers in the double-stranded polynucleotides leading to a greater density of dimers than in the single-stranded polynucleotides.

In experiments on DNA, Shafranovskaya et al.[3] and Brunk[10] thought they saw evidence for the clustering of thymine dimers in DNA. However, later experiments by Rahn and Stafford[11] and Jonker and

Blok[12] revealed an error in the experiments of Shafranovskaya et al.,[3] and Birnboim[13] was unable to confirm Brunk's[10] experiments. On the other hand, Pearson and Johns[5] found, upon analyzing products of irradiated poly dU-poly dA, the product having two dimers next to each other in reasonably large amounts.

There are several possible reasons for the inability of the above experiments in DNA to show dimer clustering: (1) perhaps dimers do not form more easily in the neighborhood of another dimer, (2) perhaps there were no other sites for dimer formation in the vicinity of a formed dimer, and (3) perhaps long-range energy transfer does not take place in DNA.

There is considerable evidence for reason number (3) above in DNA. The four bases of DNA have singlet and triplet energies which differ by hundreds of wavenumbers,[2,14] which would make energy transfer difficult. Also various experiments on sensitization of dye fluorescence by DNA[15] and quenching of phosphorescence by paramagnetic ions[16] have shown no evidence for energy transfer in DNA beyond ten or so base pairs. However, in poly dA at low temperatures, one paramagnetic ion quenched the phosphorescence of a hundred base pairs, showing that long-range energy transfer occurs.[17]

Thus, to demonstrate conclusively whether or not dimer formation is easier in the vicinity of another dimer, experiments should be done on the double-stranded polynucleotide poly dA-poly dT. These experiments would also serve to test the theoretical work of Vologodskii et al.[4] on clustering of dimers due to long-range energy transfer. They used a simple model which forced a dimer to form if the excitation migrated to a site where there was already a dimer. They then calculated a distribution function for the length of the undamaged regions as a function of dosage for both poly dA-poly dT and for DNA.

Thymine dimers are detected by liquid phase chromatography in the following way. The thymine is labeled radioactively by either ^3H or ^{14}C. After irradiation the DNA is hydrolyzed in acid (converted to individual bases plus acid-stable photoproducts) and then chromatographed. See R. O. Rahn[18] for a more complete description of the procedure. Thymine dimers are stable under this procedure.

One method for measuring defect regions is the kinetic formaldehyde method.[19,20] This method is based on the fact that the initial rate of denaturation of DNA by formaldehyde is dependent upon the number and length of denatured regions present in the DNA (including the ends of the DNA). The method has been calibrated to give the absolute number of defects and their length.[11,19,20]

Another way of measuring clustering of dimers is to use an endonuclease which makes a single strand break next to a dimer.[11,21-24] Then the resultant DNA can be denatured and the resultant fragment lengths determined by sedimentation.[21-24] This endonuclease also works on poly dA-poly dT.[21,23] Alternatively, the endonuclease can just be used to make a break in the DNA and the resultant DNA can be analyzed by the kinetic formaldehyde method since formaldehyde denatures regions having a single strand break faster than it does those with only a locally denatured region.[11]

Thus, the experiments proposed here are to irradiate poly dT and poly dT-poly dA with UV radiation (for example, from a mercury lamp - 254 nm) and measure the number of dimers formed in each by the above-described chromatography techniques. Then, the number of defects or the length of the segments between breaks generated by endonuclease should be measured for poly dT-poly dA. If the distribution of dimers formed in poly dT-poly dA is non-uniform (or the number of defects and the number of dimers is not the same--they should be the same in poly dT), then it implies that dimers form more easily in the neighborhood of another dimer. Also if the density of dimers in the defect regions in poly dA- poly dT is greater than the density in poly dT (which should be uniform), then long-range energy migration must be present and an estimate of its extent can be obtained.

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Proposition 3

APPLICATION OF A TWO-LEVEL MODEL TO THE UNTANGLING OF ABSORPTION SPECTRA

In part II, section E of this thesis, a method was given for extracting vibrational information from a tangled spectrum under the assumption that only one state had any oscillator strength in that region of the spectrum. This assumption was a good one for the origin region of naphthalene's second singlet state and will hold true for many other systems as well. However, there will also be many systems for which more than one vibronic level will have oscillator strength.

It is therefore proposed to study a two-level system with the simplifying assumption of no direct or indirect interaction between the two states to determine what information can be obtained from the absorption spectrum. This work would have two parts. First, try out the method proposed below on a model system. Second, apply the method to a real system--for instance naphthalene including another 400 wavenumbers or so of its absorption spectrum where the first a_g addition to the origin has its absorption peak.

In a two-level system with no interactions between the states the absorption cross section is proportional to[1]

$$\sigma(\omega) \propto \frac{\epsilon_p^2}{\omega} |\langle 0| \underset{\frown}{\mu} \circ \underset{\frown}{\epsilon} |p\rangle|^2 \operatorname{Im} G_{pp}(\omega) + \frac{\epsilon_{p'}^2}{\omega} |\langle 0| \underset{\frown}{\mu} \circ \underset{\frown}{\epsilon} |p'\rangle|^2 \operatorname{Im} G_{p'p'}(\omega) \tag{1}$$

where the two primary states are p and p′ with zero-order energies ϵ_p and $\epsilon_{p'}$, respectively, and where,[2]

$$\mathrm{Im}\, G_{pp}(\omega) = \frac{-\pi f_1^2(\omega)\rho_1(\omega)}{[\omega - \epsilon_p - \mathrm{Re}\,\Gamma_1(\omega)]^2 + [\pi f_1^2(\omega)\rho_1(\omega)]^2} \tag{2a}$$

$$\mathrm{Re}\, G_{pp}(\omega) = \frac{\omega - \epsilon_p - \mathrm{Re}\,\Gamma_1(\omega)}{[\omega - \epsilon_p - \mathrm{Re}\,\Gamma_1(\omega)]^2 + [\pi f_1^2(\omega)\rho_1(\omega)]^2} \tag{2b}$$

and

$$\Gamma_1(\omega) = \int_{-\infty}^{\infty} \frac{f_1^2(\epsilon_k)\rho_1(\epsilon_k)\, d\epsilon_k}{\omega - \epsilon_k} \quad . \tag{2c}$$

One can use the absorption spectrum (times ω) to get $P \equiv A\,\mathrm{Im}\,G_{pp} + B\,\mathrm{Im}\,G_{p'p'}$ where $A = \epsilon_p^2 |\langle 0|\underset{\frown}{\mu}\cdot\underset{\frown}{\epsilon}|p\rangle|^2$ and $B = \epsilon_{p'}^2 |\langle 0|\underset{\frown}{\mu}\cdot\underset{\frown}{\epsilon}|p'\rangle|^2$. Using the dispersion relation[3] between the real and imaginary parts of G, one can get $R \equiv A\,\mathrm{Re}\,G_{pp} + B\,\mathrm{Re}\,G_{p'p'}$. Taking the quotient $Q \equiv \frac{P}{R^2 + P^2}$ one can show easily that it reduces to $\frac{f_1^2(\omega)\rho_1(\omega)}{A}$ if the denominator for the p′ state in Eq. (2a) is very much larger than the denominator for the p state and A is not too much smaller than B. This says that if one is close to one state, then the procedure given in section E yields correct results, even if another state has about the same amount of oscillator strength. One would have to check whether the principal value integral for $\mathrm{Re}\,\Gamma_1$ is sensitive to $f_1^2\rho_1$ values far from where it is being evaluated. If not, then one could obtain ϵ_p in the same manner as in section E.

The above procedure assumes that one knows roughly where ϵ_p and $\epsilon_{p'}$ are. This may not always be true. If not, one could try the procedure in section E for calculating $\lambda - \epsilon_p$ using the principal value integral of Q for Re Γ and substituting R for the Re $G_{pp'}$ etc. If the principal value integral was insensitive to Q values far from the point at which it was being evaluated, then in the neighborhood of ϵ_p, one should get a straight line for $\lambda - \epsilon_p$ calculated this way. Hopefully, one would get only two places where $\mathrm{Re}\, Q + \frac{R}{R^2 + P^2} \equiv S$ yielded a straight line with a positive slope which crossed the x-axis. These places would then be ϵ_p and $\epsilon_{p'}$.

A model on which this procedure could be tried is taking $f_1^2 \rho_1$ to be several Gaussians or Lorentzians in the neighborhood of a given ϵ_p and similarly for $f_2^2 \rho_2$ and $\epsilon_{p'}$. One should eventually let the regions of $f_1^2 \rho_1$ and $f_2^2 \rho_2$ overlap. From this, one would calculate the absorption spectrum from Eq. (1) and then calculate R from the dispersion relation. Finally one would calculate Q and S. A plot of S as a function of ω would hopefully give ϵ_p and $\epsilon_{p'}$ as the only two intercepts of positively sloped regions of S. If this checked out correctly, then Q in the vicinity of these points would be $\frac{f_1^2 \rho_1}{A}$ and $\frac{f_2^2 \rho_2}{B}$. Between ϵ_p and $\epsilon_{p'}$ the peaks in Q may also correspond to peaks in $f_1^2 \rho_1$ and $f_2^2 \rho_2$.

The above procedure, although necessarily sketchy, represents the first attempt to untangle an absorption spectrum using a model having more than one state with the inclusion of the real line shape. It seems obvious that the unsolved problems of SO_2 and NO_2 will require the investigation of models of this type.

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Proposition 4

THE VARIATION OF THE TRANSITION MOMENT WITH INTERNUCLEAR DISTANCE AND ITS EFFECT ON RAMAN CROSS SECTIONS

In conventional Raman theory the term that leads to Raman intensity far off resonance comes from the linear term in the expansion of the transition dipole in terms of the vibrational coordinate Q[1]

$$
\begin{aligned}
&\langle \chi_{ev'}(Q) \langle \phi_e(q,Q) | \mu | \phi_g(q,Q) \rangle_q \; \chi_{gv''}(Q) \rangle_Q \\
&\quad = \langle \chi_{ev'}(Q) | M_e(Q) | \chi_{gv''}(Q) \rangle_Q \\
&\quad = \langle \chi_{ev'}(Q) | \chi_{gv''}(Q) \rangle_Q \, M_e(Q = Q_0) \\
&\quad + \left. \frac{\partial M_e}{\partial Q} \right|_{Q=Q_0} \langle \chi_{ev'}(Q) | Q | \chi_{gv''}(Q) \rangle \\
&\quad + \cdots \qquad (1)
\end{aligned}
$$

In Eq. (1), $M_e(Q)$ is the integration over q in the top expression, Q_0 is the equilibrium position of the ground state, and $\phi_i(q,Q)\,\chi_{iv}(Q)$ is the Born-Oppenheimer wavefunction for the iv state. In Part II, Sections B and D of this thesis, only the $M_e(Q=Q_0)$ term was included in calculations of Raman intensity. The reason for this assumption was a lack of calculations on the magnitude of the higher terms over a wide enough range of internuclear distance.

It is therefore proposed to calculate $M_e(Q)$ over a wide range of internuclear distance for a diatomic molecule. Then one should use this $M_e(Q)$ to calculate Raman excitation profiles as was done previously. Also the Raman profiles from just the $M_e(Q=Q_0)$ term should be calculated so as to assess the importance of the higher order terms and to determine how close to resonance they need to be included.

Probably one of the most efficient procedures for calculating $M_e(Q)$ is the equations-of-motion method of Rowe[2] and McKoy and coworkers.[3-5] The advantage of this method is that the matrix elements one needs in order to calculate excitation energies and transition moments are less sensitive to the inaccuracies of the ground state wavefunction used to evaluate them than in the usual procedures of solving for the wavefunctions of each state separately. A brief description of this method will now be given (condensed from Refs. 2-5).

The ground state wavefunction is approximated by (using the notation of refs. 3-5)

$$|0\rangle = |HF\rangle + \sum_{\gamma<\delta} \sum_{m<n} C^{mn}_{\gamma\delta}\, c^+_m\, c^+_n\, c_\delta\, c_\gamma\, |HF\rangle \tag{1}$$

where $|HF\rangle$ is the Hartree-Fock ground state, the c's are creation and annihilation operators, m and n are particle states and δ and γ are hole states. The approximation in Eq. (1) is that the C's are small compared to unity; if this breaks down one must go to the open shell equations-of-motion treatment

The equation

$$O^+_\lambda |0\rangle = |\lambda\rangle \tag{2}$$

defines the excitation operator O^+_λ which creates the excited state $|\lambda\rangle$ from the true ground state $|0\rangle$. If one expands O^+_λ in single particle-hole operators

$$O_\lambda^+ = \sum_{m'\gamma'} [Y_{m'\gamma'} \; c_m^+ \; c_{\gamma'} - Z_{m'\gamma'} \; c_{\gamma'}^+ \; c_{m'}] \tag{3}$$

then we can derive the equation

$$\begin{bmatrix} A & B \\ -B^* & -A^* \end{bmatrix} \begin{bmatrix} Y(\lambda) \\ Z(\lambda) \end{bmatrix} = \omega(\lambda) \begin{bmatrix} D & 0 \\ 0 & D \end{bmatrix} \begin{bmatrix} Y(\lambda) \\ Z(\lambda) \end{bmatrix} \tag{4}$$

where A, B and D are matrices and depend on the C's of Eq. (1) and $\omega(\lambda)$ is the excitation energy of the state $|\lambda\rangle$. Finally from the equation

$$O_\lambda |0\rangle = 0 \tag{5}$$

for the hermitian conjugate of O_λ^+, one can show

$$Z_{m\gamma}(\lambda) \approx \sum_{n\delta} C'^*_{m\gamma,n\delta} \; Y_{n\delta}(\lambda) \tag{6}$$

where the C′ 's are closely related to the C's. (Actually everything depends on spin as well, but this has been suppressed here.) The procedure for solving these equations is to guess a set of C's, calculate the matrix elements of A, B and D (the actual form for them is given in Ref. 3), solve the matrix equations for Y, Z and ω_λ, and then find a new set of C's from Eq. (6) until the solutions are self-consistent. The transition moment from $|0\rangle \rightarrow |\lambda\rangle$ depends on the $Y_{m\gamma}(\lambda)$'s, $Z_{m\gamma}(\lambda)$'s and the C's.[4]

To calculate the transition moment as a function of Q or internuclear distance for a diatomic molecule, one must first use a basis set to do a Hartree-Fock calculation at each value of the internuclear distance.[5] After calculating $M_e(Q)$ as discussed above, one would fit $M_e(Q)$ to some analytic form so as to be able to calculate $\langle \chi_{ev'}(Q) | M_e(Q) | \chi_{gv''}(Q) \rangle$ which will be needed to calculate the Raman cross section.[7] The vibrational wavefunctions can be calculated as was done in Part II, section D of this thesis.

One possible molecule on which to do this calculation is BeO, which has its $B^1\Sigma$ state at around 21,000 cm^{-1}[8] and which does not have too many electrons, so the calculation will take less time. Its ground state configuration is $(1\sigma)^2 (2\sigma)^2 (3\sigma)^2 (4\sigma)^2 ({}^1\pi^+)^2 ({}^1\pi^-)^2$. A possible basis set of Slater-type orbitals has been given by Schaefer.[9]

By doing this calculation for a diatomic molecule, one could find the dependence of the Raman cross section as a function of excitation energy using both the true $M_e(Q)$ and the first term of Eq. (1) -- $M_e(Q_0)$. This would help in our understanding of the Raman process.

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Proposition 5

MEASUREMENT OF EXCITED STATE VIBRATIONAL FREQUENCIES USING NANOSECOND OR PICOSECOND RESONANCE RAMAN

Although resonance Raman has been used extensively to give accurate vibrational constants for the ground state of molecules,[1,2] it has not been used for excited states. However, with the advent of time resolution of a few nanoseconds or less, experiments applying this technique to the excited state can now be tried. It is therefore proposed to obtain an excited state Raman spectrum of anthracene.

A nitrogen laser (with output at 3371 Å[3] = 29,660 cm^{-1}) would excite anthracene from its ground state to its first excited singlet state (whose 0-0 position in hexane is at 26,700 cm^{-1}).[4] The nitrogen laser would also pump a dye laser (using rhodamine 6G) to give output at around 16,700 cm^{-1}, which is where anthracene's S_1 state absorbs.[5-7] The dye laser output would yield a resonance Raman spectrum of the excited state as well as a normal Raman spectrum of the ground state and the solvent.

A pulsed nitrogen laser provides pulses of 1 MW peak power with a FWHM of 2-10 nsec.[3] One can split off part of its output with a beam splitter and use it to pump the sample. The other part of the beam can pump the dye laser. The dye pulses have about 100 kW of peak power, a FWHM in time of 2-10 nsec and a FWHM in frequency of .3 cm^{-1} or less.[3] This spectral bandwidth can easily be reduced by an order of magnitude using an etalon.[3]

For maximum resonance Raman from S_1 of anthracene, the pump pulse and the dye laser pulse should reach the cell at roughly the same time or the dye laser pulse should get there 1nsec or so later than the pump pulse. The reason for this is that the lifetime of

S_1 for anthracene is only a few nanoseconds.[8] To maximize the signal from the excited state Raman, the two beams should enter the cell collinearly from the same direction. In this way there will be the largest overlap of the two beams.

Alternatively, one could use a picosecond pulsed dye laser (operating with rhodamine 6 G)[9] instead of the nitrogen laser. The second harmonic of an amplified single pulse could excite anthracene to its S_1 state and the fundamental would excite the resonance Raman from there. The picosecond pulsed dye laser has pulses of peak power 1 GW, FWHM in time of less than 5 psec, and a FWHM in frequency of about 10 cm^{-1}.[9] The advantage of this method of excitation is that one could delay the resonance Raman exciting pulse by 50-100 psec and still not worry about relaxation out of S_1 during this time. An obvious disadvantage is the large spectral bandwidth which would cause resolution problems if the excited state frequency did not shift by more than 20 cm^{-1} from its ground state value.

For either excitation process, the Raman signal can be gathered at 90°, the exciting line can be filtered out using a dielectric coating, a spectrograph can be used for frequency resolution and an ISIT (intensified silicon intensified target) vidicon tube for detection. This vidicon tube yields practically single-photon counting detection and will allow gathering of large parts of the spectrum at one time. The vidicon can be gated so as to turn on when the dye laser pulse is exciting the resonance Raman. By delaying the latter pulse 10 nsec or so with respect to the exciting pulse, one can ascertain whether or not the new lines in the Raman spectrum arise from the S_1 state. The fluorescence of anthracene from the S_1 state occurs at much shorter wavelengths than the Raman from S_1[7] so it will not interfere with this experiment.

Since anthracene forms a photodimer at high concentrations,[10] the solution must be kept reasonably dilute. Possible solvents are hexane, ethanol, methanol, chloroform and carbon tetrachloride.[11] The advantage of using one of the latter three is that they have less vibrations to interfere with the spectrum. One should go to low temperatures so that one can resolve ground and excited state vibrations. The best solvent for these studies can be found by just looking at the Raman spectrum of the ground state (without the pump pulse) and getting the best possible spectrum in the various solvents. Obviously some of these solvents can be used at lower temperatures without forming a glass, which would probably scatter the light more.

It thus seems possible to obtain a resonance Raman spectrum from the S_1 state of anthracene using these methods. If picosecond dye laser excitation were used, one could probably use resonance Raman to measure vibrational relaxation in the excited state, analogously to the way vibrational relaxation times in the ground state are now measured.[12]

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