PHOTOCHEMICAL INVESTIGATIONS OF IONS IN THE GAS PHASE

UTILIZING ION CYCLOTRON RESONANCE SPECTROSCOPY

Thesis by

Ben Sherman Freiser

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To my parents who deserve the best.

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ABSTRACT

The photochemistry and photophysical processes of a broad range of ions have been studied in the gas phase using ion cyclotron resonance techniques. A discussion summarizing much of this work, and two papers on related topics are presented.

In paper I, "Acid-Base Properties of Molecules in Excited Electronic States Utilizing Ion Cyclotron Resonance Spectroscopy", a general method is described for obtaining excited state acid-base properties of molecules and ions in the gas phase which utilizes ion cyclotron resonance spectroscopy for studying photochemical processes involving ions. These processes, including photodissociation and photodetachment, yield in favorable instances, electronic excitation energies of ions. A comparison of the excitation energies of a base B with the corresponding acid-base complex AB yields the excited state basicity of B. Similarly, a comparison of the excitation energies of a chromophoric acid A with the complex AB yields information about the excited state acidity of A. Studies of the first type are described using the reference acids H^+ and Li^+ with the bases C_6H_5X (X = H, CN, NH_2, CHO, $COCH_3$, NO_2, OCH_3, O^-, and S^-), pyridine, and ferrocene. In several instances photodissociation spectra of solvated acid-base complexes of the type $B\overset{+}{Li}B$ have been obtained and analyzed to determine the effects of further solvation on the excitation spectra of these complexes. A comparison of the gas phase excitation spectra of a number of ions to their solution absorption is made.

Studies of the second type (excited state acidities) are described using the reference base H^- with the acids $C_6H_5CO^+$ and $C_6H_5CHOH^+$. Calculated changes in acidity and basicity are used to infer changes in electron distributions and dipole moments for excited states, and yield insight into the types of transitions involved. In particular, these studies are used to assess the controversial role played by intramolecular charge transfer in the lowest two singlet $\pi \to \pi^*$ transitions of monosubstituted benzenes. These results are compared with findings from related experiments and calculations when available.

Paper II, entitled "Electron Impact Dissociation of Cyanobenzene Radical Cations by Ion Cyclotron Resonance Spectroscopy", describes using trapped ion cyclotron resonance spectroscopy for the first time to study the electron impact dissociation of ions. Fragmentation of $C_6H_5CN^+$ to produce $C_6H_4^+$ and HCN is observed to occur at low electron energies (3-9 eV). The extent of dissociation is observed to be linear in emission current, rising from a threshold at 3.0 ± 0.5 eV to a maximum cross section estimated to be 6 $\overset{\circ}{A}^2$ at 7.5 ± 0.5 eV. The implications of these results are discussed.

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CHAPTER I

## INTRODUCTION AND BRIEF DESCRIPTION

OF THE APPARATUS

Ion cyclotron resonance spectroscopy[1] (ICR) is ideally suited for the study of photochemical and photophysical processes involving ions in the gas phase. The advantage of the technique involves the ability to generate a broad range of interesting ionic species by direct ionization, surface ionization,[2,3] penning ionization,[4] or by ion-molecule reactions, and to thermalize these species while they are trapped in a well defined spatial region.[5,6] Interactions of photons with ions are then inferred from observed changes in ion abundance monitored as a function of time as well as wavelength, enabling the study of unimolecular and bimolecular reaction kinetics.

Band intensities in photoexcitation spectra[7] of ions depend not only on the intrinsic transition probability or gas phase extinction coefficient, $\epsilon_g(\lambda)$, but also on the quantum yield, $\varphi_d(\lambda)$, for the process being monitored. The measured quantity is the photoexcitation cross section, $\sigma_d(\lambda)$, which is proportional to the product of these variables (eq 1). If the quantum yield is relatively constant over an absorption

$$\sigma_d(\lambda) \propto \epsilon_g(\lambda)\varphi_d(\lambda) \tag{1}$$

band (Figure 1, band I), then $\sigma_d(\lambda)$ will reflect the absorption spectrum and directly yield vertical excitation energy. If, on the other hand, φ_d varies significantly over an absorption band (Figure 1, band II),

Figure 1. Comparison of expected photodissociation cross section $\sigma_d(\lambda)$ and absorption spectrum $\epsilon_g(\lambda)$ for cases where the photodissociation quantum yield of $\varphi_d(\lambda)$ is constant (I) and varying (II) over the absorption band.
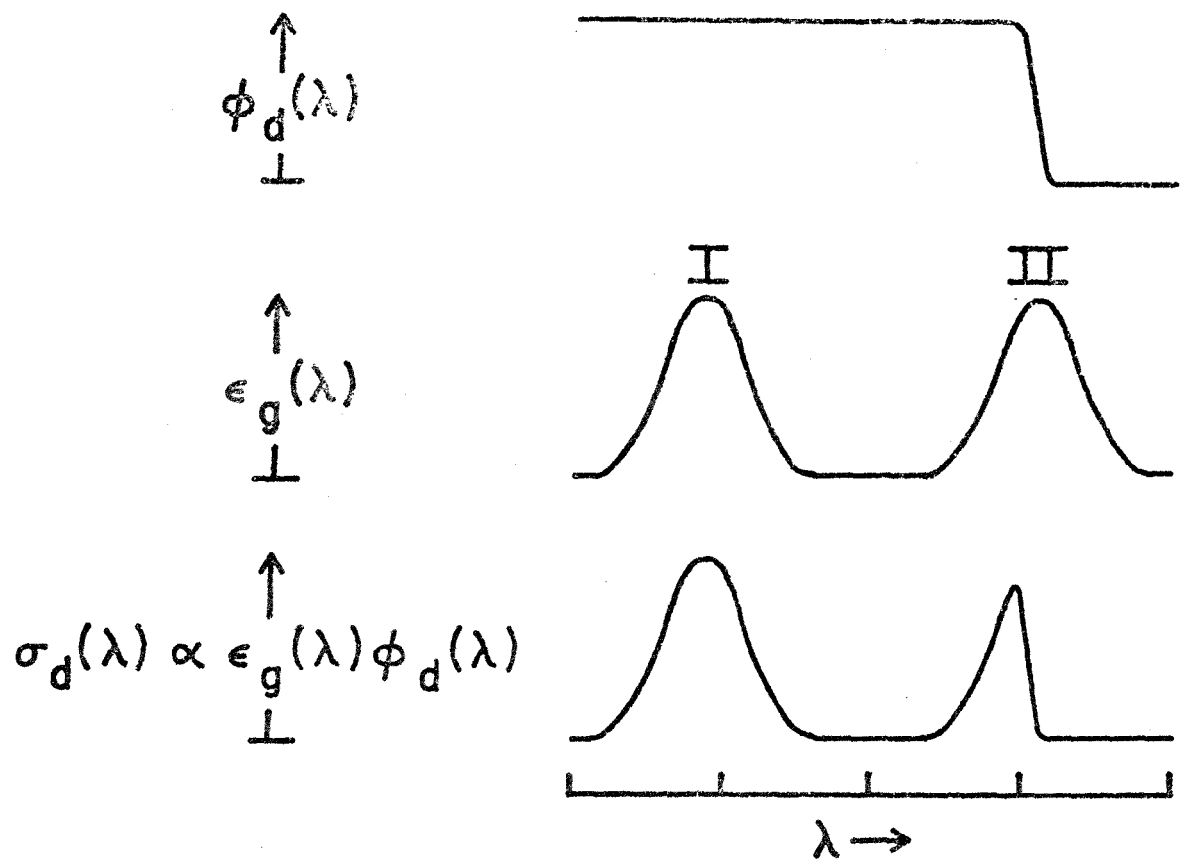
$$\phi_d(\lambda)$$

$$\epsilon_g(\lambda)$$

I II

$$\sigma_d(\lambda) \propto \epsilon_g(\lambda)\phi_d(\lambda)$$

$$\lambda \rightarrow$$

then $\sigma_d(\lambda)$ will not yield exactly the vertical excitation energy. The latter would occur, for example, in the vicinity of the thermodynamic threshold for the photoprocess being monitored, below which $\varphi_d(\lambda) = 0$. In comparison to direct absorption measurements in solution or in plasmas, the absorption maxima determined by this method should yield an intrinsic measure of the vertical transition energies of the ions free of effects due to solvent, counterions, and any other neutral or ionic species which absorb in the region of interest. A meaningful comparison to the theoretical transition energies in addition to solvent shift data may therefore be obtained. Processes amenable to study include electron photodetachment[8-17] (process 2), ion photodissociation (processes 5 and 7),[7, 18-38] and production of excited electronic states with modified reactivity[39] (processes 4 and 8) and/or modified photochemistry[37, 38] (e.g., multiphoton processes 3, 6, and 9). Processes 3, 4, and 6 have not to date been observed in the ICR.

$$AB^- + h\nu_1 \; \rightarrow \; [AB^-]^* \quad
\begin{array}{ll}
\longrightarrow AB + e & (2) \\
\xrightarrow{h\nu_2} AB + e & (3) \\
\xrightarrow{\text{neutral}} C^- + D & (4) \\
\longrightarrow A^- + B & (5) \\
\xrightarrow{h\nu_2} A^- + B & (6)
\end{array}$$

$$AB^+ + h\nu_1 \; \rightarrow \; [AB^+]^* \quad
\begin{array}{ll}
\longrightarrow A^+ + B & (7) \\
\xrightarrow{\text{neutral}} C^+ + D & (8) \\
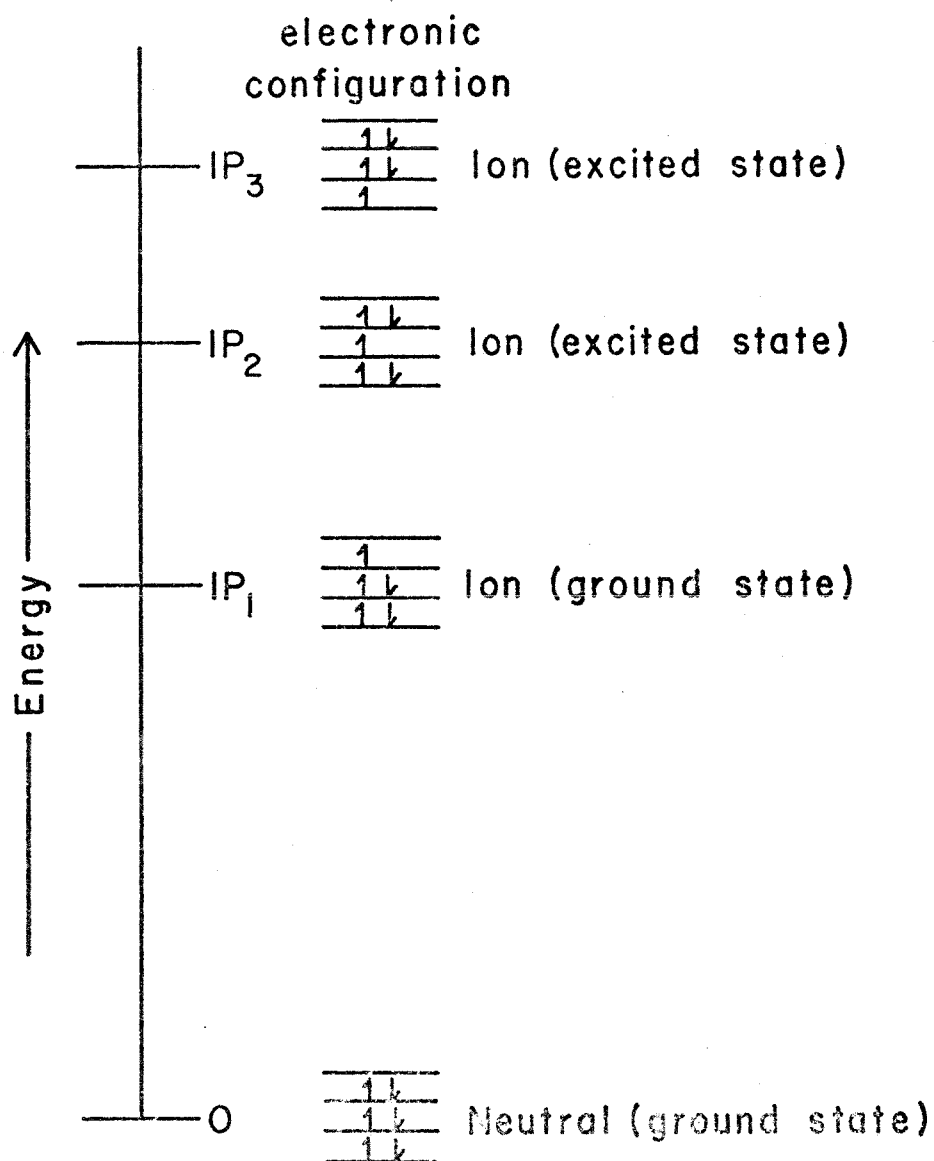\xrightarrow{h\nu_2} A^+ + B & (9)
\end{array}$$
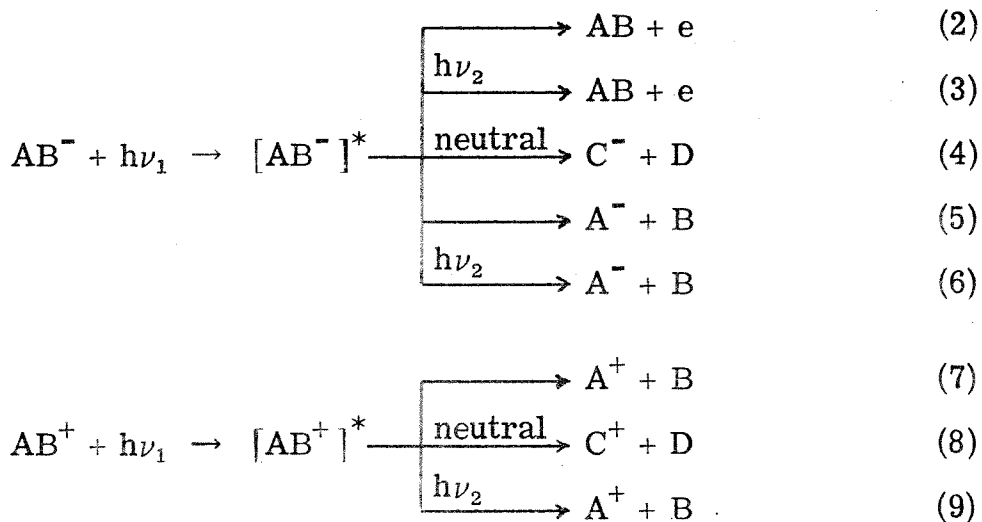
Thresholds determined by Brauman and co-workers for photo-detachment of electrons from negative ions (process 2) have yielded electron affinities and related thermochemical data important in describing the intrinsic acidity of numerous organic and inorganic molecules.[8-17] These studies have also uncovered, in selected cases, information about excited states of negative ions.[9-11]

Dunbar and co-workers have demonstrated the application of ICR techniques to study an even wider range of photochemical processes involving gaseous ions, including photodissociation[19-32] (processes 5 and 7) and photoinduced reactions[39] (processes 4 and 8). These studies have thus far been limited primarily to radical cations. Photodissociation of the parent ion of methyl chloride with polarized light yields methyl cations with an angular distribution characteristic of the symmetry of the excited state.[29, 30] The interpretation of excitation functions for such photodecomposition processes is facilitated by the availability of photoelectron spectra which detail many of the excited states of radical cations.

As shown in Figure 2, photoelectron spectroscopy yields ionization potentials of neutrals corresponding to the energies required to remove electrons from the highest filled orbital (IP_1) and successively higher energy orbitals (IP_2, IP_3, etc.) deeper in the valence shell. Starting with an even electron neutral, IP_1 produces the radical cation in its ground state, and IP_2 and higher ionization potentials produce the ion in excited electronic states. Note, however, that in no case does ionization produce excited electronic states of the ion in which an

Figure 2. Comparison of photoelectron spectroscopy to photo-

dissociation spectroscopy.

Photoelectron Spectroscopy

electronic
configuration

IP$_3$ Ion (excited state)

IP$_2$ Ion (excited state)

IP$_1$ Ion (ground state)

Energy →

O   Neutral (ground state)

Photodissociation Spectroscopy

+ hν
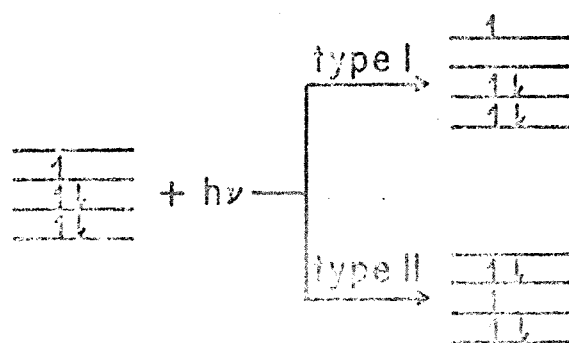
type I

type II

electron occupies the lowest unfilled orbital. In photodissociation spectroscopy the ground state radical cation is irradiated and two possible transitions can occur. A Type I transition corresponds to excitation of an electron from the highest filled orbital to the lowest unfilled orbital. This produces an excited state of the ion not detailed by photoelectron spectroscopy. A Type II transition corresponds to promotion of an electron from an inner valence orbital to the highest filled orbital, producing an excited state of the ion which is observed in photoelectron spectroscopy. If the structure of the ground state of the ion is not very much different from that of the neutral, the energy required for a Type II transition where, for example, the electron excited is in the second highest filled orbital, will just be $IP_2 - IP_1$ as determined by photoelectron spectroscopy. Thus, if the energy axis of the photoelectron spectrum is adjusted such that IP_1 is zero on the photodissociation energy scale, overlap of the photodissociation spectra and the photoelectron spectrum aids in the interpretation of the transitions involved. The complementary nature of the information obtained in both experiments is strongly reflected in studies of unsaturated hydrocarbons.[19, 24-26, 28, 29, 32, 37, 38] Differing absorption characteristics make it possible to identify structural isomers with photodissociation data. Dunbar and co-workers have clearly demonstrated this interesting application of photodissociation data in the case of butene cations,[26] $C_7H_8^+$ cations,[27] and various alkyl-benzene cations.[25, 32] Application of lasers to obtain high resolution spectra of ions has also been demonstrated.[31]

The effort launched at Caltech in this field has been directed toward spectroscopy and photochemistry of even electron gaseous ions. The study of these species is of importance not only because of the paucity of data on this subject, but because many of these ions are stable in solution enabling direct comparisons to be made. Demonstrating such experiments, we reported the photodissociation of perfluoroallyl cations generated from perfluoropropylene.[36] The excitation function for the only observed process (10) was interpreted as

$$C_3F_5{}^+ + h\nu \; \rightarrow \; CF_3{}^+ + C_2F_2 \tag{10}$$
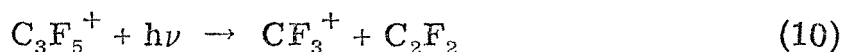
arising from the lowest $\pi - \pi^*$ singlet excitation of the perfluoroallyl cation, with the observed onset and λ_{max} being in the same range as the lowest $\pi - \pi^*$ singlet excitations reported for allyl cations in solution.[40] In addition, a possible relationship between collisional activation (where electronic excitation of the reactant ion in high energy collisions is inferred) and the decomposition of ions in photochemically excited states was suggested to explain the observation that the photodissociation reactions reported for $C_3F_5{}^+$ and several other polyatomic ions all show prominant metastables related to the corresponding decomposition processes.

A direct comparison of the gas phase photodissociation and solution absorption spectra of benzoyl cation, protonated benzene, and protonated mesitylene was afforded by the availability of the solution spectra of these ions.[6] From the results it was inferred that the quantum yields for photodissociation of these species do not vary

significantly with wavelength and are thus very likely close to unity.
In some instances the solution spectra had extra peaks attributed to
neutral or ionic impurities which obscured the true spectrum of the
ion. Finally, the comparison of the gas phase and solution spectra
surprisingly revealed no solvent shifts. Further study has shown that
the lack of solvent shift is not a general phenomena.[35] The maxima
observed for the conjugate acids of benzaldehyde, acetophenone, and
nitrobenzene in concentrated H_2SO_4, for example, are at shorter
wavelengths compared to the corresponding maxima in the gas phase.
From these examples it was concluded that solvent shifts will occur
for ions having acidic protons which can interact with the solvent.

Another area of research having great potential is the photo-
dissociation of weakly bound complexes which utilizes ionic "shift
reagents" for characterizing excited electronic states. We reported
the photodissociation spectra of Li^+ complexes with monosubstituted
benzenes demonstrating that information relating to electron distribu-
tions and acid-base properties of molecules in excited electronic states
can be derived.[33,35] Similar information was obtained from studies
on the corresponding protonated species.[34,35] Chapter II of this thesis
presents a detailed discussion of this topic.

Besides changing molecular properties in excited states (e.g.,
excited state basicities) absorption of light by an ion may modify its
reactivity (exemplified in processes 4 and 8) and/or its photochemistry
(exemplified by processes 3 and 9). Processes 4 and 8 are perhaps

the most common found in solution photochemistry, and in addition to being of intrinsic interest are of synthetic and mechanistic value. To observe these processes under the experimental conditions used in ICR, the excited intermediate must have a lifetime on the order of 0.1 - 1 sec. That this appears to be rare is indicated by the fact that only one paper has been published on the subject[39] and even it is under suspicion.

We recently reported the laser photodissociation of benzene[38] and cyanobenzene[37] radical cations by a sequential two photon process 9 involving a long lived intermediate. This work demonstrated the unique capability of the ICR as a technique for studying long lived excited states, since containment of the ion prevents deactivation with the wall, which is usually a limiting factor in spectroscopic studies at low pressure. In addition, these techniques allow transitions occurring below thermodynamic threshold, previously inaccessible by photodissociation spectroscopy, as well as the absorption spectra of excited ions to be examined.[37] Finally, these results suggest that photoinduced reactions be sought utilizing this type of excited intermediate.

This thesis represents an update on the Caltech effort in the area of photochemistry and spectroscopy of ions in the gas phase. The work summarized above has already appeared in the literature and is referenced in Table I. Chapter II presents an in-depth discussion on the properties of molecules and ions in excited states, and solvent effects on ion excitation spectra.

Table I. Bibliography of Published Work Related to This Thesis

1. Observation of Ion Ejection Phenomena in Ion Cyclotron Double
    Resonance Experiments
        B. S. Freiser, T. B. McMahon, and J. L. Beauchamp
        Int. J. Mass Spectrom. and Ion Phys., 12, 249 (1973)

2. Gas Phase Ion Chemistry and Photochemistry of Ions Generated
    from Perfluoropropylene; Photodissociation of the Perfluoroallyl
    Cation
        B. S. Freiser and J. L. Beauchamp
        J. Am. Chem. Soc., 96, 6260 (1974)

3. Laser Photodissociation of Benzene Radical Cations. Evidence for
    A Two Photon Process Involving A Long Lived Intermediate
        B. S. Freiser and J. L. Beauchamp
        Chem. Phys. Lett., 35, 35 (1975)

4. Photochemistry of Organic Ions In The Gas Phase. Comparison Of
    The Gas Phase Photodissociation and Solution Absorption Spectra
    Of Benzoyl Cation, Protonated Benzene, and Protonated Mesitylene
        B. S. Freiser and J. L. Beauchamp
        J. Am. Chem. Soc., 98, 3136 (1976)

5. Sequential Deuterium Exchange Reactions Of Protonated Benzenes
    With D_2O In The Gas Phase By Ion Cyclotron Resonance Spectroscopy
        B. S. Freiser, R. L. Woodin, and J. L. Beauchamp
        J. Am. Chem. Soc., 97, 6893 (1975)

6. Gas Phase Proton Affinities Of Molecules In Excited Electronic
    States By Ion Cyclotron Resonance Spectroscopy
        B. S. Freiser and J. L. Beauchamp
        J. Am. Chem. Soc., 98, 265 (1976)

7. Photochemistry Of Weakly Bound Li^+ Complexes: A Method For
    Determining Shifts In Charge Distribution Accompanying Electronic
    Excitation
        B. S. Freiser, R. H. Staley, and J. L. Beauchamp
        Chem. Phys. Lett., 39, 49 (1976).

8. Sequential Two Photon Dissociation of Cyanobenzene Cation
        B. S. Freiser, T. E. Orlowski, and J. L. Beauchamp
        Chem. Phys., in press

9. Electron Impact Dissociation Of Cyanobenzene Radical Cations By
    Ion Cyclotron Resonance Spectroscopy
        B. S. Freiser and J. L. Beauchamp
        Chem. Phys. Lett., in press (included as Chapter III in this
        thesis)

Studies of phenomena related to electron impact excitation and dissociation of ions present a formidable challenge to the experimentalist. It is shown in Chapter III that ICR methods are applicable to the study of these processes.

Apparatus for Photochemistry Studies

The ICR instrumentation and experimental techniques for studying photochemical processes involving ions in the gas phase have been previously described in detail.[1,7,33-38] The "working end" of the apparatus is shown schematically in Figure 3. A McMahon-Beauchamp type trapped ion cell[6] is arranged with the source trapping region adjacent to a 1" sapphire window on the end of the vacuum enclosure. Ions initially formed by pulsing the electron beam (or substitute source) are stored in the source region of the ICR cell, irradiated, and then sampled. By varying the trapping time, the temporal behavior of ion concentration can be monitored. Some typical data are shown in Figure 4 for toluene cation which is photodissociated using the 488 nm line from an Ar^{+} laser via reaction 11. From the exponential decay

$$C_6H_5CH_3{}^+ + h\nu \rightarrow C_7H_7{}^+ + H \qquad (11)$$
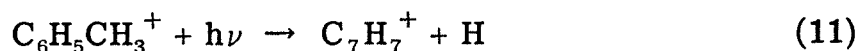
of the $C_7H_8{}^+$ with the laser on, and knowing the intensity of the light used, an estimate of the cross section for the process can be obtained at that wavelength using the equations detailed below. Varying the wavelength yields the photodissociation profile, which can be related to the absorption spectrum of the ion.[7]

Figure 3. Ion cyclotron resonance trapped ion apparatus for observing photochemical and photophysical processes involving ions.
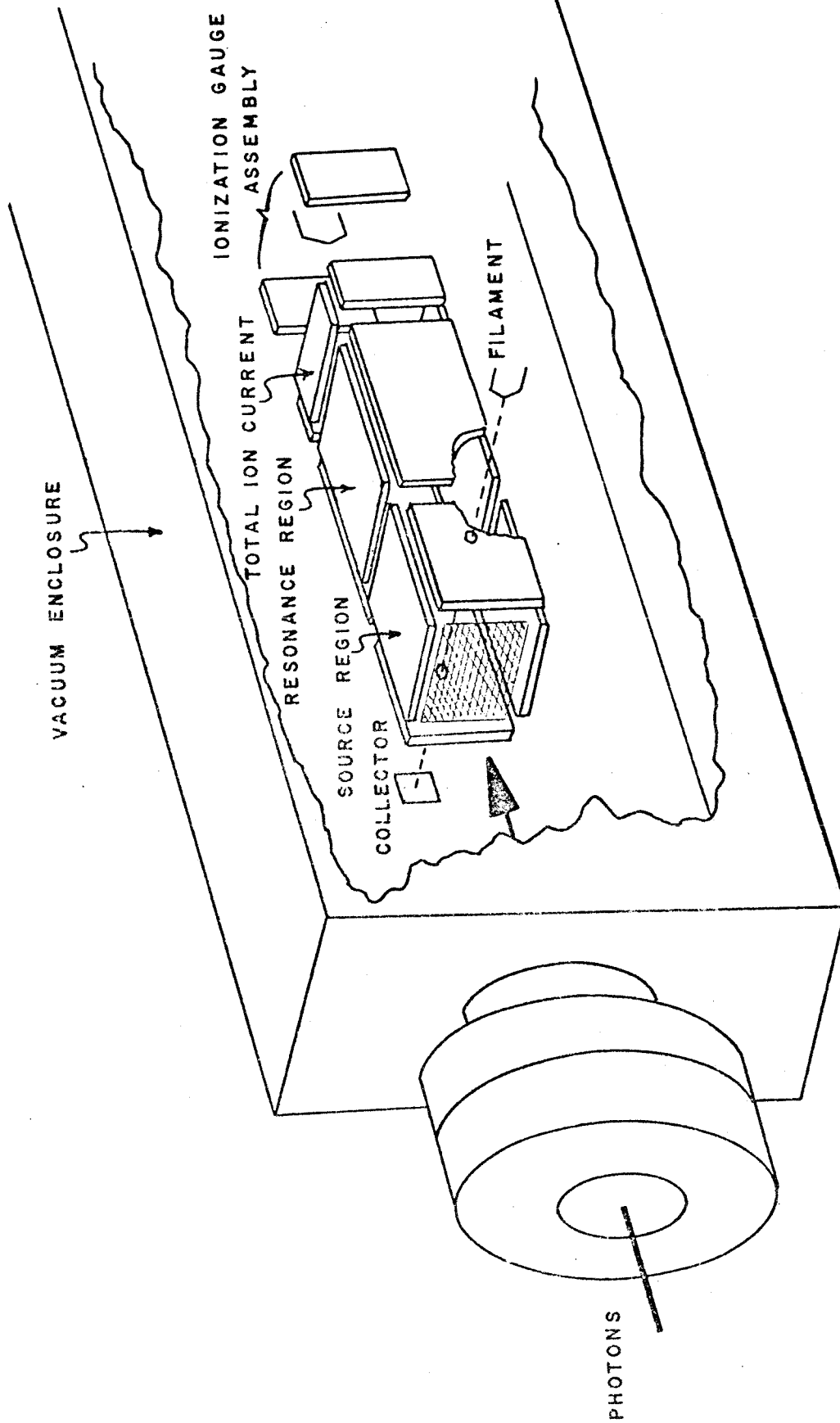
15

IONIZATION GAUGE ASSEMBLY

VACUUM ENCLOSURE

TOTAL ION CURRENT

RESONANCE REGION

SOURCE REGION
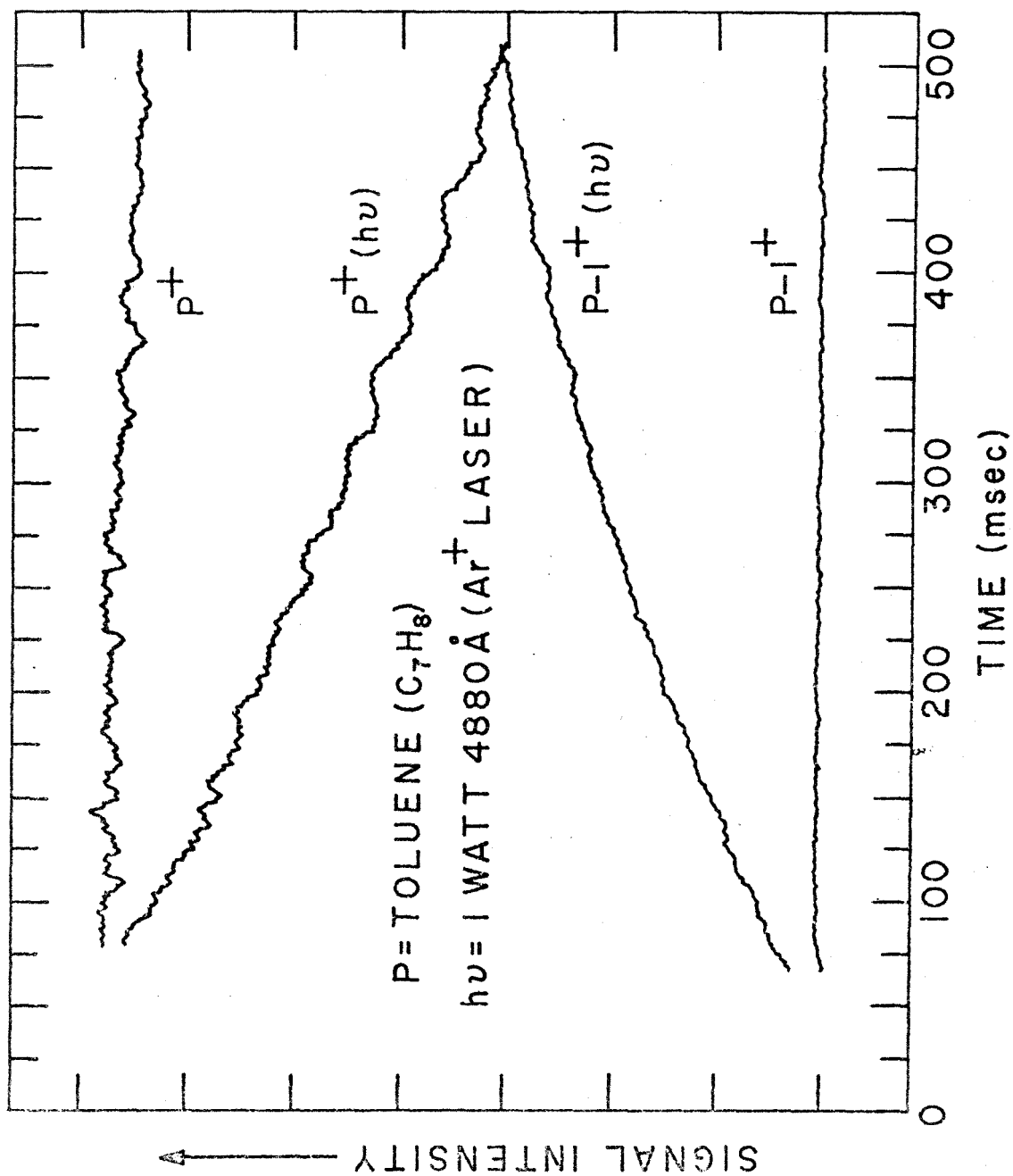
COLLECTOR

FILAMENT

PHOTONS

Figure 4. Variation of ion abundance with time in toluene, with and

without irradiation. When the laser is turned on, the

parent ion is observed to steadily decay, with buildup of

of the $C_7H_7^+$ product ion.

The apparatus also includes an electronic shutter which is synchronized with the trapped ion timing sequence such that light is admitted to the ICR cell only during a portion of the ion storage time. This feature permits ions to undergo a number of nonreactive collisions prior to irradiation to allow deactivation of any electronically or vibrationally excited species which could possibly complicate the measurements. Another obvious advantage of using the shutter is it enables the study of the photochemistry and spectroscopy of products formed in ion molecule reactions, thus making it possible to examine a greater range of species than can be formed by direct electron impact ionization. The utilization of this feature is illustrated in the sequence of reactions 12 and 13 in which the reagent methoxide ion is generated and then reacts with acetic acid to generate the acetate

$$CD_3ONO + e \rightarrow CD_3O^- + NO \tag{12}$$

$$CD_3O^- + CH_3CO_2H \rightarrow CH_3CO_2^- + CD_3OH \tag{13}$$
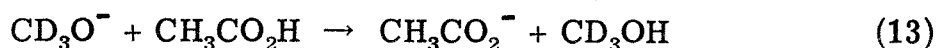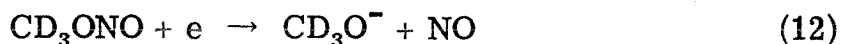
anion. The variation of ion abundance with time is shown in Figure 5. When the light is admitted to the cell, the photodetachment reaction 14

$$CH_3CO_2^- + h\nu \rightarrow CH_3CO_2 + e \tag{14}$$
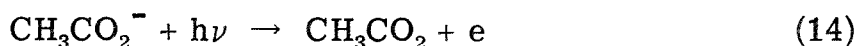
is observed. Simultaneously, the remaining reagent ion CD_3O^- (reformed by scavenging photoelectrons produced by reaction 14) is ejected from the cell. As observed in Figure 5, the acetate anion decays with time when the shutter is open. The extent of photodetachment is determined by the light intensity, the cross section for

Figure 5. Formation of $CH_3CO_2^-$ in a mixture of CD_3ONO and

CH_3CO_2H is indicated in the absence of irradiating light.

The experiment is then repeated except that irradiating

light is admitted into the ICR cell 540 msec after initi-

ating ionization. The subsequent decay of $CH_3CO_2^-$ is

due to photodetachment, and the reaction is complete at

~ 1 sec. The remaining CD_3O^- reagent ion is ejected

from the cell when the light is turned on.
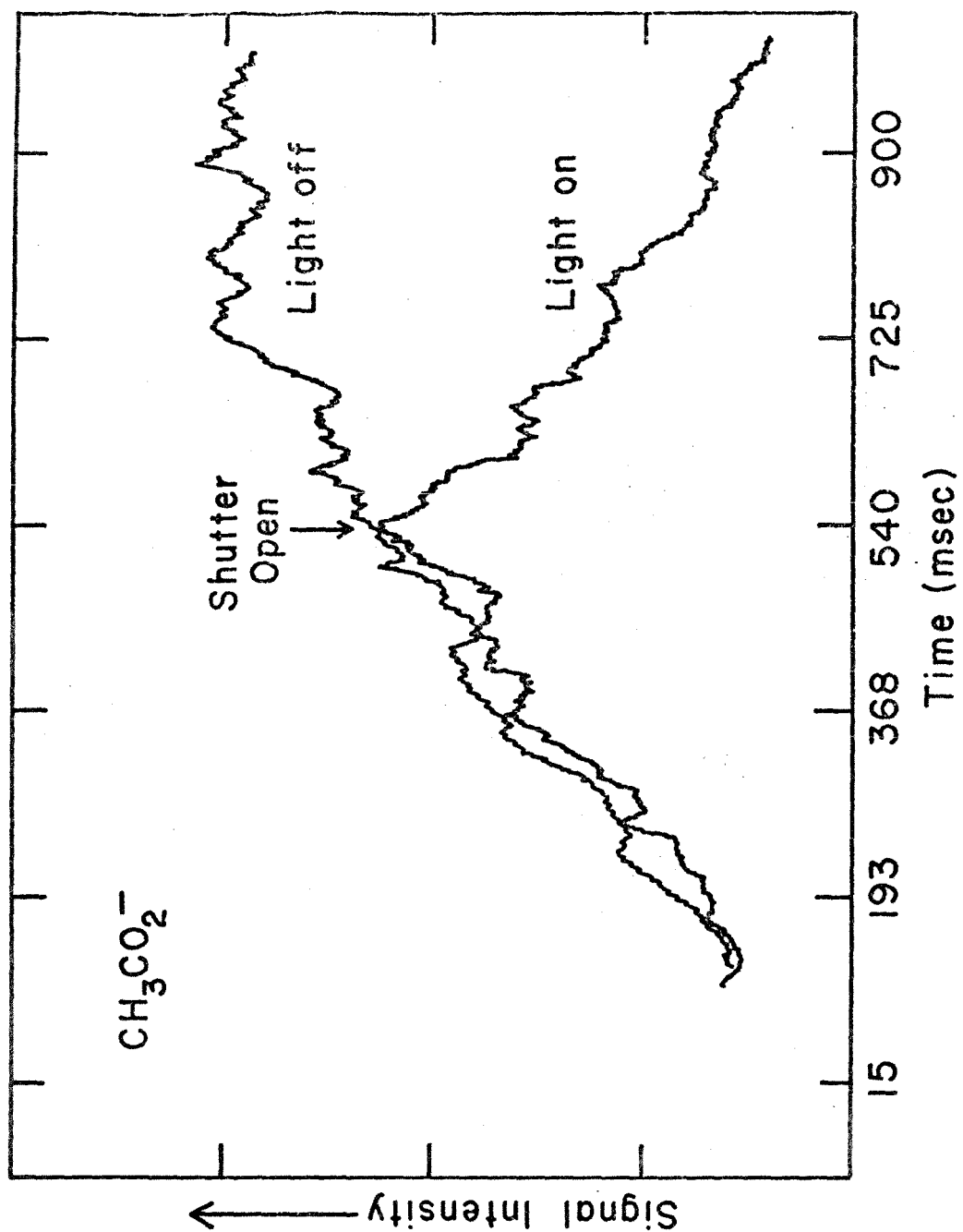
the process, and the irradiation period. In this case it is vital that irradiation proceed <u>after</u> the formation of $CH_3CO_2^-$ since the photo-detachment of CD_3O^- would yield erroneous results.

Finally, this instrument is tough and versatile and can be moved at a moments notice.

Determining Cross Sections and Extinction Coefficients From ICR Trapped Ion Data

Photodissociation and photodetachment, generalized by reaction 15, are pseudo first order processes. The rate of decay of A, dA/dt,

$$A + h\nu \rightarrow \text{products} \tag{15}$$

can be written as in eq 16, where f (unitless) is the overlap factor

$$\frac{dA}{dt} = - fI\sigma A \tag{16}$$

between the light beam and the ion cloud, I (photons $\sec^{-1}cm^{-2}$) is a measure of the light intensity, σ (cm^2) is the cross section for the particular photoprocess, and A (ions cm^{-3}) is the ion concentration. Solving equation 16 readily yields equations 17 and 18, where A and A_0

$$\ln A/A_0 = - fI\sigma t \tag{17}$$

$$\frac{d \ln A/A_0}{dt} = - fI\sigma \tag{18}$$

are the ion concentrations with the light on and with the light off, respectively. Thus from a plot of the data obtained in a trapped ion

experiment (with and without light) as indicated in eq 17 ($\ln A/A_0$ vs t), a measure of $If\sigma$ is obtained using eq 18. With a knowledge of the light intensity I, an estimate of the cross section is obtained. The overlap factor f will have a value between 0 and 1 depending on the conditions employed. We will here assume that it is 1. Because f is not known and changes from experiment to experiment, relative cross sections (comparing A with B) are more accurate and readily determined than absolute cross sections. It should be noted, however, that caution must be exercised in comparing the relative photode-struction of an ion produced by electron impact to one produced at some later time in an ion-molecule reaction for the obvious reason that the irradiation times are different.

Once a cross section σ (cm^2) is obtained, it can be multiplied by a constant factor (derived in eq 19) to yield the extinction coefficient

$$\epsilon(\ell\ mol^{-1}cm^{-1}) = \sigma(cm^2ion^{-1}) \times 6.023 \times 10^{23}\ (ion\ mol^{-1}) \times 10^{-3}\ (\ell\ cm^{-3})$$

$$= 6.023 \times 10^{20}\ \sigma\ (cm^2) \tag{19}$$

$\epsilon\ (\ell\ mol^{-1}cm^{-1})$ for direct comparison to other measurements (e.g., solution spectra).

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CHAPTER II

ACID BASE PROPERTIES OF MOLECULES IN EXCITED ELECTRONIC STATES UTILIZING ION CYCLOTRON RESONANCE SPECTROSCOPY

B. S. Freiser and J. L. Beauchamp[1]

Contribution No. 5378, from the Arthur Amos Noyes Laboratory of

Chemical Physics, California Institute of Technology

Pasadena, California 91125

Abstract: A general method is described for obtaining excited state acid-base properties of molecules and ions in the gas phase which utilizes ion cyclotron resonance spectroscopy for studying photochemical processes involving ions. These processes, including photodissociation and photodetachment, yield in favorable instances electronic excitation energies of ions. A comparison of the excitation energies of a base B with the corresponding acid-base complex AB yields the excited state basicity of B. Similarly, a comparison of the excitation energies of a chromophoric acid A with the complex AB yields information about the excited state acidity of A. Studies of the first type are described using the reference acids H^+ and Li^+ with the bases C_6H_5X (X = H, CN, NH_2, CHO, $COCH_3$, NO_2, OCH_3, O^-, and S^-), pyridine, and ferrocene. In several instances photodissociation spectra of solvated acid-base complexes of the type $BLiB^+$ have been obtained and analyzed to determine the effects of further

solvation on the excitation spectra of these complexes. A comparison of the gas phase excitation spectra of a number of ions to their solution absorption spectra is made.

Studies of the second type (excited state acidities) are described using the reference base H^- with the acids $C_6H_5CO^+$ and $C_6H_5CHOH^+$. Calculated changes in acidity and basicity are used to infer changes in electron distributions and dipole moments for excited states, and yield insight into the types of transitions involved. In particular these studies are used to assess the controversial role played by intramolecular charge transfer in the lowest two singlet $\pi \to \pi^*$ transitions of monosubstituted benzenes. These results are compared with findings from related experiments and calculations when available.

One of the most important and useful concepts in chemistry is that of the acid-base properties of molecules. Several treatises have been written on the subject, including classic papers by Brønsted and Lewis among others.[2] Despite different points of view, a general description emerges: a base is a specie which is electron donating and an acid is one which is electron accepting. This definition alone suggests an intimate relationship between the acid-base properties of a molecule and its charge distribution. Since charge densities are often modified by electronic excitation, it is expected that the acid-base properties of a molecule in an excited state will also vary from its properties in the ground state. Conversely, a determination of excited state acid-base

properties can be used to infer associated changes in electron density and dipole moment. Determining these quantities has been a subject of considerable interest both theoretically and experimentally and, because of their interrelationship, determining any one property sheds light on the others.

The direct measure of acid-base properties of molecules in excited states in solution remains an active area of research.[3-5] These studies mainly utilize absorption data and fluorescence data in conjunction with the Förster cycle[3] to determine changes in pK in excited singlet and triplet states.[4] Most of this work is confined to Brønsted acids and bases, though some work on Lewis acid systems has been reported.[5] New and promising research areas involve utilization of excited acid-base properties to promote otherwise inactive chemical reactions[6] and the application of pulsed picosecond lasers to study the kinetics of excited state proton transfer reactions. Work having indirect significance to excited state acid-base properties includes calculations on charge distributions of molecules in their ground and excited states[7-9] from which dipole moments can be obtained. In addition, there are numerous experimental approaches which yield dipole moments of molecules in excited electronic states.[10-17] For molecules in metastable excited states having sufficiently long lifetimes, the usual methods for obtaining dipole moments in ground states may be successfully applied.[14,15] For short-lived systems, alternate methods have been devised utilizing the effects of electric fields on absorption spectra[10-13] (electrochromism) and

the influence of solvent on the spectra[10a, 16, 17] (solvatochromism).
These results aid in understanding the types of transitions involved,
provide a test for the accuracy of theoretical calculations, and again
suggest excited state acid-base properties.

The bond dissociation energy D(A—B) determined for the general
reaction 1 defines acid-base strengths as considered throughout this

$$AB \rightarrow A + B \qquad \Delta H_{rxn} \equiv D(A-B) \qquad (1)$$
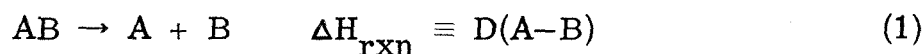
paper. Thus, for a particular reference acid A, B_2 is a stronger base
than B_1 if $D(A-B_2)$ is greater than $D(A-B_1)$. Similarly, for a partic-
ular reference base B, A_2 is a stronger acid than A_1 if $D(A_2-B)$ is
greater than $D(A_1-B)$.

Application of gas phase methods[18] such as flowing after-
glow,[19, 20] high pressure mass spectrometry,[18, 21, 22] drift
tubes,[23, 24] and ion cyclotron resonance spectroscopy[25-31] (ICR) have
been instrumental in determining intrinsic ground state acid-base
properties in the absence of complicating solvation effects. The
reactions studied are generally the equilibria processes 2 and 3. For

$$AB_1 + B_2 \rightleftharpoons AB_2 + B_1 \qquad (2)$$
$$A_1B + A_2 \rightleftharpoons A_2B + A_1 \qquad (3)$$
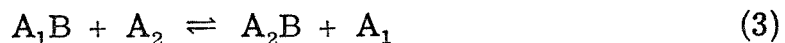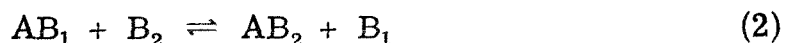
process 2, numerous studies have been reported using the reference
acids H^+,[18, 19-21, 25, 26] Li^+,[27] and more recently $CpNi^+$[28] to deter-
mine the basicities of a wide variety of n- and π-donor neutral bases
as well as of anionic bases in the case of H^+. For process 3, relative

acidities have been tabulated for a great number of cationic and neutral acids using the reference bases H[-],[18, 22, 29] F[-],[18, 29, 30] Cl^{-},[30] and Br^{-}.[31] In all of these cases, the criteria for study is that one of the species must be positively or negatively charged.

In this paper we report a straightforward method for determining the gas phase acid-base properties of molecules in excited electronic states using the techniques of ion cyclotron resonance spectroscopy.[32, 33] The determination of excited state basicities is discussed first. The method is general and follows directly from the thermochemical cycle in Scheme I, where A is a reference acid, B is
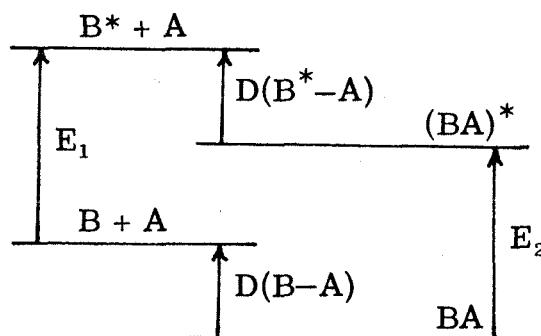
Scheme I

a neutral or negatively charged base in the ground state, B^* is the base in an excited state, E_1 is the excitation energy of the base, E_2 the excitation energy of its conjugate acid, and $D(B-A)$ and $D(B^*-A)$ define the base strengths in the ground and excited states, respectively. The determination of binding energies in excited electronic states relative to the ground state is then determined from eq 4. Since

$$\Delta D(B-A) = D(B^*-A) - D(B-A) = E_1 - E_2 \qquad (4)$$

$\Delta D(B-A)$ is a thermodynamic quantity, E_1 and E_2 in eq 4 should correspond to adiabatic transition energies. Unfortunately, measurements of the 0-0 transition energies cannot be accurately determined due to the lack of vibrational structure in these spectra. However, if the band shapes of the base and conjugate acid are similar, using vertical energies does not introduce large errors.

Using H^+ for A, Scheme I can be applied in determining proton affinities in excited states, and corresponds to the Förster cycle[3] utilized in solution work. The proton affinity PA(B) of a neutral or anionic base B is defined as the heterolytic bond dissociation energy for process 1 where A is H^+. The excited state proton affinity $PA(B^*)$ is determined relative to the ground state proton affinity PA(B) using eq 5 which follows directly from eq 4 and the definition of proton

$$\Delta PA(B) = PA(B^*) - PA(B) = E_1 - E_2 \tag{5}$$

affinity. When B is a neutral species, E_1 is obtained from the gas phase absorption spectrum of B, and E_2 is obtained using ICR techniques developed for examining the photodissociation of gaseous ions,[32, 35-37] the latter phenomenon generalized by eq 6. The measured quantity in

$$C^+ + h\nu \rightarrow D^+ + E \tag{6}$$

reaction 6 is the photodissociation cross section, $\sigma_d(\lambda)$, which is proportional to the product of the intrinsic transition probability or gas phase extinction coefficient, $\epsilon_g(\lambda)$, and the photodissociation quantum yield, $\varphi_d(\lambda)$, as written in eq 7. If the quantum yield for

$$\sigma_d(\lambda) \propto \epsilon_g(\lambda)\varphi_d(\lambda) \tag{7}$$

photodissociation is relatively constant over an absorption band, then $\sigma_d(\lambda)$ will reflect the absorption spectrum and directly yield the vertical excitation energy.[36] If, on the other hand, φ_d varies significantly over an absorption band, then $\sigma_d(\lambda)$ will not yield exactly the vertical excitation energy. The latter would occur, for example, in the vicinity of the thermodynamic threshold for dissociation, below which $\varphi_d(\lambda) = 0$.

When B is an anion such as phenoxide ($C_6H_5O^-$), E_2 is obtained from the gas phase absorption spectrum of the conjugate acid, and E_1 is obtained from the excitation spectrum of the anion. Excited states of anions are generally higher in energy than the electron affinity of the corresponding neutral EA(B); hence they lie in the photodetachment continuum.[38-40] Following absorption, excited states decay by autodetachment[38-40] or dissociation.[41-43] In the former case, peaks appear in the photodetachment spectrum; in the latter case, eq 7 is applicable with $\sigma_d(\lambda)$ being directly determined by monitoring either the disappearance of the primary ion or the appearance of corresponding photofragment ions.

The alkali ions, especially Li^+, have received considerable attention both theoretically and experimentally as reference Lewis acids to measure base strengths of molecules.[27, 44-46] Interesting differences in both the quantitative and qualitative ordering of base strengths using Li^+ compared to H^+ arise[27] due to the strictly

electrostatic bonding of Li^+ compared to the covalent bonding available to the proton.[45] The core electrons on Li^+ interact repulsively with electrons on the base (Pauli Principle) preventing the close contact necessary for covalent bonding.[45] Thus, while important information can be obtained about excited state proton affinities using H^+, Li^+ studies yield a more straightforward analysis of the changes in charge distribution of a neutral base accompanying excitation since the purely electrostatic bonding in Li^+ does not perturb the nature of the chromophore.

A potential energy diagram for the formation of BLi^+ in its ground state as well as in a selected excited state is shown in Figure 1. The determination of Li^+ binding energies of molecules in excited states relative to the ground state follows directly using eq 4 with $A = Li^+$ to yield eq 8, where E_1 is determined from the gas phase ab-

$$\Delta D(B-Li^+) = D(B^*-Li^+) - D(B-Li^+) = E_1 - E_2 \qquad (8)$$

sorption spectrum of B and E_2 is obtained readily by monitoring the photodissociation reaction 9.

$$BLi^+ + h\nu \rightarrow B + Li^+ \qquad (9)$$

During the course of the above studies on weakly bound Li^+ complexes, it was found that at long times or at high pressures these complexes react further to form Li^+ bound dimers directly by reaction 10. The dimer species are observed to photodissociate via reaction 11 allowing a comparison of their spectra to that of the corresponding

Figure 1.   Potential energy diagram for the formation of BLi$^+$ in its ground state as well as in a selected excited state.

$$BLi^+ + B \rightarrow B\overset{+}{L}iB \tag{10}$$

$$B\overset{+}{L}iB + h\nu \rightarrow BLi^+ + B \tag{11}$$
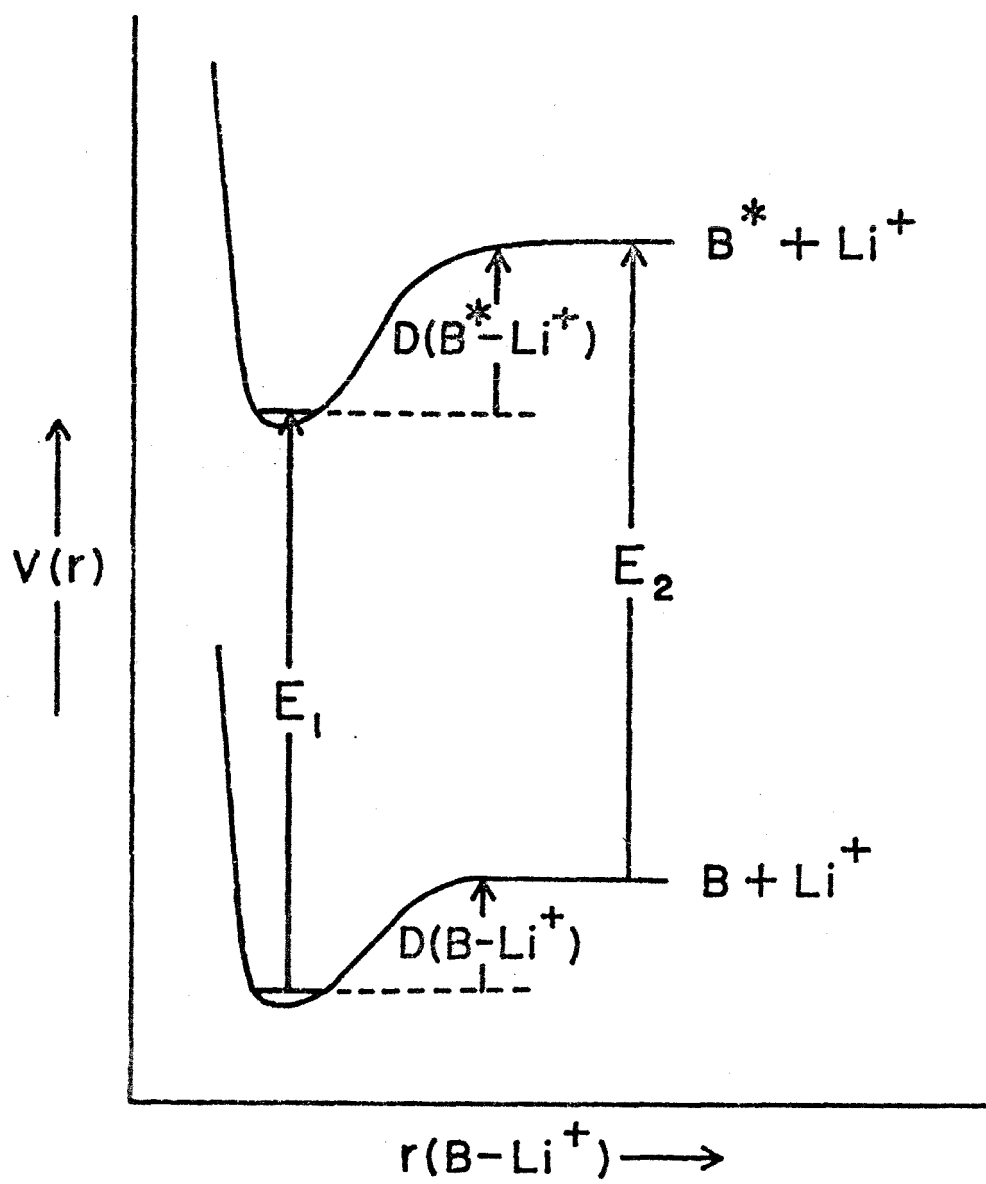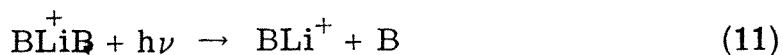
neutral and monomer complex. These results yield information relating to the effects of further solvation on the electronic excitation energies of the acid-base complex.

Scheme II can be used to detail the change of acidity of a mole-cule or ion in the analogous manner to Scheme I. This scheme yields
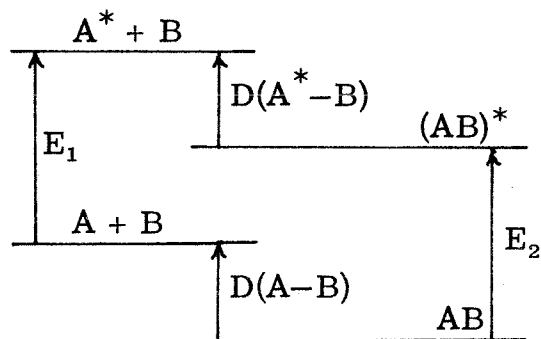
Scheme II

eq 12, where $\Delta D(A-B)$ is the change in the acidity of A between its

$$\Delta D(A-B) = D(A^*-B) - D(A-B) = E_1 - E_2 \tag{12}$$

excited state acidity, defined $D(A^*-B)$, and its ground state acidity, defined $D(A-B)$, and where E_1 and E_2 are obtained from the excitation spectrum of the isolated and complexed acid, respectively. As noted above, for this analysis to be straightforward, the reference base B must not greatly change the nature of the chromophore. For cationic acids $(A = R^+)$ and using H^- as the reference base, eq 12 becomes

eq 13. This equation is used to deduce information about the excited

$$\Delta D(R^+-H^-) = D(R^{+*}-H^-) - D(R^+-H^-) = E_1 - E_2 \qquad (13)$$

state acidities of benzoyl cation and protonated benzaldehyde.

Scheme III is used to determine solvent effects on absorption

spectra of ions, where A is the gaseous ground state species, A* the
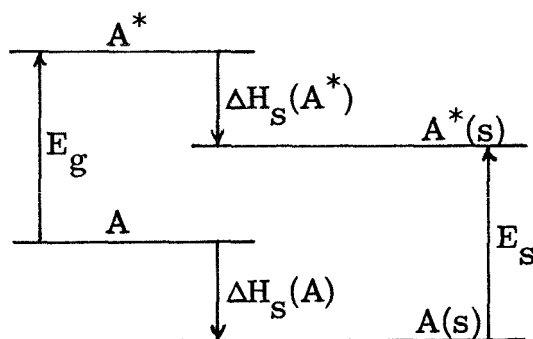
Scheme III

gaseous excited state species, A(s) is the solvated ground state species,

$A^*(s)$ is the solvated excited state species, E_g is the excitation energy

in the gas phase, E_s the excitation energy in solution, and $\Delta H_s(A)$ and

$\Delta H_s(A^*)$ are the heats of solvation for the ground and excited states,

respectively. Solvent shift is an effective spectroscopic tool both for

determining the character of absorption bands and for yielding insight

into the intermolecular forces between solute and solvent.[47] From

Scheme III, for example, it is clear that the solvent shift $E_g - E_s$

yields information about the changes in solvation energy between the

ground and excited states, $\Delta H_s(A) - \Delta H_s(A^*)$. Several ions whose

spectra have been obtained in both gas and solution phase will be dis-

cussed.

Most of the ions and neutrals examined in this study are mono-

substituted benzenes. The detailed characterization of excited elec-

tronic states of these species remain controversial. In particular, for

the neutral species, the two lowest singlet $\pi \rightarrow \pi^*$ excitations have been

interpreted in two ways. The observation that the uv spectra of sub-

stituted benzenes are largely uniform and greatly resemble that of the

parent compound, despite the reduction in symmetry and perturbation

of the electronic system by the substituent, have led to one interpreta-

tion that these bands correspond to the benzene transitions shifted to

lower energies.[48] Using this interpretation, bands corresponding to

the benzene 203.5 nm primary band ($^1A_{1g} \rightarrow {}^1B_{1u}$) and to the 256 nm

secondary band ($^1A_{1g} \rightarrow {}^1B_{2u}$) are found usually shifted in a regular way

in monosubstituted benzenes such that the ratios of λ_{max} for the sec-

ondary and primary bands are $\lambda_{sec}/\lambda_{prim} \simeq 1.24$. These transitions

can be assigned $^1A_1 \rightarrow {}^1B_2$ and $^1A_1 \rightarrow {}^1B_1$ in the lower C_{2v} symmetry.

More recently it has been suggested that for certain substituents these

transitions correspond to internal charge transfer bands in which elec-

tron density shifts either from the ring to the substituent or from the

substituent to the ring depending on the nature of the substituent.[10b, 49]

Similar interpretations can also be applied to ionic monosubstituted

benzenes such as benzoyl cation[36] and phenoxide anion.[10b]

If internal charge transfer is important in these species, dra-

matic effects on their acid-base properties in their lowest excited

states are expected. Hence, the present studies provide further information relating to the nature of the electronic excitations.

Experimental

ICR instrumentation and experimental techniques for studying photochemical processes involving ions in the gas phase have been previously described in detail.[32, 34-36] Methods for generating alkali ion complexes have also been described.[27] Pressures utilized for these experiments were typically 10^{-7} torr and ion trapping times approached 2 sec. A 2.5 kW mercury-xenon arc lamp was used in conjunction with a 0.25 m Bausch and Lomb monochromator set for a resolution of 10 nm, except for Li^+ complexes with nitrosobenzene, ferrocene, and p-methoxybenzaldehyde for which 13 nm resolution was used, to obtain photodissociation spectra. Neutral absorption spectra were obtained on a Cary 17 using a 1 cm quartz gas cell. All chemicals were commercial samples of high purity, and were used as supplied except for freeze-pump-thaw cycles to remove non-condensable gases. Mass spectrometry revealed no detectable impurities.

Results

Excited State Basicities. The gas phase spectra of several bases B and their conjugate acids BH^+ between 200 and 400 nm are displayed in Figures 2-6 and summarized in Table I. The spectra of the cations were obtained by monitoring their photodissociation. In several instances (eqs 14-18) the photoproducts were investigated.

Figure 2. (a) Comparison of the gas phase absorption spectrum of benzaldehyde with the photodissociation spectrum of its conjugate acid.

(b) Comparison of the gas phase absorption spectrum of cyanobenzene with the photodissociation spectrum of its conjugate acid. The absorption spectra of the neutrals were recorded at low resolution to facilitate comparison.
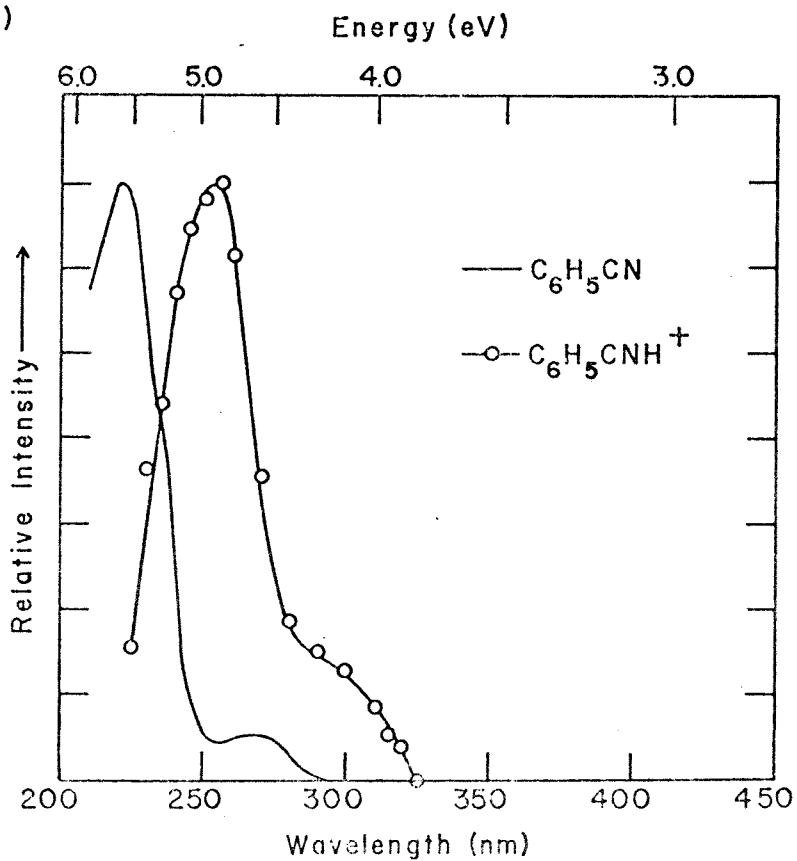
(a)
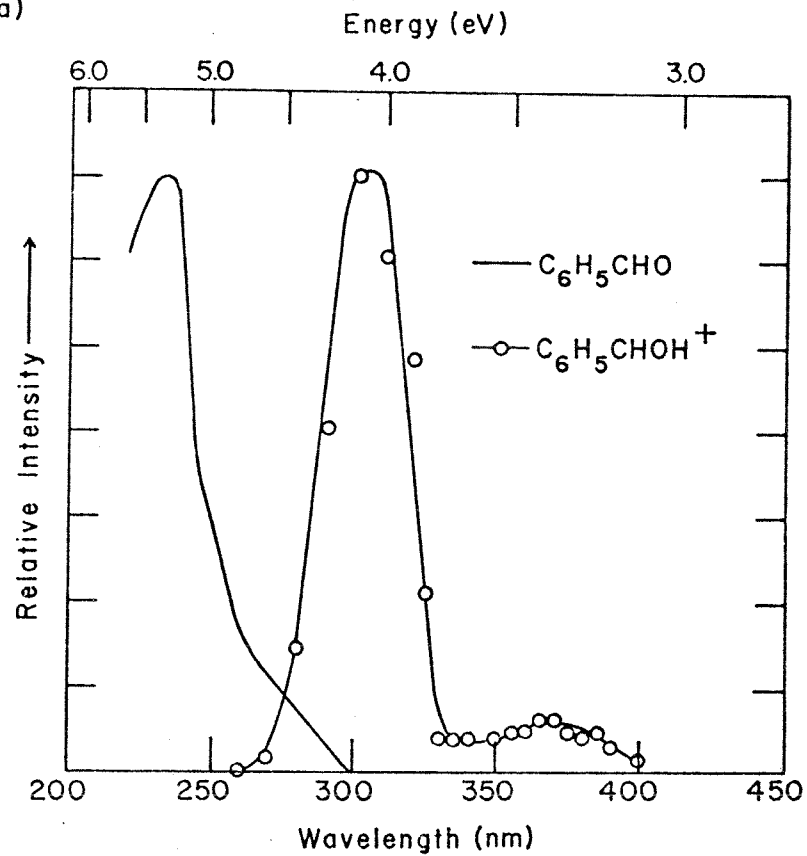
(b)

Figure 3. (a) Comparison of the gas phase absorption spectrum of acetophenone with the photodissociation spectrum of its conjugate acid.

(b) Comparison of the gas phase absorption spectrum of nitrobenzene with the photodissociation spectrum of its conjugate acid. The absorption spectra of the neutrals were recorded at low resolution to facilitate comparison.

Figure 4. Comparison of the gas phase absorption spectrum of
pyridine with the photodissociation spectrum of its
conjugate acid.

Figure 5. (a) Comparison of the gas phase absorption spectrum of benzene with the photodissociation spectrum of its conjugate acid.

(b) Comparison of the gas phase absorption spectrum of mesitylene with the photodissociation spectrum of its conjugate acid. The absorption spectra of the neutrals were recorded at low resolution to facilitate comparison.
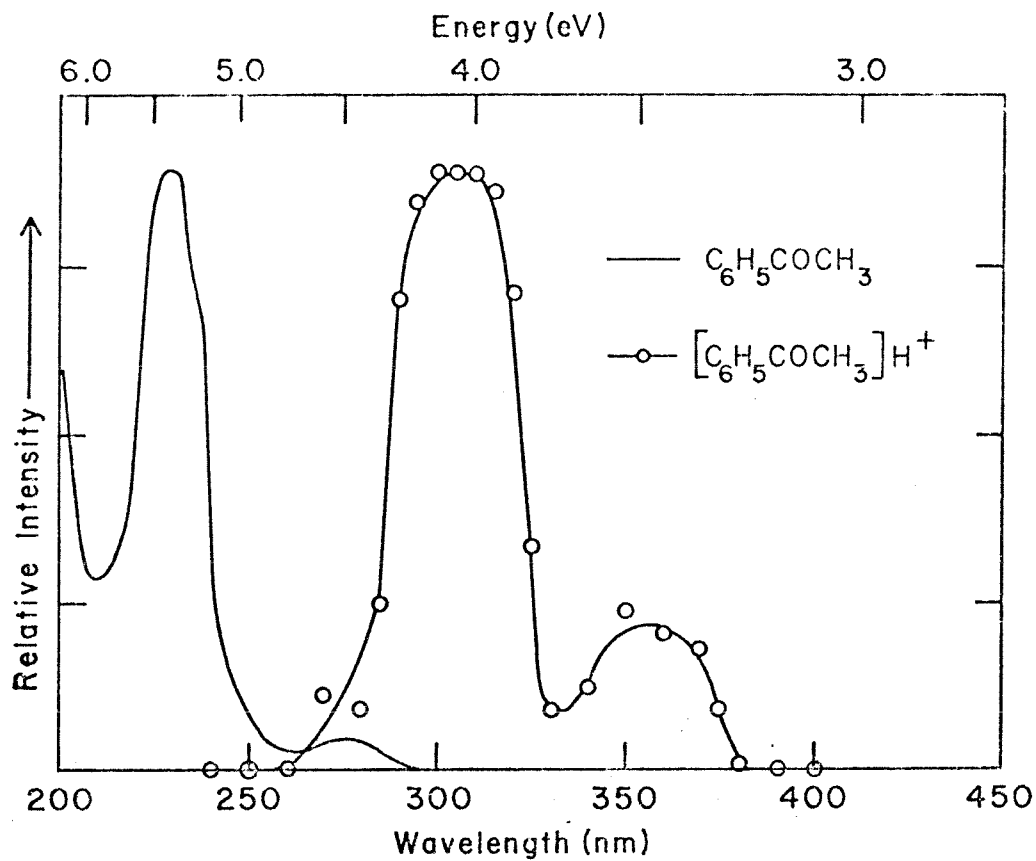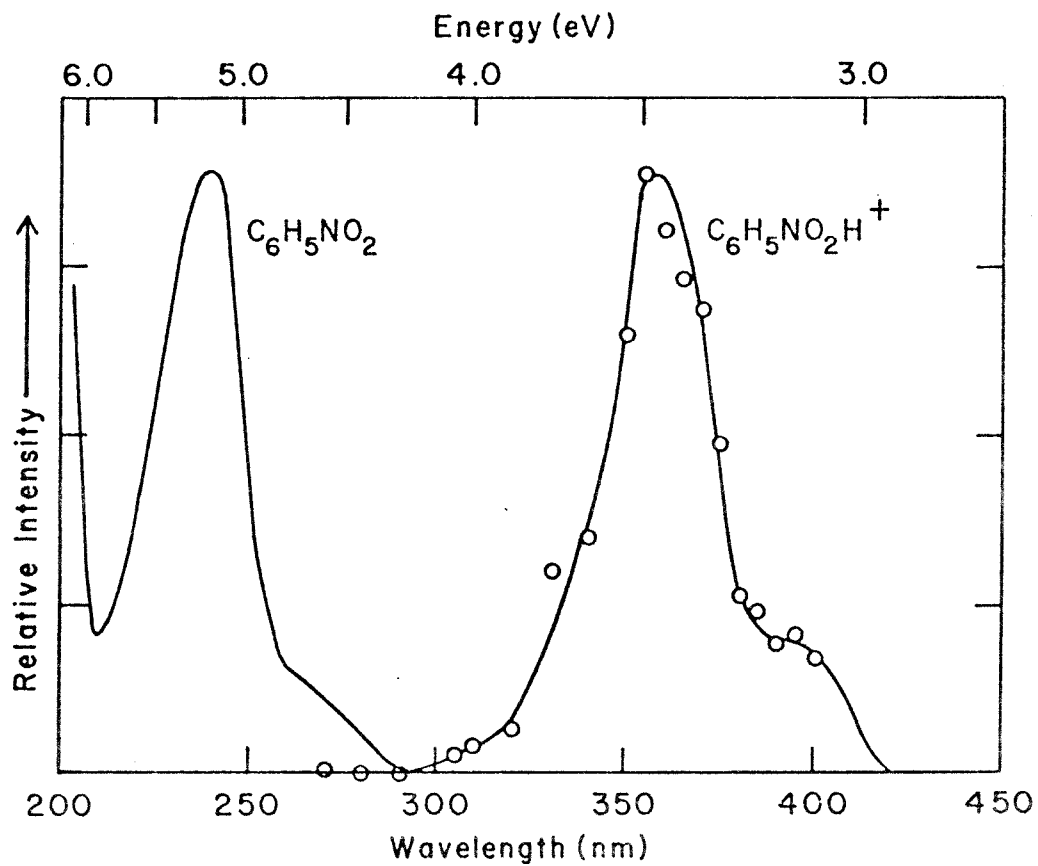
(a)

(b)

Figure 6. Comparison of the gas phase absorption spectrum of anisole with the photodissociation spectrum of its conjugate acid.
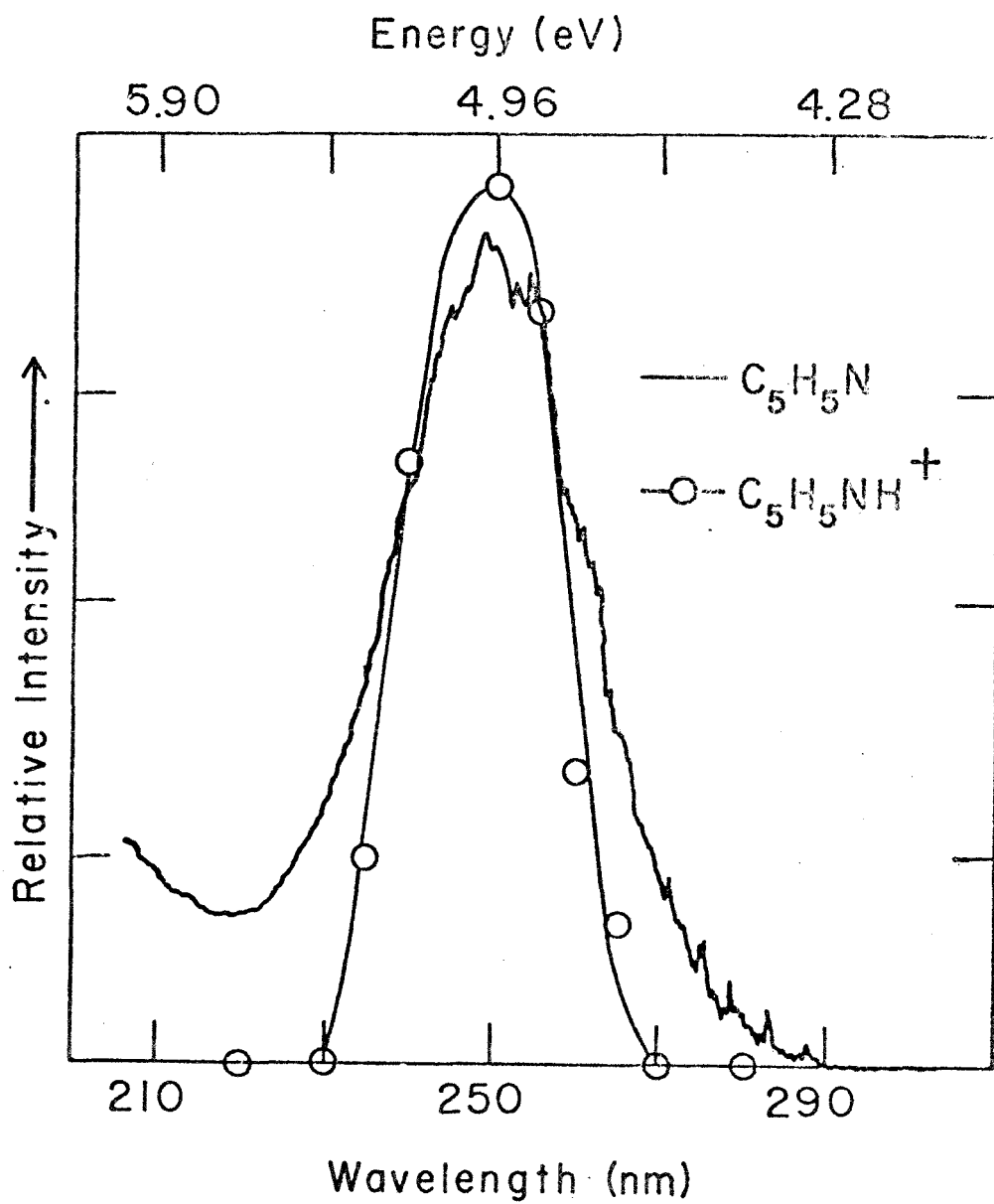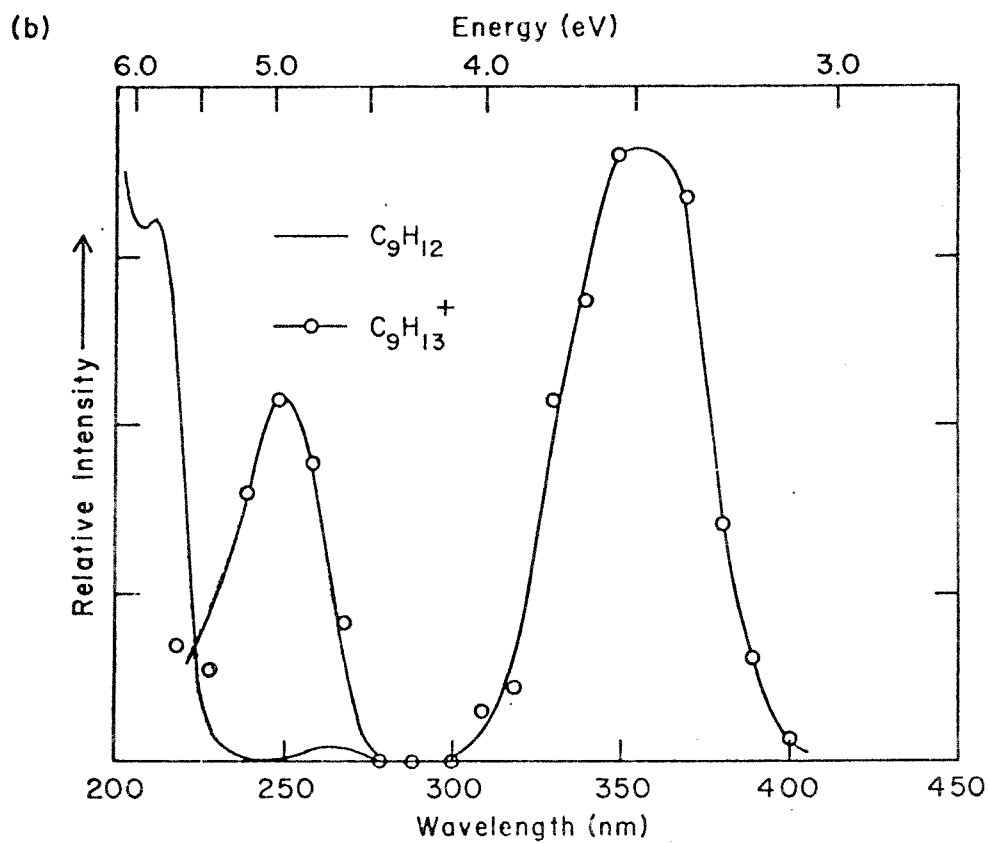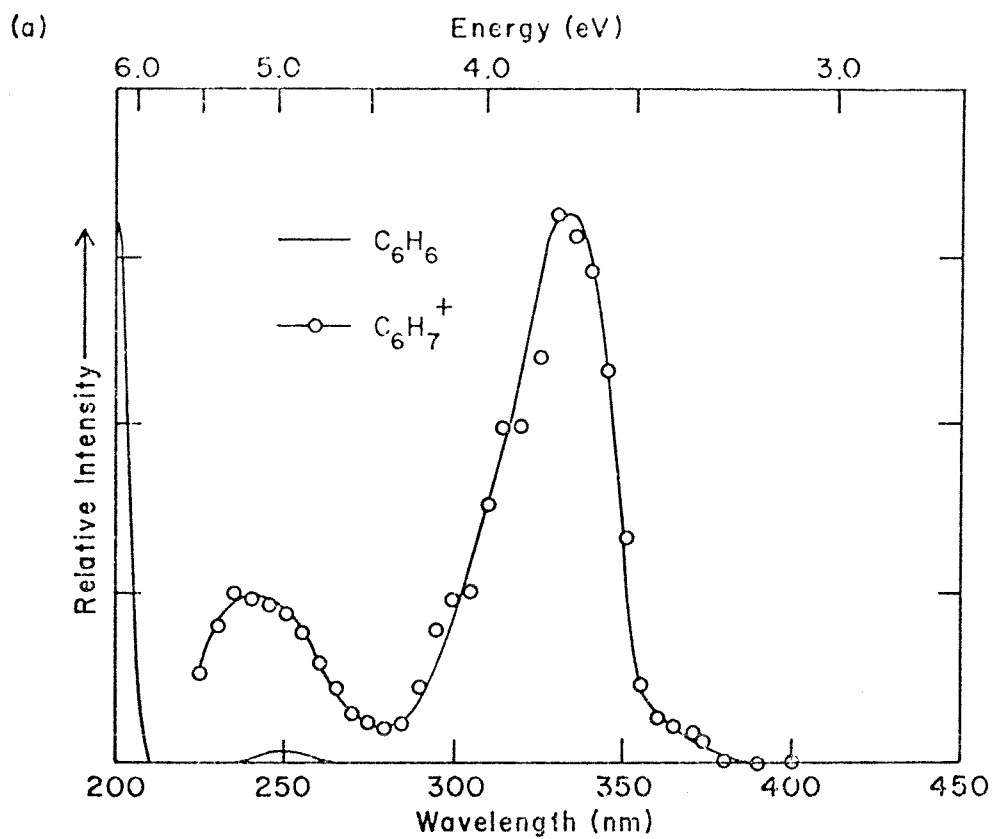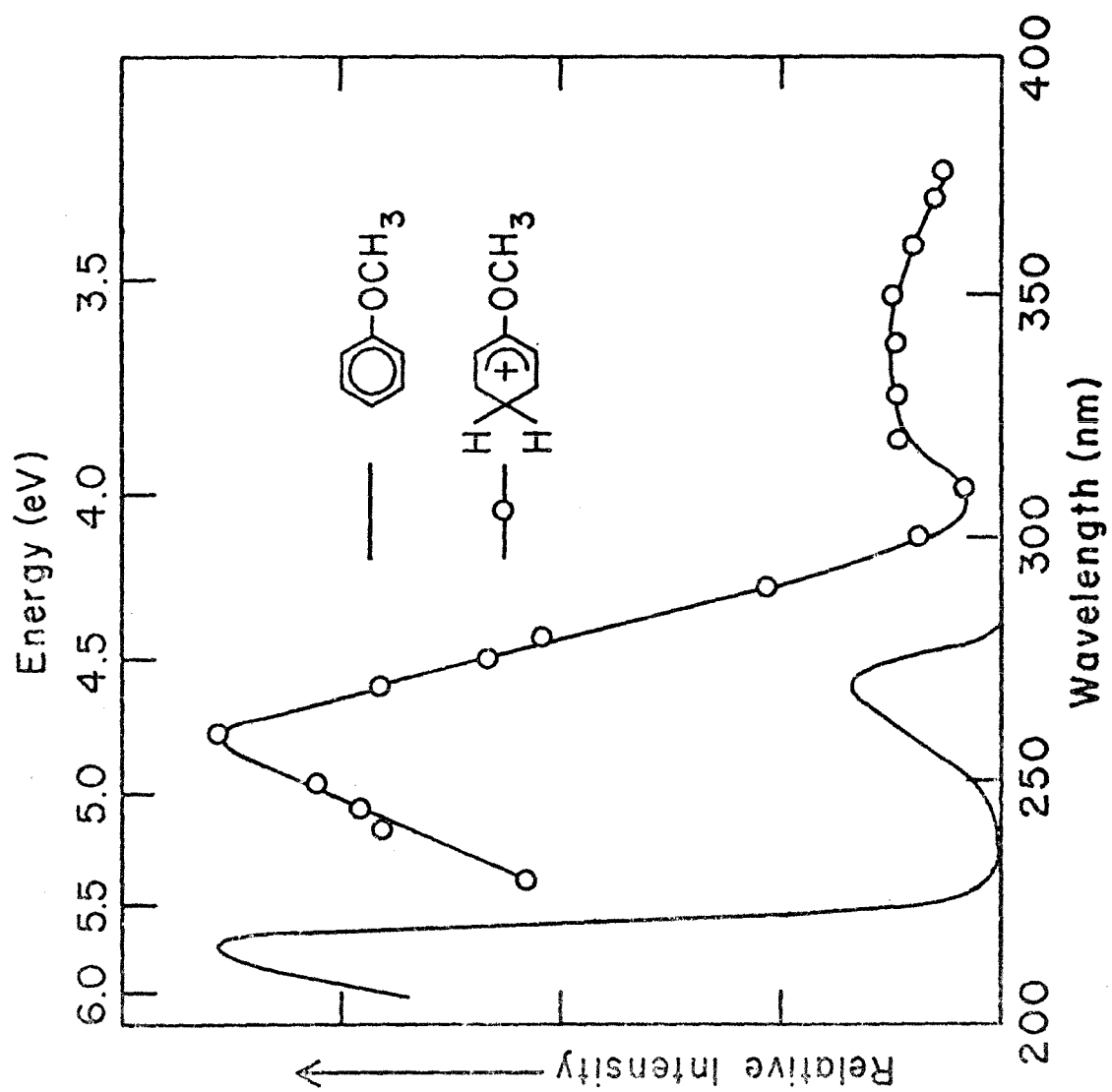
Table I. Spectroscopic and Thermochemical Data Related to Proton Affinities of Electronically Excited States of Selected Neutral Bases

Compound	PA(B)[a]	Neutral λ_{max}[b]	rel[c] int	Conjugate Acid λ_{max}[b]	rel[c] int	PA(B*)[a]	ΔPA[a]
Benzaldehyde	198.1	232	1.00	303	1.00	227.1	29
	198.1	275[d]	0.11	368	0.09	224.1	26
Cyanobenzene	194.1	224	1.00	254	1.00	209.1	15
	194.1	274	0.07	293	0.20	201.1	7
Acetophenone	203.1	230	1.00	305	1.00	233.1	30
	203.1	275	0.05	355	0.24	226.1	23
Nitrobenzene	191.6	240	1.00	357	1.00	230.6	39
	191.6	280	0.12	~400	0.19	222.6	31
Pyridine	218.1	250	1.00	250	1.00	218.1	0
	218.1	275	e	f	f	<218.1	<0
Benzene	182.7	201[g]	1.00	245	0.25	205.7	23
	182.7	253[g]	0.03	330	1.00	208.7	26
Mesitylene	197	212	1.00	250	0.60	217	20
	197	264	0.02	355	1.00	225	28
Anisole	198.4	216	1.00	260	1.00	220.4	22
	198.4	268	0.20	340	0.14	220.4	22

[a]PA(B) and PA(B*) in kcal/mol. ΔPA = PA(B*) - PA(B); values for PA(B) are relative to PA(NH₃) = 202.3 ± 2 kcal/mol (J. F. Wolf, I. Koppel, R. W. Taft, R. H. Staley, and J. L. Beauchamp, unpublished results; P. Kebarle, 1976 ASMS Annual Conference on Mass Spectrometry, San Diego).

Table I. (Continued)

[b]Wavelength, ± 10 nm for conjugate acid spectra.

[c]Band intensities relative to the more intense peak which is assigned a value of 1.00.

[d]These bands are low intensity shoulders for which λ_{max} is difficult to define precisely. An error of 10 nm introduces an uncertainty of approximately 5 kcal/mol in ΔPA.

[e]Unresolved band.

[f]Band not observed.

[g]K. Kimura and S. Nagakura, Mol. Phys., 9, 117 (1965).

$$C_6H_5CHOH^+ + h\nu \rightarrow C_6H_7^+ + CO \tag{14}$$

$$C_6H_5CNH^+ + h\nu \rightarrow C_6H_5^+ + HCN \tag{15}$$

$$C_5H_5NH^+ + h\nu \rightarrow C_5H_4N^+ + H_2 \tag{16}$$

$$\text{[structure]} + h\nu \rightarrow C_6H_5^+ + H_2 \tag{17}$$

$$\text{[structure]} + h\nu \rightarrow \begin{cases} C_9H_{11}^+ + H_2 & (18a) \\ C_9H_9^+ + 2H_2 & (18b) \\ C_8H_9^+ + CH_4 & (18c) \end{cases}$$
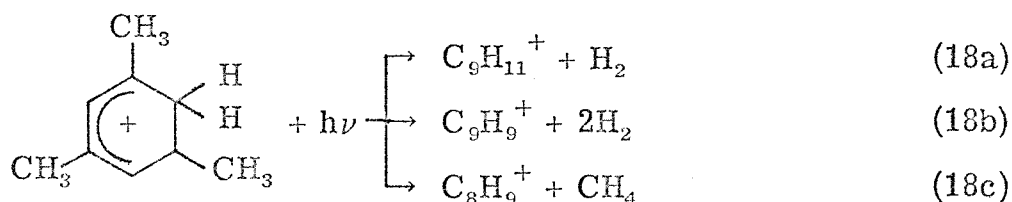
For simplicity throughout this paper we use W_0 to denote the ground state and W_1 and W_2 (when applicable) to indicate the first and second strongly allowed states observed for the above bases and their conjugate acids.
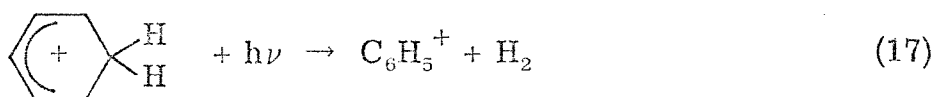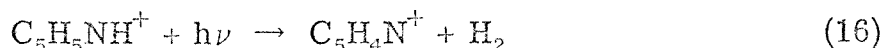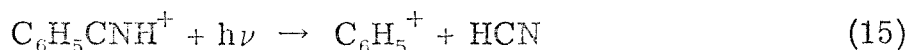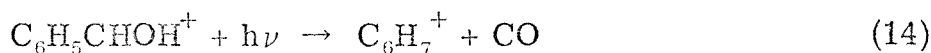
Figures 2 and 3 compare the neutral absorption spectra of benzaldehyde, cyanobenzene, acetophenone, and nitrobenzene to the photodissociation spectra of their conjugate acids. These species have all been shown in other studies to be substituent protonated.[50] Due to the similarity in the band shapes of the neutral molecules and their conjugate acids, as indicated above, vertical excitation energies are used to determine E_1 and E_2 in eq 5 without introducing large errors.

The most pronounced effect of excitation on base strength is observed for the W_2 state of nitrobenzene, estimated to be 39 kcal/mol more basic than the ground state. This would correspond to an increase of about 28 pK units! Similar but smaller increases in proton

affinity are calculated for the excited states of benzaldehyde, cyanobenzene, acetophenone, and the W_1 state of nitrobenzene (Table I).

Protonated aniline was not observed to undergo photodissociation. This suggests, but is not proof, that the spectrum lies to higher energies (unattainable with the present apparatus) as is observed for the absorption spectrum of anilinium in solution.[51]

Figure 4 compares the gas phase spectrum of pyridine with the photodissociation spectrum of the protonated species obtained by monitoring reaction 16. The long wavelength tail ascribed to the $n \rightarrow \pi^*$ transition[52] is not observed in the protonated species. The $\pi \rightarrow \pi^*$ transition,[52] however, shows no shift, indicating no change in base strength in the excited state.

Figures 5 and 6 compare the gas phase absorption spectra of benzene, mesitylene, and anisole to the photodissociation spectra of their conjugate acids. These species have been shown to be ring protonated.[50,53] Ring protonation occurs in the para position for anisole.[53] Assuming correlation, as previous solution studies suggest,[4] substantial increases in proton affinity are calculated for the excited states of these species with, for example, ΔPA = 26 and 23 kcal/mol being noted for the W_1 and W_2 excited states in benzene.

As noted above, excitation energies of negative ions can be obtained by monitoring either photodissociation or photodetachment

processes, and used in conjunction with eq 4 to yield excited state base strengths. The specific examples mentioned here are observed to undergo photodetachment.

The photodetachment threshold is frequently a good estimate of the electron affinity.[38-40] Recent photodetachment experiments by J. H. Richardson have indicated that complex molecular ions can be expected to exhibit unusual photodetachment cross sections arising from transitions to excited electronic states of the ion.[40] The use of these excitation energies to elucidate excited state properties of anionic bases was not considered. A series of phenoxides as well as thiophenoxide provide an interesting application of this analysis. Figure 7, showing the relative photodetachment cross section of phenoxide as a function of wavelength obtained by J. H. Richardson[40], is typical of the above mentioned species. Based on proton transfer data it is concluded that the lower intensity, nearly linear cross section at longer wavelengths ($>$ 400 nm) corresponds to photodetachment of an electron from the highest occupied molecular orbital.[40] The maximum at 332 nm, also observed in solution[54] (ca. 300 nm), is attributed to a $\pi \rightarrow \pi^*$ transition to an excited electronic state of the ion. The photodetachment cross section for the ions $o-CH_3C_6H_4O^-$, $o-ClC_6H_4O^-$, $m-ClC_6H_4O^-$, and $C_6H_5S^-$ were also reported[40] to have an excitation maximum very near 330 nm (Table II). Experimentally, the lowest transitions in the absorption spectra for the corresponding phenols are nearly identical to each other,[55] with thiophenol being only slightly different.[56]

Figure 7. Relative cross section for the photodetachment of $C_6H_5O^-$ (taken from reference 40) with a Xenon lamp and a bandwidth of 14.1 nm (O), multiplied by 10 (Δ).
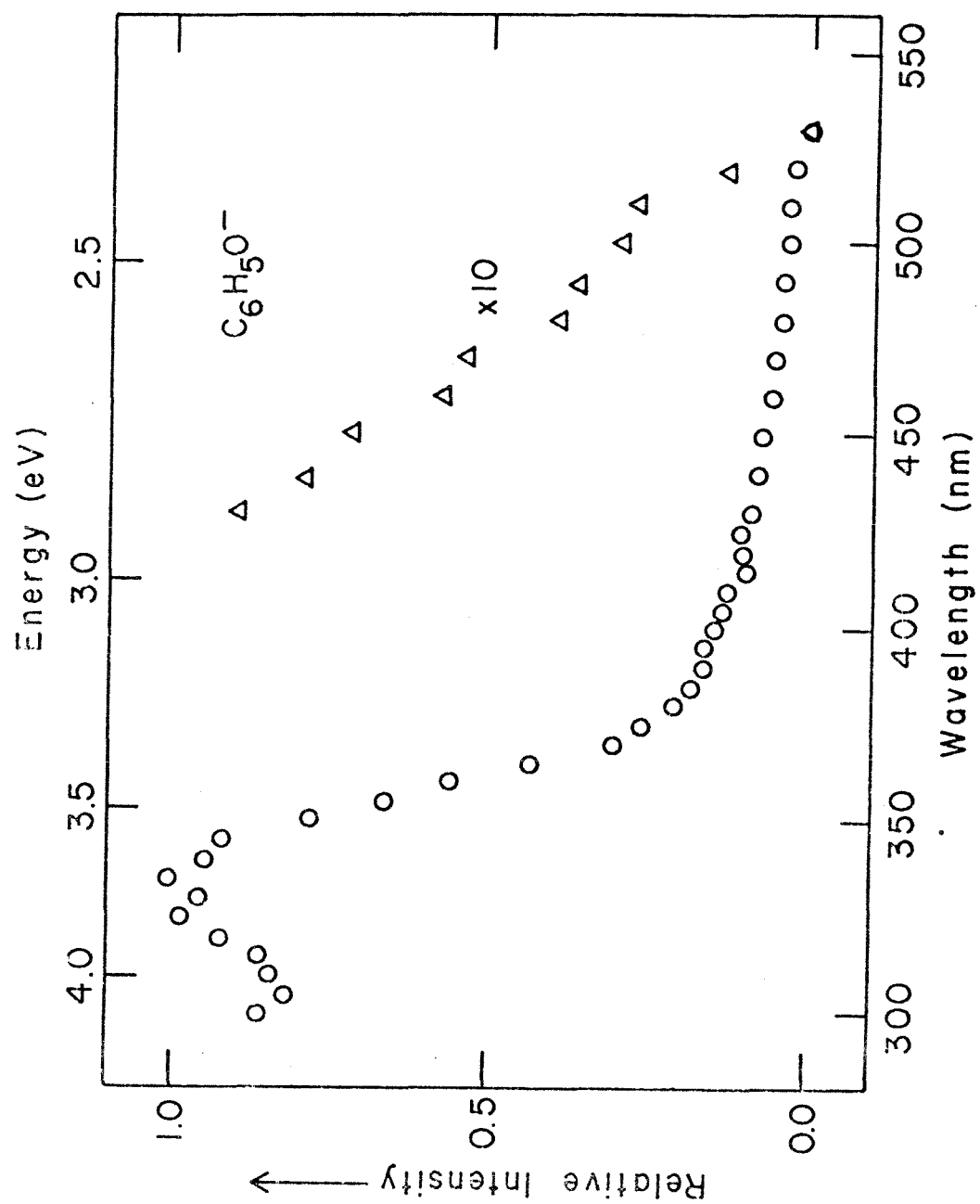
Table II. Spectroscopic and Thermochemical Data Related to Proton Affinities of Electronically Excited States of Selected Anionic Bases

Compound	Anion[a] λ_{max}[b]	Neutral (conjugate acid) λ_{max}[b]	$\Delta PA(B)$[c]
Phenol	332	270[d]	-20
o-Methylphenol	330	268[e]	-20
o-Chlorophenol	340	276[e]	-20
m-Chlorophenol	330	270[e]	-20
Thiophenol	332	270[d]	-20

[a]Data on anions from Reference 40.

[b]Wavelength, $\pm$ 10 nm.

[c]$\Delta PA(B) = PA(B^*) - PA(B)$ in kcal/mol.

[d]K. Kumura and S. Nagakura, Mol. Phys., 9, 117 (1965).

[e]Reference 55.

An analysis of the spectra indicate that the first two $\pi \rightarrow \pi^*$ transitions in phenolate correspond to the first two in phenol.[10b, 40] It is therefore probable that the maximum at 330 nm in phenolate corresponds to the transition $W_0 \rightarrow W_1$ and that $W_0 \rightarrow W_2$ is at shorter wavelengths. The W_1 state in phenol lies at 270 nm and using eq 5 one obtains a $\Delta PA(B)$ of -20 kcal/mol, that is, a decrease in basicity in the excited state. Identical results are noted for the other species.

Changes in basicity in excited states have been determined using Li^+ as the reference acid. The compounds, for which spectra are reported in this study, form Li^+ complexes directly (i.e., bimolecularly) via reaction 19 at low pressures (ca. 10^{-7} torr), indicating a minimum

$$B + Li^+ \rightarrow BLi^+ \tag{19}$$

lifetime of approximately 150 msec.[57] During the 2 sec trapping time, 10-20 collisions with the neutral species stabilize and deactivate the complex.

Figures 8-12 compare the gas phase absorption spectra of several bases to the photodissociation spectra of the corresponding Li^+ complexes obtained by monitoring process 9 between 200-700 nm. Due to the similarity of the band shapes in the spectra of the neutral molecules and their complexes, vertical energies are again used instead of adiabatic energies to estimate $E_1 - E_2$, and therefore $\Delta D(B-Li^+)$ in eq 8 without introducing large errors. The results are summarized in Table III.

Figure 8. (a) Comparison of the gas phase absorption spectrum of benzaldehyde with the photodissociation spectrum of the corresponding Li^+ complex.

(b) Comparison of the gas phase absorption spectrum of nitrobenzene with the photodissociation spectrum of the corresponding Li^+ complex. The absorption spectra of the neutrals were recorded at low resolution to facilitate comparison.

(a)

(b)

Figure 9. (a) Comparison of the gas phase absorption spectrum of acetophenone with both the photodissociation spectrum of the corresponding Li^+ complex and Li^+ bound dimer.

(b) Comparison of the gas phase absorption spectrum of nitrosobenzene with both the photodissociation spectrum of the corresponding Li^+ complex and Li^+ bound dimer. The absorption spectra of the neutrals were recorded at low resolution to facilitate comparison.
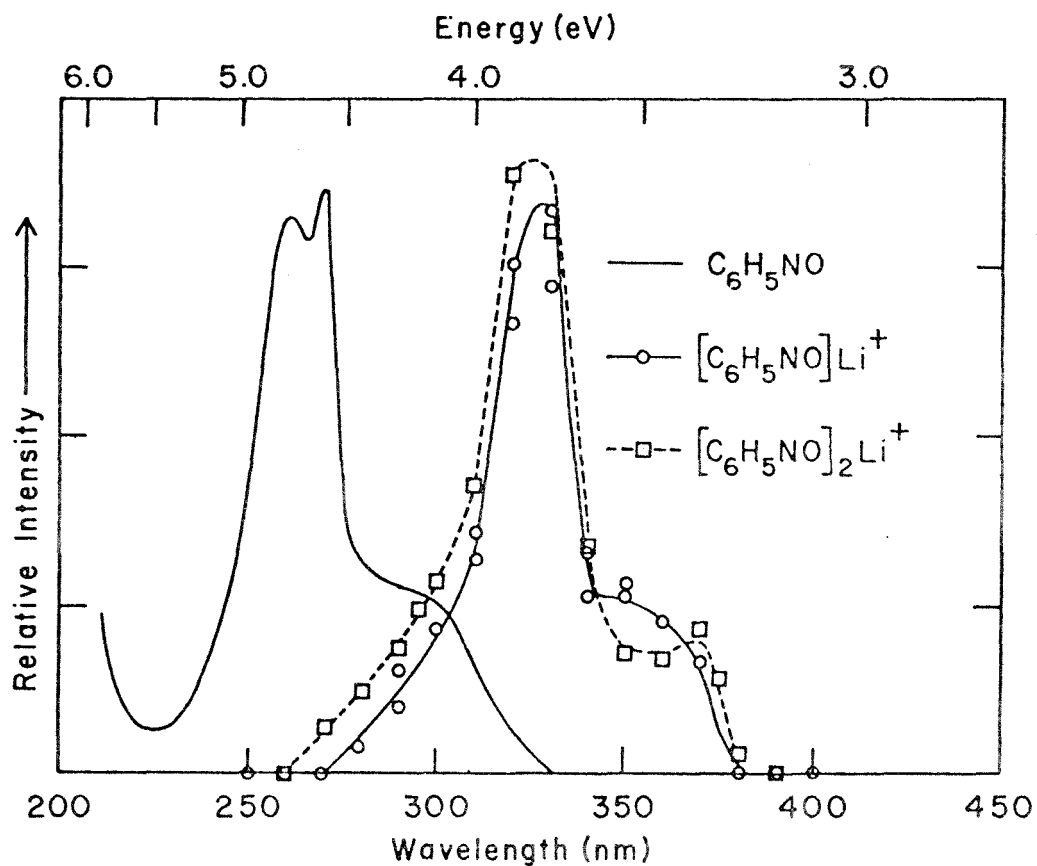
Figure 10. (a) Comparison of the gas phase absorption spectrum
of cyanobenzene with the photodissociation spectrum of
the corresponding Li^+ complex.

(b) Comparison of the gas phase absorption spectrum of
aniline with the photodissociation spectrum of the cor-
responding Li^+ complex. The absorption spectra of the
neutrals were recorded at low resolution to facilitate
comparison.

(a)
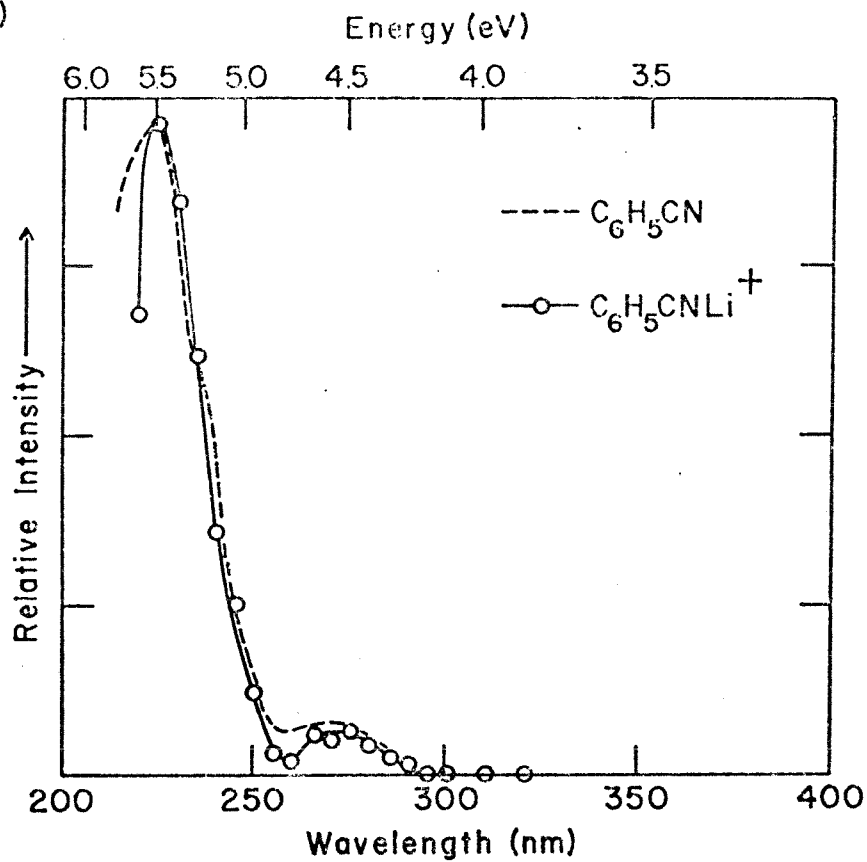
(b)
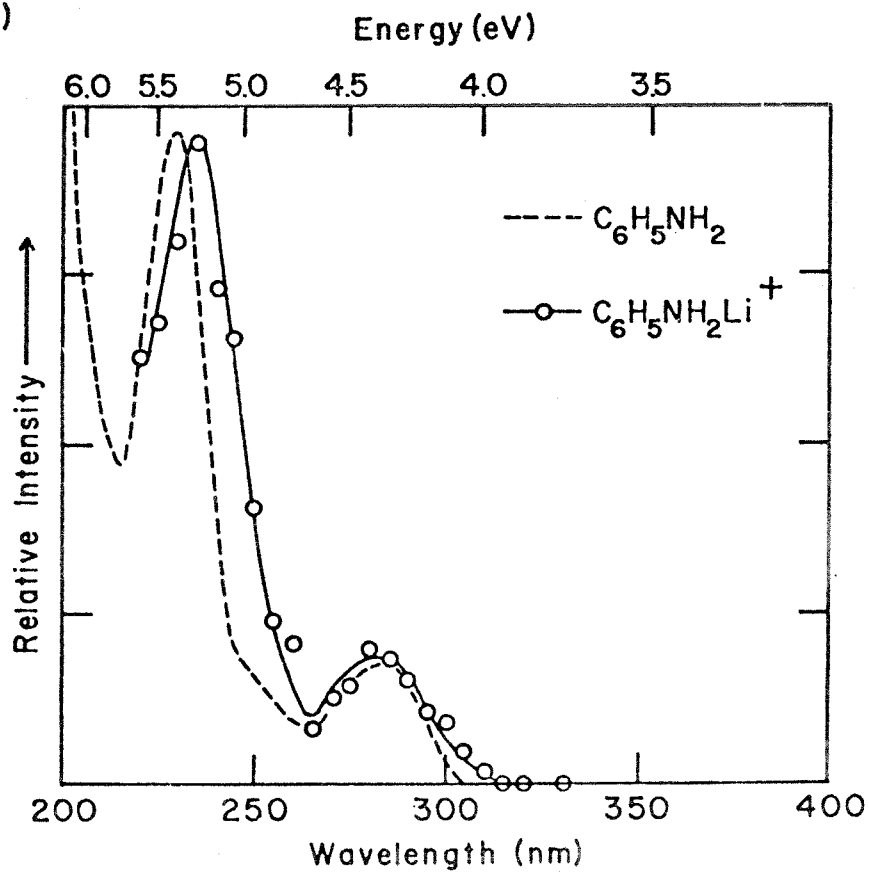
Figure 11. Comparison of the gas phase absorption spectrum of p-methoxybenzaldehyde with the photodissociation spectrum of the corresponding Li^+ complex. The absorption spectrum of the neutral was recorded at low resolution to facilitate comparison.
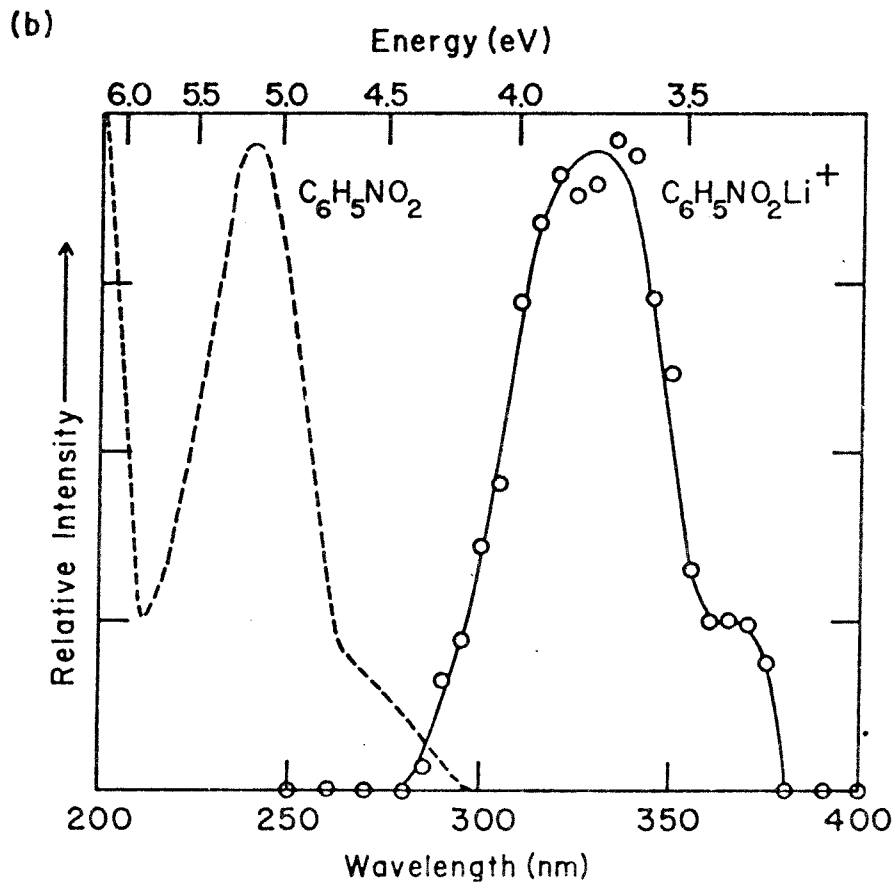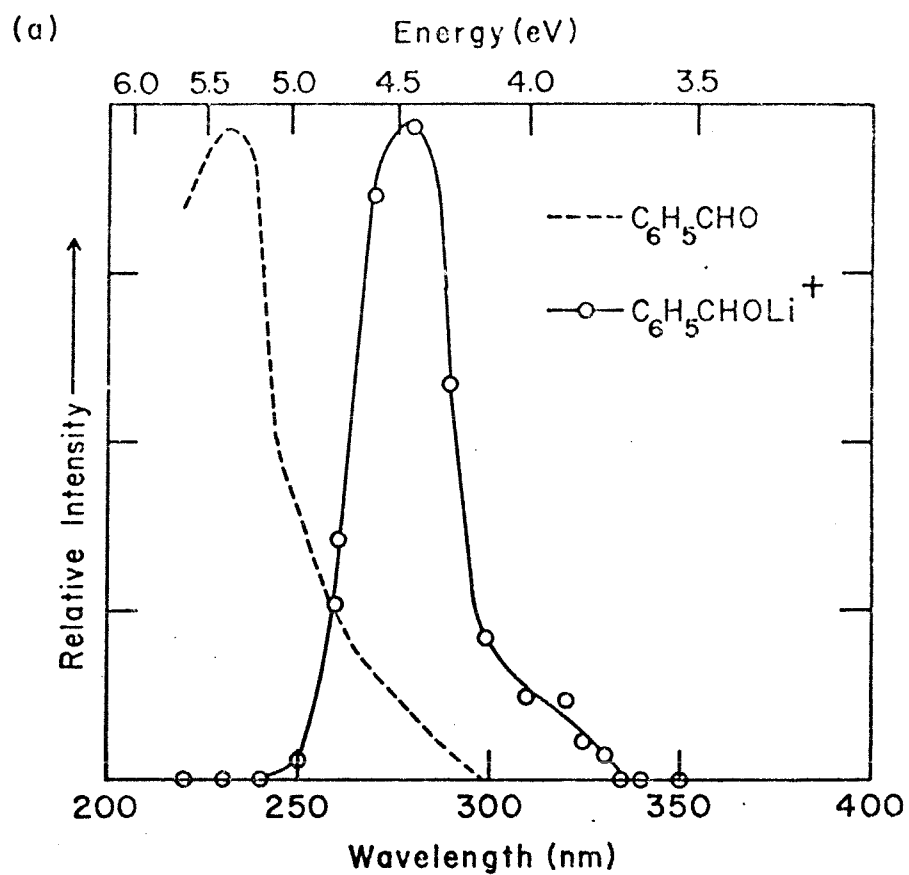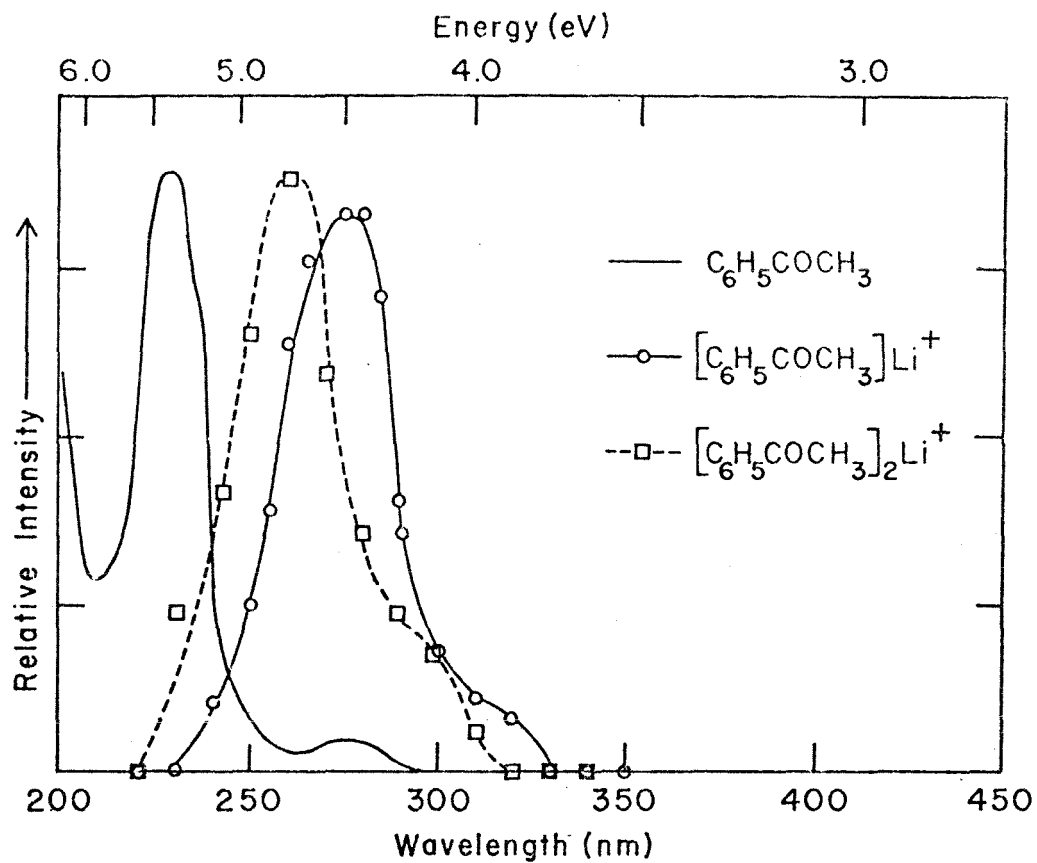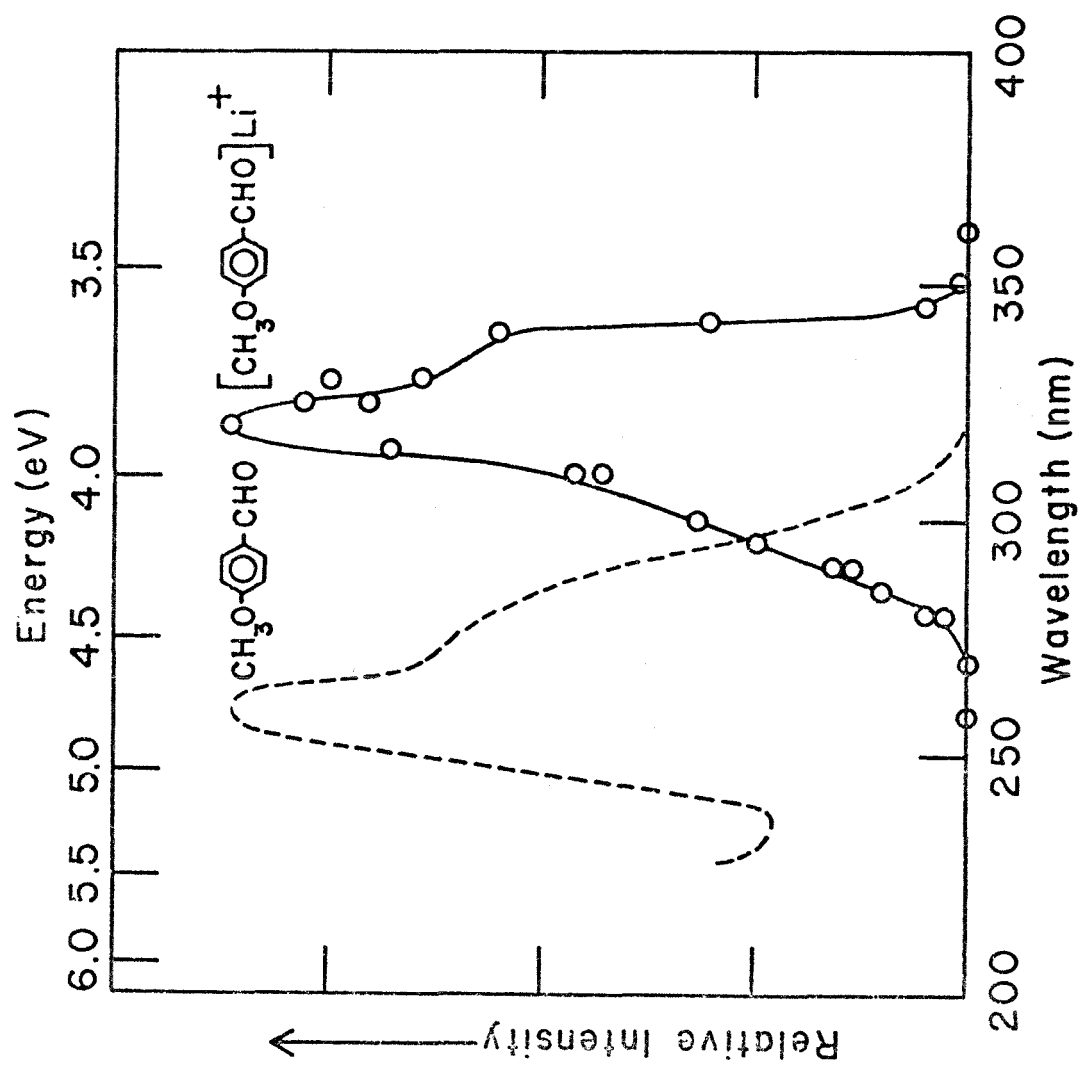
Figure 12. (a) Photodissociation spectrum of the Li^+ complex of

ferrocene.

(b) Absorption spectrum of ferrocene vapor at 35 °C

(taken from Reference 58). The Roman numerals were

used by the authors of the previous work and are used

here to facilitate comparison.

(a)

Energy (eV)

[Ferrocene]Li$^+$

(b)

Energy (eV)

Ferrocene
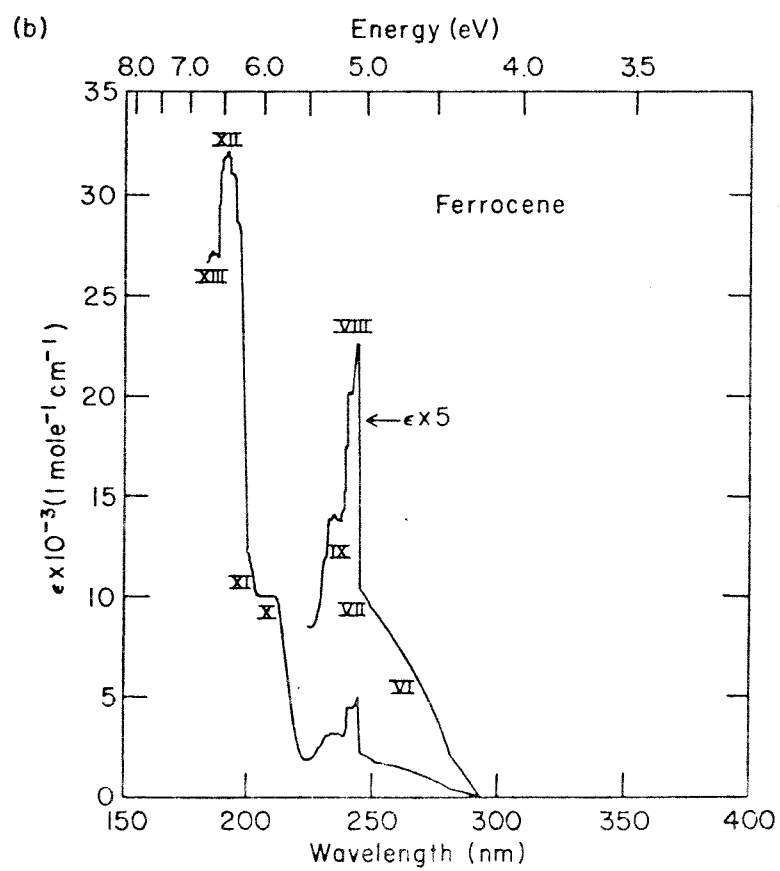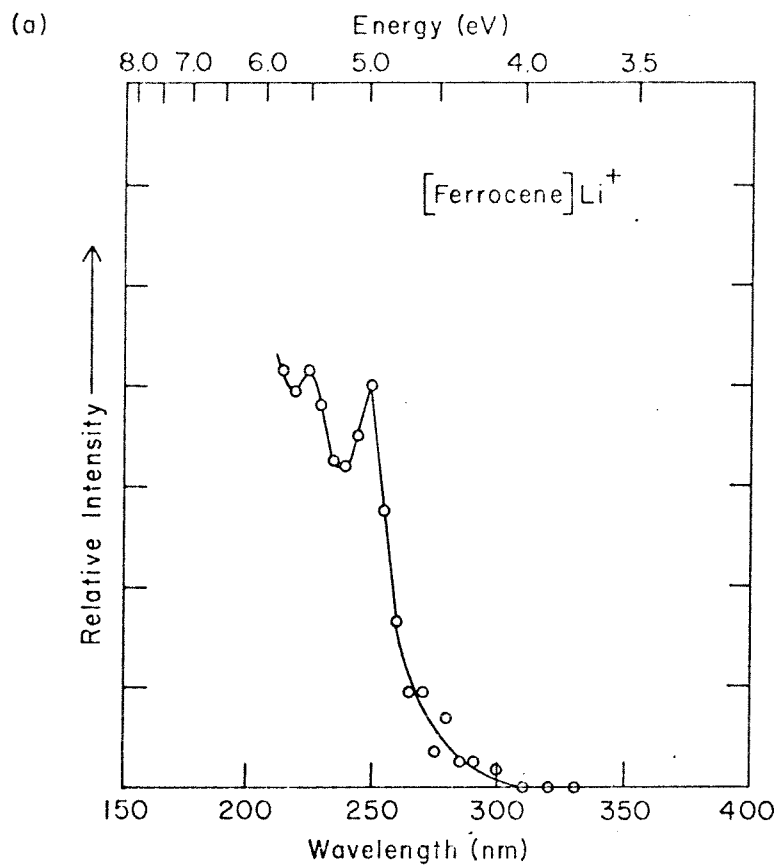
Table III. Spectroscopic and Thermochemical Data Relating Li^+ Binding Energies of Excited Electronic States of Selected Bases

Compound	Neutral		Complex		
	λ_{max}[a]	rel[b] int	λ_{max}[a]	rel[b] int	$\Delta D(B-Li^+)$[c]
Benzaldehyde	232	1.00	280	1.00	21
	275	0.11	310	0.12	12
Nitrobenzene	240	1.00	330	1.00	32
	280	0.12	370	0.19	25
Cyanobenzene	224	1.00	225	1.00	1
	274	0.07	270	0.07	- 1
Aniline	230	1.00	235	1.00	3
	282	0.19	280	0.21	- 1
Acetophenone	230	1.00	275	1.00	20
	275	0.05	310	0.12	12
Nitrosobenzene	265	1.00	325	1.00	20
	300	0.37	360	0.27	16
p-Methoxy-benzaldehyde	260	1.00	320	1.00	21
	290	0.50	335	0.45	13
Ferrocene[d]	194				
	202				
	211				
	234		225[e]		- 5
	244		250[e]		3
	266		280[e]		5

[a]Wavelength, ± 10 nm.

[b]Band intensities relative to the more intense peak which is assigned a value of 1.00.

Table III. (Continued)

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[c] $\Delta D(B-Li^+) = D(B^*-Li^+) - D(B-Li^+)$ in kcal/mol.

[d] Taken from Reference 58.

[e] Unresolved band.

Appreciable shifts are observed for both transitions in benzal –

dehyde, nitrobenzene, acetophenone, and nitrosobenzene (Figures 8 and

9), with the most pronounced effect for the W_2 state of nitrobenzene

indicating an increase in Li^+ binding energy of 32 kcal/mol relative to

the ground state. In comparison, however, no significant shifts are

observed for the corresponding transitions cyanobenzene and aniline

(Figure 10). Interestingly, the complexes of Li^+ with benzene and

fluorobenzene were not observed to photodissociate appreciably over

this wavelength region.

The spectrum of the Li^+ complex with p-methoxybenzaldehyde

is shown to be similar in shape but shifted to lower energies relative to

the uncomplexed neutral (Figure 11). That only the low energy

absorption is present, and none at higher energies relative to the

neutral spectrum, indicates that Li^+ is bound entirely to CHO, CHO

being much more basic than OCH_3. Furthermore, the changes in excited

state base strengths for the W_1 and W_2 states in p-methoxybenzaldehyde

are identical to those in benzaldehyde (Table III).

Figure 12 compares the photodissociation spectrum of the Li^+

complex of ferrocene to the absorption spectrum of ferrocene vapor at

35 °C obtained by McGlynn et al.[58] The Roman numerals in the vapor

spectrum were used by the authors of the previous work and are used

here to facilitate the comparison. Bands VI, VIII, and IX appear to be

present in the photodissociation spectrum of the complex with only

minor shifts noted relative to the vapor spectrum (Table III). No other

absorptions in the complex were noted between 220 nm and 700 nm

$(45, 500 \text{ cm}^{-1} - 14, 288 \text{ cm}^{-1})$. In particular, band XII, having an extinction coefficient of greater than $30, 000 \text{ } \ell \text{ mol}^{-1}\text{cm}^{-1}$ and interpreted as ligand to metal $(L \rightarrow M)^{59, 60}$ was not observed in the Li^+ spectrum at the wavelengths studied.

Figure 9 compares the gas phase absorption spectra of acetophenone and nitrosobenzene to the photodissociation spectra of both their corresponding Li^+ complexes and Li^+ bound dimer complexes. The latter were obtained by monitoring the appearance of BLi^+ product in process 11, since monitoring the disappearance of the dimer complex directly was hampered by the limited mass range of the present apparatus. The cross section for photodissociation of the dimer complex, relative to the monomer complex, therefore could not be estimated to see if a factor of two would be obtained.

The spectra of the neutral, monomer, and dimer are similar in appearance for acetophenone (Figure 9a) and nitrosobenzene (Figure 9b) with only small shifts to higher energy (~5 kcal/mol) noted for both W_1 and W_2 in the dimer complex of acetophenone relative to the monomer and to lower energy for W_1 in nitrosobenzene (+2 kcal/mol). These results are summarized in Table IV.

Excited State Acidities. The gas phase spectra of $C_6H_5CO^+$ and $C_6H_5CHOH^+$, obtained by monitoring reactions 14 and 20, and of their

$$C_6H_5CO^+ + h\nu \rightarrow C_6H_5^+ + CO \tag{20}$$
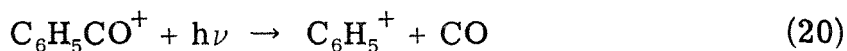
corresponding conjugate bases C_6H_5CHO and $C_6H_5CH_2OH$ between 200-400 nm are displayed in Figure 13 and summarized in Table V. Using

Figure 13. (a) Comparison of the photodissociation spectrum of

benzoyl cation with the gas phase absorption spectrum

of its conjugate base, benzaldehyde.

(b) Comparison of the photodissociation spectrum of

protonated benzaldehyde with the gas phase absorption

spectrum of its conjugate base, benzyl alcohol. The

absorption spectra of the neutrals were recorded at low

resolution to facilitate comparison.

(a)
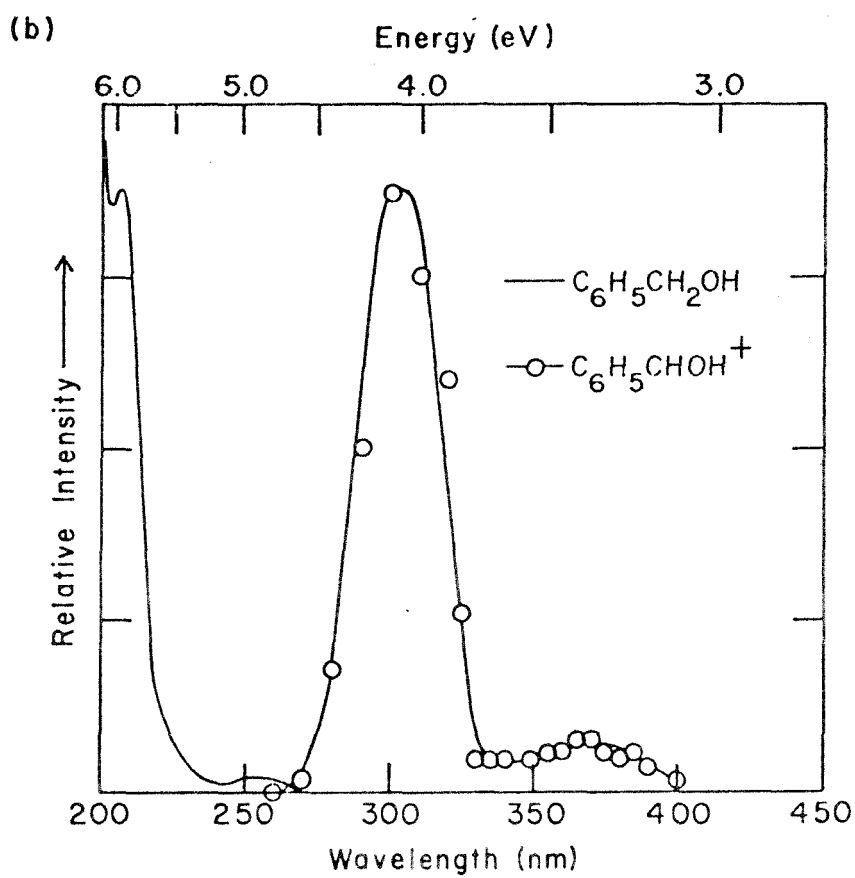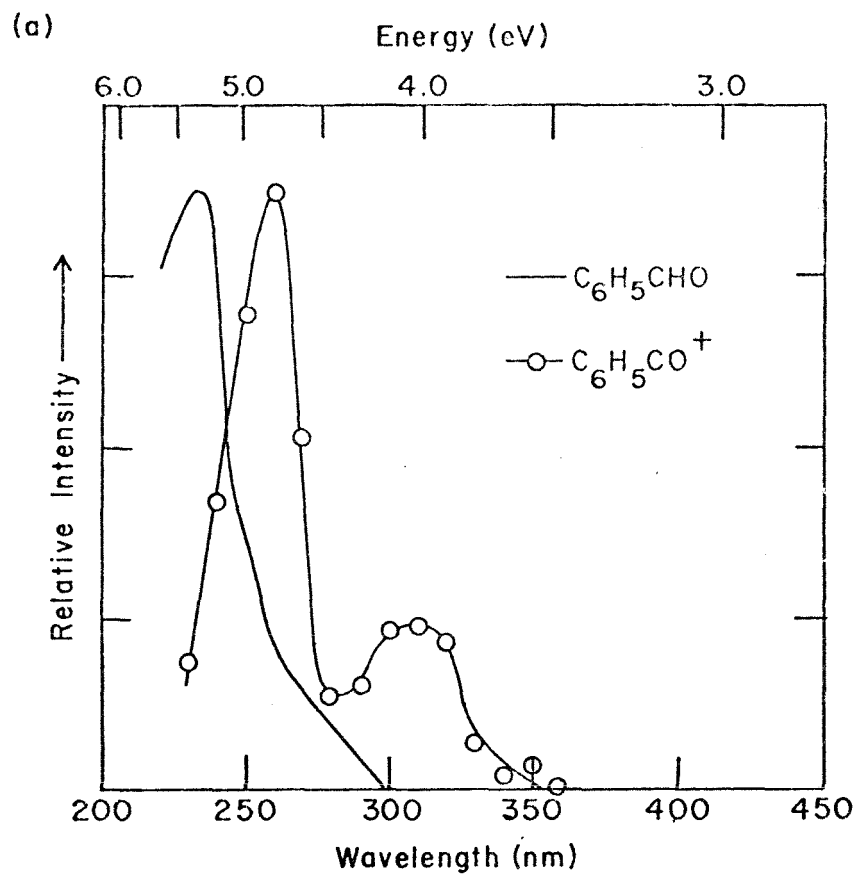
Table IV. Spectroscopic and Thermochemical Data Comparing Li^+
Monomer and Dimer Complexes

Compound	BLi^+		$B\overset{+}{Li}B$		$\Delta D(BLi^+{-}B)^c$
	λ_{max}^a	rel^b int	λ_{max}^a	rel^b int	
Acetophenone	275	1.00	262	1.00	-5
	310	0.12	295	0.22	-5
Nitrosobenzene	325	1.00	324	1.00	0
	360	0.27	368	0.21	2

^{a}Wavelength, $\pm$ 10 nm.

^{b}Band intensities relative to the more intense peak which is assigned a value of 1.00.

$^c\Delta D(BLi^+{-}B) = D(BLi^{+*}{-}B) - D(BLi^+{-}B)$ in kcal/mol.

eq 13 and the data from the figure, the changes in the bond dissociation energies for the cation acids in excited states relative to their ground states for the processes 21 and 22 may be estimated. The results are

$$C_6H_5CO^+ + H^- \rightarrow C_6H_5CHO \tag{21}$$

$$C_6H_5CHOH^+ + H^- \rightarrow C_6H_5CH_2OH \tag{22}$$
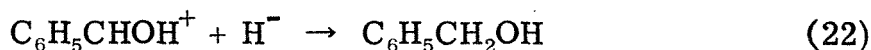
summarized in Table V and indicate, for example, that benzoyl cation has a lower $D(R^+-H^-)$ in its two excited states (decreased acidity) relative to its ground state by about 13 kcal/mol.

Comparison of Gas Phase Excitation Spectra to Solution Absorption Spectra. Many of the ionic species for which gas phase spectra have been obtained in this study have been observed in solution. We recently reported that the photodissociation spectra of benzoyl cation, protonated benzene, and protonated mesitylene were identical to the direct absorption spectra obtained in HF and BF_3 for benzoyl cation and concentrated H_2SO_4 for the latter ions.[36] In Table VI we include these examples, as well as several more for which the comparison can be made. It is apparent from the table that lack of a solvent shift is not a general rule. The maxima observed for the conjugate acids of benzaldehyde, acetophenone, and nitrobenzene in concentrated H_2SO_4 occur at shorter wavelengths compared to the corresponding maxima in the gas phase spectra. Similarly, the maxima for phenoxide and thiophenoxide occur at shorter wavelength in solution than in the gas phase.

Table VI. Comparison of the Gas Phase Photoexcitation Spectra to the Solution Absorption Spectra

Species	Gas Phase λ_{max}[a]	Solution Solvent	Solution λ_{max}[a]	Ref.	$\Delta H_S(A^*)-\Delta H_S(A)$[b]
$C_6H_5CO^+$	260	H_2SO_4	260	c	0
	310		310	c	0
$C_9H_{13}{}^+$	250	HF, BF_3	250	d	0
	355		355	d	0
$C_6H_7{}^+$	245	HF, BF_3	e		
	330		330	f	0
$C_6H_5CHOH^+$	303	H_2SO_4	293	g	3
	368		323	g	11
$[C_6H_5COCH_3]H^+$	305	H_2SO_4	295	g	3
	355		322	g	8
$C_6H_5NO_2H^+$	357	H_2SO_4	e		
	~400		350	h	10
$C_5H_5NH^+$	250	HCl, C_2H_5OH	250	i	0
$C_6H_5O^-$	e	KOH, H_2O, CH_3OH	235	j	
	332		287	j	14
$C_6H_5S^-$	e	KOH, H_2O	263	k	
	332		302	k	9

[a]Wavelength, ± 10 nm for gas phase spectra.

[b]$\Delta H_S(A^*)$ - $\Delta H_S(A)$ in kcal/mol corresponds to the change in solvation energy of the ion between its excited and ground states.

Table VI. (Continued)

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[c]G. A. Olah, C. U. Pittman, Jr., R. Waack, and M. Doran, _J. Am. Chem. Soc._, 88, 1488 (1966).

[d]Reference 61.

[e]Band not observed.

[f]V. H. Luther and G. Pockels, _Z. Electrochem._, 59, 159 (1955).

[g]W. L. Paul, P. J. Kovi, and S. G. Schulman, _Spectrosc. Letts._, 6, 1 (1973).

[h]S. G. Schulman, L. B. Sanders, and J. D. Winefordner, _Photochem. Photobiol._, 13, 381 (1971).

[i]M. L. Swain, A. Eisner, C. F. Woodward, and B. A. Brice, _J. Am. Chem. Soc._, 71, 1341 (1949).

[j]Reference 47.

[k]J. S. Kwiatkowski, M. Berndt, and J. Fabian, _Acta Phys. Pol._, A38, 365 (1970).

Discussion

Excited State Base Strengths. The results from both the excited state proton and Li^+ affinities are straightforward and suggest that the $W_0 \rightarrow W_1$ and $W_0 \rightarrow W_2$ transitions in benzaldehyde, acetophenone, nitrosobenzene, nitrobenzene, and p-methoxybenzaldehyde have large contributions due to internal charge transfer as evidenced by large changes in base strength. The results for the same transitions in aniline and cyanobenzene, however, suggest no rearrangement which affects the Li^+ binding energy and possibly minor rearrangement which has only a small effect on the proton binding energies.

These findings are in qualitative agreement with the change in dipole moment measured for several of these transitions (Table VII). Changes of greater than 4D were measured for nitrobenzene, benzaldehyde, and nitrosobenzene and less than 1D for aniline and cyanobenzene.[10-12] Analysis of solvent effects, as well as calculations on these systems, leads to similar conclusions. The ICR method provides a powerful tool and has the advantage that, unlike excited state dipole measurements,[11, 12] the sign of the dipole change is evident.

No dissociation was observed for Li^+ complexes of benzene and fluorobenzene. Unlike the previous examples, Li^+ is π bonded to the ring in these compounds. The effect of π-bonded Li^+ on the spectra could not be determined. That protonated benzene (benzenium ion) absorbs suggests the difference in bonding of H^+ and Li^+ expected.

A complete understanding of the excited states of benzenium ion ($C_6H_7^+$) has not been achieved, as evidenced by the variety of theoretical

Table VII. Changes in Dipole Moment on Electronic Excitation
$(\pi \rightarrow \pi^*)$ in Several Substituted Benzenes

Compound	State	$|\Delta\mu|$[a]	Ref.
Nitrobenzene	W_1	4.8	b
	W_1	3.9	c
	W_2	4.0	b
	W_2	7.6	c
Benzaldehyde	W_1	4.3	b
	W_2	3.5	b
Nitrosobenzene	W_1	9.1	b
Cyanobenzene	W_1	0.31	d
Aniline	W_1	0.85	e
Phenol	W_1	0.20	e
p-Fluorophenol	W_1	0.44	e
Fluorobenzene	W_1	0.3	f

[a] $|\Delta\mu|$ in Debye is the absolute change in dipole moment.

[b] Reference 10a.

[c] Reference 10b.

[d] Reference 12.

[e] Reference 11.

[f] Reference 13.

models proposed in the literature.[61-63] For this reason the large
change in proton affinity estimated for the excited states in benzene as
well as the following interpretations are also speculative. The ΔPA
observed for benzene, mesitylene, and anisole are all comparable
(Table I), indicating that the affect that CH_3O, as well as CH_3, has on
benzene is the same in its ground and excited states. This is somewhat
contrary to studies indicating an increased quinoid like structure I in
the excited state of anisole,[11] for example, yet substantiates other
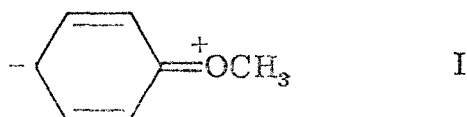
evidence that the excitation is associated with at most a small contribu-
tion of electron density from CH_3O to the ring.[10b]

The spectroscopy of phenol and phenolate have been studied exten-
sively in solution.[10b] For phenol, measurements of the change in
dipole moment[11] as well as calculations[10b] indicate only a small
internal charge transfer component (substituent to ring) if any is involved
in the first two singlet transitions of this molecule. The calculations
predict an increase in the charge transfer components upon ionization
of phenol to phenolate, which is in qualitative agreement with the de-
crease in proton affinity noted for phenolate in its excited states (Table
II). This arises since ionization of phenol to form phenolate results in
a marked energy decrease of both the first two singlet $\pi \rightarrow \pi^*$ transitions.
Similar results are obtained for thiophenolate.

Photodissociation of the Li^+ complex of p-methoxybenzaldehyde
is illustrative of an application of these studies as a probe to determine

binding sites in polyfunctional molecules. For a disubstituted benzene, attachment of Li^+ may initially occur at either site. If one site is considerably more basic than the other, ion molecule reactions will shortly produce all of the complexes having Li^+ bound at that site. If, however, the sites are comparable in basicity, ion molecule reactions will produce an equilibrium mixture of complexes bound at either site. The presence of one or both structural isomers can be detected by their unique excitation spectrum. The Li^+ complex of p-methoxy-benzaldehyde was studied as an example. The methoxy group is electron donating while the aldehyde group electron withdrawing. The two lowest singlet $\pi \rightarrow \pi^*$ excitations in this compound are expected to result in a net increase of negative charge on the aldehyde (as observed for benzaldehyde) and a net decrease of negative charge on the methoxy. This would result in a shift to higher or lower energies of the transitions present in the neutral depending on whether Li^+ is bound to the CH_3O or CHO groups, respectively. Figure 11 shows that the spectrum of the Li^+ complex of p-methoxybenzaldehyde is shifted to lower energies than the isolated neutral. No absorptions to higher energies are noted. This result indicates that CHO is substantially more basic than CH_3O with respect to Li^+ as the reference acid. Although $D(B-Li^+)$ has not been measured directly for anisole or benzaldehyde, this result is in accord with the reported ordering of $D(B-Li^+)$ being higher for CH_3CHO than CH_3OCH_3.[27] Furthermore, while the methoxy shows its effects on the spectrum of benzaldehyde (both λ_{max} of p-methoxybenzaldehyde at longer wavelengths than benzaldehyde, Table III), it does not enhance

the change in Li$^+$ affinity $\Delta D(B-Li^+)$ compared to benzaldehyde (Table III). It is concluded that internal charge transfer from CH$_3$O to the ring is not an important component in the $\pi \rightarrow \pi^*$ transitions. These results are in accord with the relatively small changes in dipole moment observed for phenol and O-alkylated derivatives.[10, 11]

The symmetry of ferrocene dictates that its dipole moment in any of its states must be zero. Hence there is no change in dipole moment upon excitation. The lack of substantial shifts noted for the excitation spectrum of the Li$^+$ complex, despite the fact that charge transfer transitions are associated with large changes in polarizability, is a graphic illustration that changes in dipole moment rather than polarization is the important factor. Large shifts are predicted to occur for nonsymmetric inorganic complexes, and can be used to detail the charge transfer transitions in these compounds.

The photodissociation of Li$^+$ bound dimers yields information about changes in the absorption spectrum of an acid-base complex when an additional base is added. This information provides insight into the difference between purely gas phase spectra and spectra obtained in solution. The effect of the second base is to weaken the interaction of Li$^+$ with the original base. Thus the shift in the spectra of the dimer complex is not expected to be as great as in the monomer complex relative to the isolated neutral. This is observed for the aceto-phenone system (Figure 9a). Similarly, interactions of Li$^+$ in solution will weaken its interaction with the base and smaller shifts are predicted.[64] The dimer and monomer complexes of nitrosobenzene,

however, have the same absorption maxima (Figure 9b). This can be
rationalized as follows. In comparing the changes of dipole moment
in Table VII to the changes in $\Delta D(B-Li^+)$ in Table III, the largest
change of dipole moment, 9.1 D for nitrosobenzene, is not manifest
in the shifts observed with Li^+. Assuming that the dipole measurement
is not in error, this indicates that Li^+ is in fact bonded to nitrogen and
not oxygen (Species II), and thus experiences a smaller change in
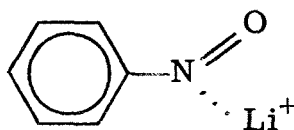
II

dipole moment. The fact that the photoexcitation spectra of the dimer
and monomer complex have the same maxima suggests that, in the
dimer, Li^+ bonds to the oxygens (Species III). In this configuration
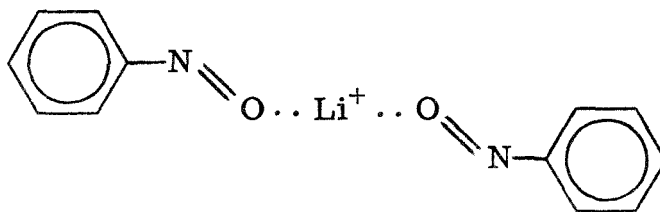
III

Li^+ experiences a larger change in dipole moment than in Structure II
which would shift the spectra to longer wavelengths, but the second
base weakens the interaction counteracting this shift. The net effect is
that the monomer and dimer spectra have the same maxima.

Excited State Acid Strengths. The first two singlet $\pi \to \pi^*$ transitions in benzoyl cation, benzaldehyde, protonated benzaldehyde, and benzyl alcohol are all correlated facilitating discussion as well as enabling quantitative determination of excited state acid-base properties. From a comparison of benzoyl cation and protonated benzaldehyde to their respective conjugate bases (Figure 11 and summarized in Table V), it is observed that in both cases $D(R^+-H^-)$ decreases in the excited state. This indicates that the transitions in these cations involve transfer of electron density from the ring to the substituent. This is in complete accord with charge distribution calculations performed on benzoyl cation.[65]

Solvent Effects. Solvent effects (shifts) arise both as a result that the solvent configuration surrounding a specie in its ground state may not be the lowest energy configuration when the specie is in its excited state and, secondly, because the solvation energy for the species in the two states may differ.

The absence of any solvent shift for benzoyl cation, $C_6H_7^+$ and $C_9H_{13}^+$ in highly acidic media has already been noted with surprise.[36] The new examples listed in Table VI do, however, indicate that this will not always be the rule and suggest a plausible explanation for the lack of shift in the former examples. The spectra of $C_6H_5CHOH^+$, $[C_6H_5COCH_3]H^+$, and $C_6H_5NO_2H^+$ in H_2SO_4 are all shifted to higher energies relative to their gas phase spectra. These ions all have acidic protons which upon going from the gas phase to solution become less acidic due to the increased interaction of the solvent. This effect

is identical to that described for BLi^+ compared to $B\overset{+}{L}iB$. The ions for which no shifts are observed <u>do not</u> possess acidic protons.

Comparison of $\triangle PA(B)$, $\triangle D(B-Li^+)$, and Changes in Dipole Moment. Figure 14 compares the change in basicity upon excitation determined using H^+ and Li^+ as reference acids. The data (although limited) follow the linear relationship 23, where the thermodynamic

$$\triangle PA(B) = 0.76 \; \triangle D(B-Li^+) + 15 \tag{23}$$

quantities are in kcal/mol. There are two points of interest: (1) in Figure 14, $\triangle PA(B)$ is always greater than $\triangle D(B-Li^+)$; (2) the proton affinities of these compounds are all near 200 kcal/mol while the $D(B-Li^+)$ probably center near 50 kcal/mol. Except for cyanobenzene, $\triangle D(B-Li^+)/D(B-Li^+)$ is greater than $\triangle PA(B)/PA(B)$, indicating that while covalent bonding of H^+ enhances PA relative to $D(B-Li^+)$, it does not play an important role in determining $\triangle PA(B)$. Thus, changes in basicity arise primarily from electrostatic interactions.

In comparing the changes of dipole moment in Table VII to the changes in PA (Table I) or changes in $\triangle(B-Li^+)$ (Table III) a number of interesting points surface. As mentioned above, substantial changes in $\triangle D(B-Li^+)$ and $\triangle PA(B)$ are noted in these species whose change in dipole moment is greater than 4D, and little or no change in those species where the change in dipole moment is less than 1D. Several inconsistencies are noted. For nitrobenzene and benzaldehyde the change in dipole moment for W_1 is greater than for W_2, which is the opposite expected from their spectral shifts. This could indicate either

Figure 14. Comparison of the change in basicity upon excitation measured using H^+ as the reference acid to that measured using Li^+ as the reference acid.
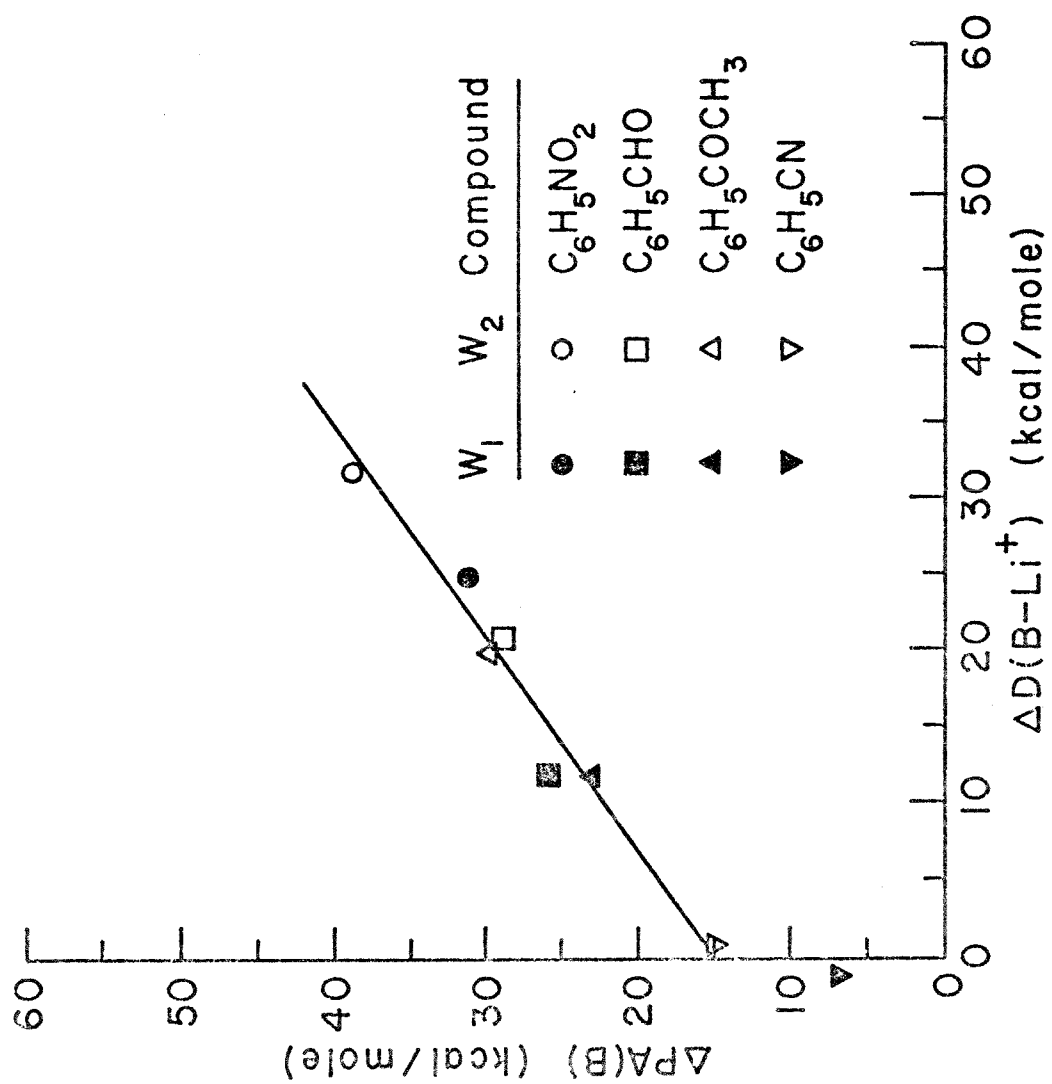
an enhanced role of polarization in the W_2 states of these molecules or an error in the dipole change determination. Also, as noted earlier, the largest change in dipole moment (Table VII) of 9.1 D for nitrosobenzene is not manifest in the spectral shifts observed with Li^+. This apparent inconsistency was explained above by invoking a nitrogen bonded Li^+ complex.

Conclusions

A general method for obtaining information about excited state acid-base properties has been described and applied to a number of interesting systems and problems. Since most previous studies have been confined to solution, the ICR technique brings a new dimension to the type of information which can be obtained. The spectra of ions in the gas phase allow an intrinsic measure of excited state properties and frequently permits an evaluation of solvation effects. Using Li^+ and H^+ as shift reagents allows the study of changes in dipole moment and charge density with greater specificity and sensitivity than solvent shift studies. Furthermore, the site specificity has the advantage, over direct dipole change measurements, that the sign of the change is evident.

The spectra of Li^+ bound dimers allow comparison to the lowest excitation in the monomer complexes. Information about internal solvation and structure in these complexes was obtained.

Further work both on the theoretical as well as experimental level can be expected to yield exciting and significant results in this area.

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CHAPTER III

ELECTRON IMPACT DISSOCIATION OF CYANOBENZENE RADICAL

CATIONS BY ION CYCLOTRON RESONANCE SPECTROSCOPY

B. S. Freiser and J. L. Beauchamp

Contribution No. 5332, from the Arthur Amos Noyes Laboratory of

Chemical Physics, California Institute of Technology

Pasadena, California 91125

Abstract: Trapped ion cyclotron resonance spectroscopy has been
used for the first time to study the electron impact dissociation of
ions. Fragmentation of $C_6H_5CN^+$ to produce $C_6H_4^+$ and HCN is ob-
served to occur at low electron energies (3-9 eV). The extent of
dissociation is observed to be linear in emission current, rising
from a threshold at 3.0 ± 0.5 eV to a maximum cross section
estimated to be 6 $\mathring{A}^2$ at 7.5 ± 0.5 eV. The implications of these
results are discussed.

1. Introduction

Quantitative study of the electron impact dissociative excitation
of ions and neutrals still offers a formidable challenge to the experi-
mentalist. Such data are important in describing processes occurring
in environments such as plasmas or gas discharges where there are
appreciable concentrations of energetic electrons [1]. Although dia-
tomic ions have been studied, including H_2^+ [2, 3], D_2^+ [2, 3], O_2^+ [4],
and N_2^+ [4], there is a paucity of data describing the electron impact
dissociative excitation of polyatomic ions. We wish to report that ion

cyclotron resonance spectroscopy (ICR) appears to hold considerable promise for routine investigation of these processes. To illustrate the experimental methodology, we present results for the low energy (3-9 eV) electron impact dissociation of $C_6H_5CN^+$ (reaction 1)

$$C_6H_5CN^+ + e \rightarrow C_6H_4^+ + HCN \quad . \tag{1}$$

2. Experimental

The ion cyclotron resonance spectrometer used in the present study is a modified V-5900 series manufactured by Varian Associates [5]. The ICR cell is one which has been used extensively for studies of ion photoexcitation processes and has been described in detail [6-8]. Parent cations from cyanobenzene ($\sim 5 \times 10^{-7}$ torr) were formed and subsequently excited in a continuous electron beam, while being trapped for up to 150 msecs. Ion formation was accomplished by switching the electron energy to a value (11.5 eV) lying above the ionization potential of C_6H_5CN (9.73 eV) [9] for 15 msec. Cyanobenzene was obtained from Matheson, Coleman, and Bell and used as supplied except for freeze-pump-thaw cycles to remove noncondensable gases. Mass spectrometry revealed no detectable impurities.

3. Results

Experiments were performed varying the electron excitation energy, the trapping time, and the emission current. Since the space potential in the source region is affected by the electron beam [10], variations in either emission current or electron energy can have an effect on the trapping efficiency and possibly the spatial distribution of

the stored ions. To account for these effects, we have made the simplifying assumption that at low conversion ($<$ 10%) the ratio $[C_6H_4^+]/[C_6H_5CN^+]$ is proportional to the electron impact dissociation cross section.

Figure 1 compares the relative dissociation cross section for process 1 as a function of excitation energy to both the photoelectron spectrum of cyanobenzene reported by Rabalais and Colton [9] and to the photodissociation spectrum of $C_6H_5CN^+$ reported in an earlier study [8]. The energy axis of the photoelectron spectrum is adjusted such that the first vertical ionization potential of cyanobenzene is zero on the photodissociation and electron impact dissociation energy scales. The electron energy scale in fig. 1a has been corrected for the space potential of the electron beam which has the effect of reducing the electron energy. The space charge depression of the potential, ΔV, at the electron beam is given approximately by

$$\Delta V = \frac{i_e}{5.93 \times 10^7 \, (V_0)^{\frac{1}{2}} C} \tag{2}$$

where C is the capacitance per unit length between the electron beam and the cell, i_e is the electron beam current in amperes, V_0 is the nominal electron energy (eV) and the factor 5.93×10^7 is the velocity in cm/sec of a 1.0 eV electron [10]. This depression can be substantial at the emission currents and electron energies employed. For example, with C = 8.3×10^{-14}f calculated for the geometry of the ICR cell utilized in these studies, at 5 μa emission and 4 eV electron energy, ΔV is approximately 0.5 eV.

Figure 1. (a) Relative dissociation cross section for process 1 as a function of excitation energy.
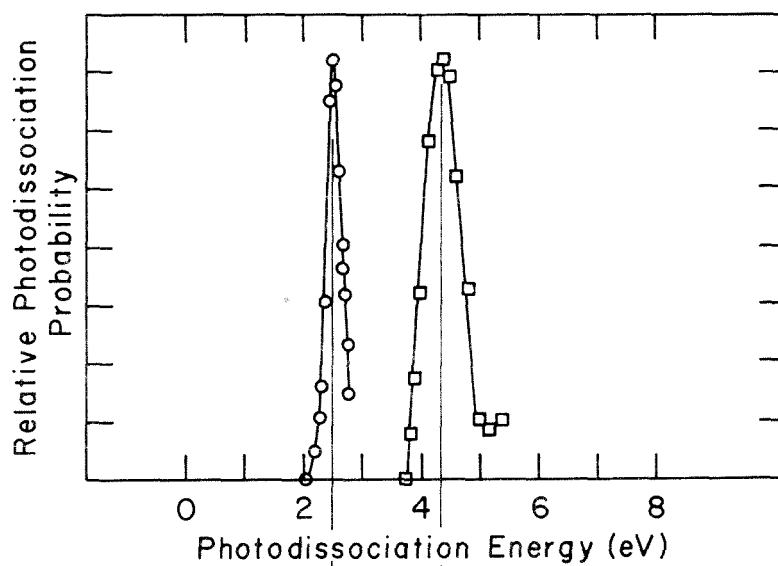
(b) Photodissociation spectra obtained for the one photon process 4 ($\Box$) and the two photon process 5 ($\bigcirc$).

(c) Photoelectron spectrum of cyanobenzene. The energy axis of the photoelectron spectrum is adjusted such that the first vertical ionization potential of cyanobenzene is zero on the photodissociation and electron dissociation energy scale.
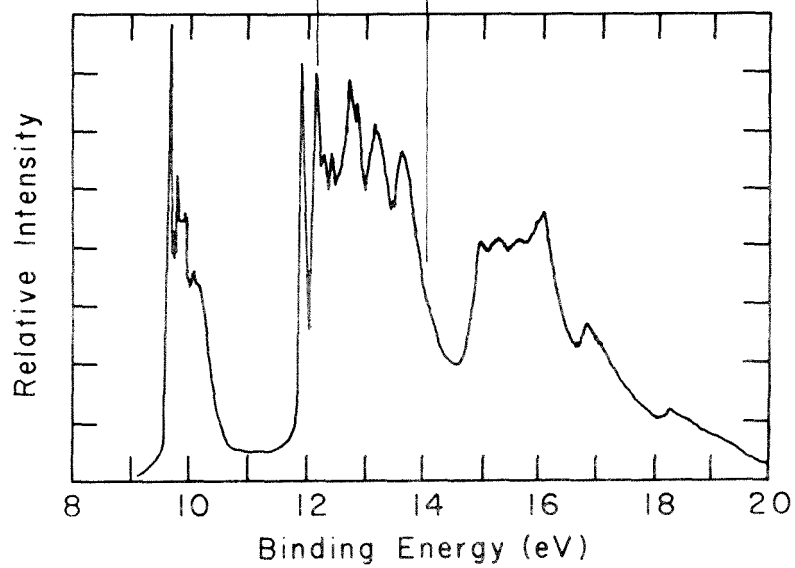
(a)
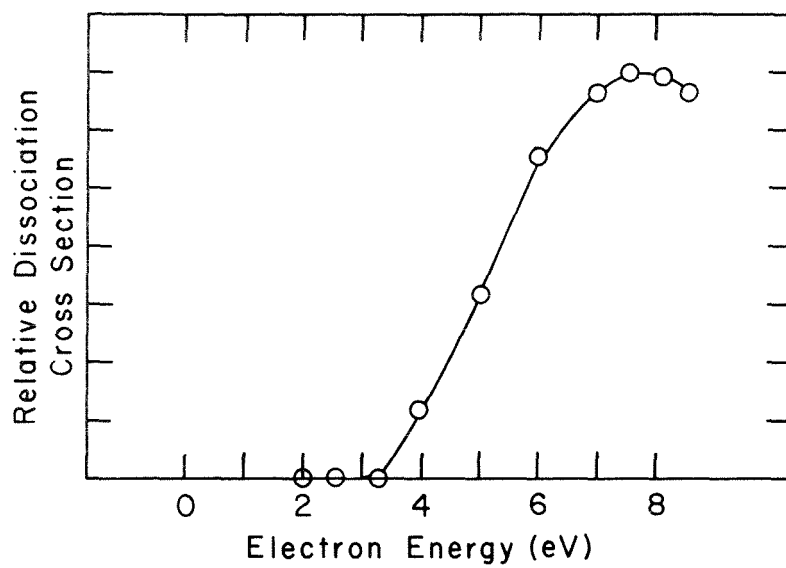
(b)

(c)

Figure 2 illustrates the linear dependence of the apparent dissociation rate on emission current. The rates were obtained by monitoring the temporal variation of ion abundances at 7.5 eV excitation energy. A cross section $\sigma \sim 6$ Å^2 is estimated at 7.5 eV using eq. (3),

$$\sigma(\text{Å}^2) = \frac{MA}{6.28 \times 10^{12}} \times 10^{16} \approx 1.6 \times 10^3 \, MA \qquad (3)$$

where M is the slope in sec^{-1} μa^{-1} obtained from fig. 2, A is the area of the electron beam in cm^2 (0.30 cm $\times$ 0.076 cm), and 1.6×10^3 is a constant of proportionality. This value is probably a minimum since $C_6H_4^+$ is somewhat reduced in intensity due to reaction with the parent neutral [8]. More importantly, since less than 100% of the ions remain spatially localized in the electron beam, the cross section may be underestimated.

4. Discussion

The photodissociation spectrum (fig. 1b) consists of a band at high energy obtained by monitoring process 4 and a band at low energy

$$C_6H_5CN^+ + h\nu \rightarrow C_6H_4^+ + HCN \qquad (4)$$
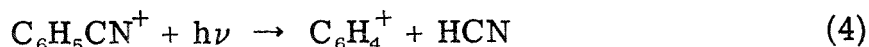
attributed to a two photon process 5 [8]. Comparison of the photo-

$$C_6H_5CN^+ \rightleftharpoons [C_6H_5CN^+]^* \rightarrow C_6H_4^+ + HCN \qquad (5)$$
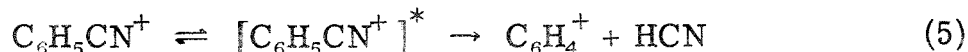
dissociation spectra to the photoelectron spectrum indicates that the high energy band arises from a $\pi \rightarrow \pi^*$ transition and the lower energy absorption proceeds through a $\pi \rightarrow \pi$ transition [8].

Figure 2. Apparent dissociation rate for process 1 as a function of

emission current at an electron energy of 7.5 eV.
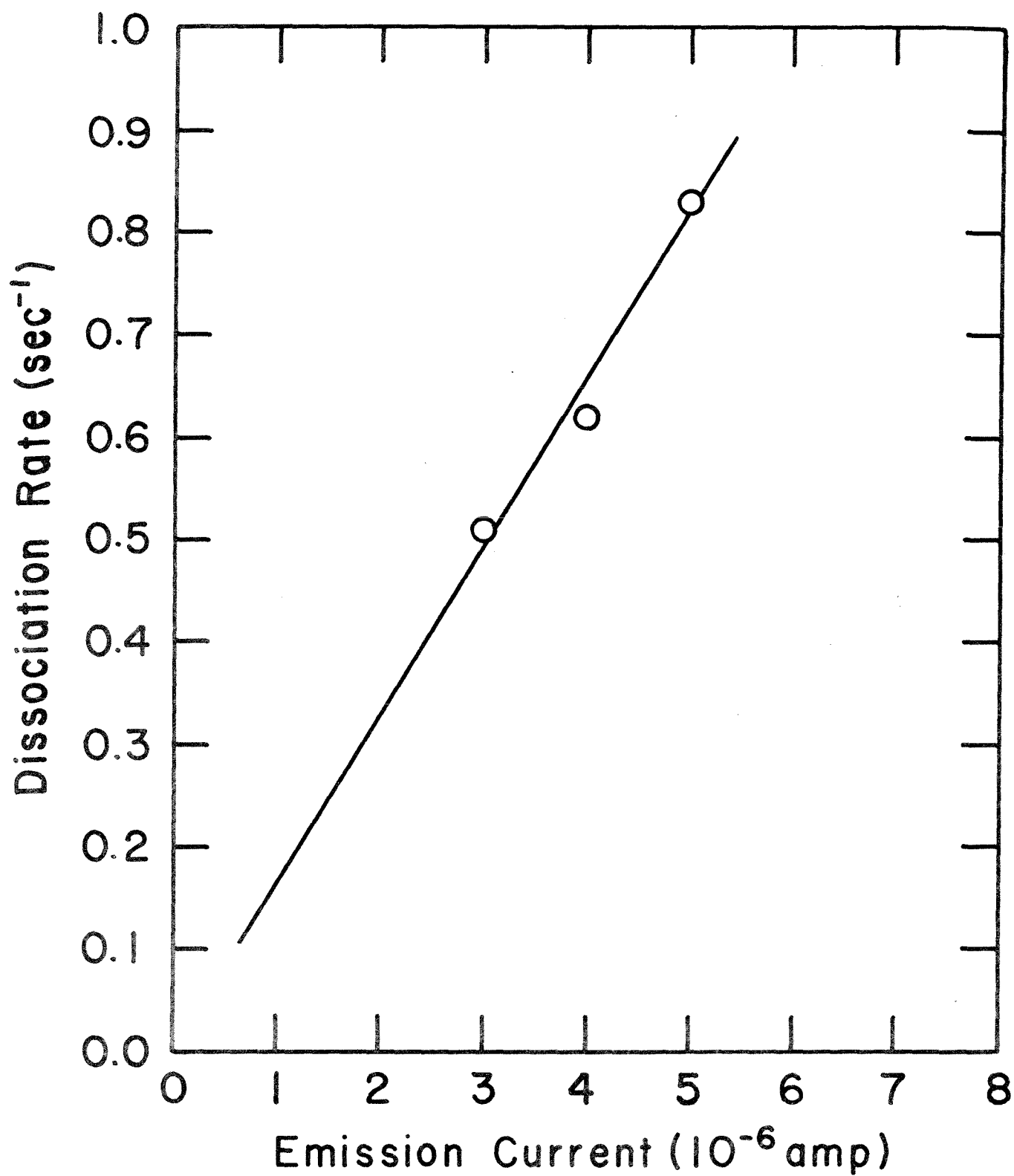
The cross section for electron impact dissociation (fig. 1a) is observed to rise from a threshold of 3.0 ± 0.5 eV, near the thermodynamic threshold of 3.2 eV [11], to a maximum at 7.5 ± 0.5 eV. A comparison of fig. 1a and 1b suggests that electron excitation proceeds by the same $\pi \rightarrow \pi^*$ transition as observed for the photodissociation process 4. Comparison to fig. 1c, however, indicates the presence of other states which, in the absence of the usual photon absorption selection rules, could be involved.

In summary, this work demonstrates the capabilities of ion cyclotron resonance spectroscopy as a technique for studying electron impact dissociative excitation of polyatomic ions. This technique affords the possibility of exciting states of ions inaccessible by photon absorption (e.g., spin forbidden) by monitoring either dissociation processes or modified reactivity [12]. Finally, this work indicates that electron impact excitation of ions should be considered as a possible complication in experiments involving ion trapping in the space charge of a continuous electron beam [11, 13], when the product of the emission current and the trapping time approaches 10^{-7} amp sec.

Acknowledgment

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PROPOSITION I

Photochemistry of Dinitrogen Complexes

Abstract

It is proposed that the photochemistry of dinitrogen complexes

of transition metals be examined because the findings may pro-

vide useful information about the structure and reactivity of

these interesting model compounds as biological N_2-fixation

catalysts as well as suggest useful alternate light-involved

fixation processes. Particular attention will be placed on the

photochemistry of mono- and bi-nuclear osmium complexes

with direct emphasis on means of observing nitrogen reduction

to ammonia.

Dinitrogen is an important raw material for the fertilizer and

plastic industries. While it has the obvious advantage of being plentiful,

it is so inert that considerable energy must be consumed during its

processing. Thus, there is a large effort in progress to find a new and

effective catalyst for its activation. That such catalysts might exist is

shown by nitrogen-fixing bacteria which can produce ammonia from

dinitrogen and water at ordinary temperature and pressure, using chem-

ically mild reducing agents such as sugars.[1,2] The reaction is catalyzed

by the enzyme nitrogenase. While the physical characteristics of the

enzyme are fairly well-known,[1] the actual nature of the active site is

not. The various mechanisms proposed for the activity of nitrogenase

all attribute the active site for the process to the presence of the

transition metals Fe and Mo.[1] There is as yet, however, no concrete evidence as to which metal is at the active site, whether a single metal is responsible for activation, and what the oxidation state is of the metal atom or atoms present. While biochemists are trying to answer these questions by the isolation and study of the enzymes, chemists are preparing and testing model compounds with the hope of eventually not only understanding but simulating enzymatic activity in vitro.

Within the last decade nonenzymatic reduction reactions involving transition metal complexes under mild conditions have been reported.[3-10] These systems can be roughly divided into protic and aprotic. Early work mainly involved aprotic systems.[3,4] Volpin and co-workers, for example, utilized a combination of complexes of Cr, Mo, W, Fe, and Ti together with $LiAlH_4$, Grignard reagents, alkylaluminum derivatives, alkali metal naphthalides, and other reducing agents to reduce N_2 at room temperature. Addition of ligands such as CO was found to inhibit reduction, suggesting that the catalysts formed a complex with N_2.[3] ESR studies[4] indicated the possibility of a binuclear metal complex of N_2, but this was not isolated. Since, with few exceptions, unambiguously characterized compounds could not be isolated, coupled with the fact that the nitrogenases are protic systems, aprotic systems proved to be a disadvantage.[9]

Allen and Senoff started the "protic age" with the discovery of $Ru(NH_3)_5N_2^{2+}$.[11] The N_2 in this complex was found to be directly coordinated to the metal ion in a linear arrangement analogous to the metal carbonyls, in which back π-bonding from filled nonbonding orbitals of

the metal to empty π-orbitals on N_2 occurs. The increase of electron density in its π^* orbitals destabilizes N_2, as evidenced by a 200 cm^{-1} decrease in its stretching frequency, thus in theory making it more susceptible to reduction.[12]

Allen and Senoff's work inspired an intense search for other dinitrogen complexes which might serve as possible models for enzymatic N_2 fixation. The result of this effort is a respectable number of new dinitrogen complexes.[2, 8, 9] As these new complexes became available, attempts at reducing the complexed N_2 were made. Despite the increased electron density on nitrogen, these attempts were fruitless usually resulting only in the displacement of nitrogen.[8, 9] The dinitrogen complexes appeared to be almost as inert as dinitrogen itself, prompting the discoverers of the original dinitrogen complex to express doubt whether such complexes really do play a part in enzymatic fixation. Recently, however, Shilov et al. have found that V(II) in the presence of Mg^{2+} reduces N_2.[10] In addition, Chatt and co-workers made the exciting discovery that mononuclear, bis-dinitrogen complexes of Mo and W react in protic media (H_2SO_4 in CH_3OH) under ambient conditions to yield up to 90% ammonia.[7] These results are of obvious significance indicating that reaction can occur at a single metal site, and demonstrating quite definitely that it is possible to reduce N_2 under mild conditions. Hence, the prospect of finding a suitable system for the catalytic reduction of nitrogen once again looks quite promising.

Another relatively new and promising area in this field is the activation of dinitrogen complexes by the absorption of light. The

observation that dinitrogen complexes decomposed by light led Sigwart and Spence to make the first study in this area on mono- and binuclear Ru-N_2 complexes.[13] They found that upon irradiation in the uv, the Ru(II) complexes were oxidized to Ru(III). This result indicated the exciting possibility that the nitrogen had been reduced in the process, although no products were found. Despite the great potential of this finding, it was not until relatively recently that the mechanism of this reaction was reinvestigated and determined.[14] Hintze and Ford found, rather disappointingly, that the solvent, not nitrogen, is reduced during the photooxidation.[14] To explain these results they postulated a charge transfer to solution (CTTS) state lying below the metal to ligand charge transfer (MLCT) state. The relatively few other studies on the photochemistry of Ru(III) complexes have likewise indicated that MLCT excitation results in processes other than ligand reduction, namely, phosphorescence, ligand substitution, CTTS, and energy transfer (sensitization).[14] Chatt, however, has recently reported that irradiation of the bis-dinitrogen complex, cis-[W(N_2)$_2$(PMePh)$_4$], in methanol at room temperature (inactive in the dark) yields 83% ammonia and 3% hydrazine.[8] Similarly, irradiation of other W and Mo bis-dinitrogen complexes has been found to promote reactions at the dinitrogen ligand.[8]

Proposed Research

The photochemistry of complexes containing dinitrogen, although in its infancy, already has indicated a great potential. Thus it is

proposed that a series of photochemical and spectroscopic studies be launched involving mono- and binuclear (including mixed binuclear) complexes in various oxidation states. Chatt's results, for example, clearly suggest that a detailed spectroscopic analysis and wavelength-dependence photochemical study on the "magical" bis-dinitrogen complexes would be fruitful.

Since this is essentially uncharted territory, one can choose from the wide variety of complexes presently available, and produce new and interesting results. It is proposed that complexes containing Os, however, would be particularly well suited for these studies for the following reasons:

(1) No work on the photochemistry of these complexes has been reported.

(2) The Os—N_2 bond is among the strongest (M—N_2) bonds as evidenced by a greatly lowered γ_{N_2} stretch, e.g., in $[Os(NH_3)_5N_2]X_2$.[15] This is a result of the great π donating ability of Os. Coinciding with this, Os complexes are in general much more stable than other metal complexes (e.g., Ru,[16] W, Mo) and specifically, are less air sensitive, and thus are more amenable to study. Finally, and perhaps most importantly, the greater π-donating ability of Os is known to enhance nucleophilicity of the dinitrogen.

(3) Complexes of Os are readily synthesized. These include a wide variety of mononuclear complexes, bis compounds, binuclear complexes, mixed binuclear complexes, and complexes in a variety of oxidation states.[2, 8, 9]

(4) Assignments of uv absorptions on selected Os complexes have been made which indicate the presence of a number of MLCT states.[17] Together with the enhanced back donation from the metal in the ground state, MLCT transitions should increase the susceptibility of N_2 to attack by a proton donor.

For the above reasons, complexes of Os are likely candidates for initial study.

Questions to be explored in these studies would include:

(1) Will H_2 inhibition of N_2 fixation in biosystems be observed with model systems even in the presence of light? The results will bear significantly on the possibility of competitive H_2 binding and/or redox reactions elsewhere in the enzyme system. Hopefully, H_2 will not react with the complex to give the corresponding hydrides.[18]

(2) Will other competitive processes such as charge transfer to solution (CTTS) prevent reduction of N_2 as in the Ru complexes? The CTTS transitions are not well understood and perhaps variation of the solvent could prevent this from occurring. A careful study would be interesting.

(3) If substitution is competing with reduction, can the proper choice of ligand prevent this? For example, using ligands of high basicity increases electron density on the metal ion, which in turn increases the metal nitrogen bond making dissociation more difficult.[2]

(4) Will the bis dinitrogen complex "perform" as well as Chatt's complexes? How does the electronic spectra of these compounds compare to the single N_2 complexes, i.e., do they have a very low lying MLCT below CTTS?

(5) If the mononuclear $M-N_2$ complex is successfully photoreduced to produce NH_3, what further light would this shed on the role of the second metal in the enzyme which is postulated to be necessary for fixation?

(6) Inasmuch as energy transfer processes are important in bio-systems, what would be the effect of conducting the photochemical reactions in the presence of various photosensitizers to try to facilitate the reduction of N_2?

(7) Will it be possible to observe intermediate reduction products by the use of fast scan techniques, flash photolysis, and ESR flash? Study of the intermediates is significant because such information is indispensable for the simulation of N_2 assimilation in vitro and for the development of catalysts for the reduction of gaseous dinitrogen, e.g., to hydrazine under normal conditions.

(8) As a corollary study, it would be interesting to examine $d \rightarrow \pi^*$ transitions in metal complexes having such ligands as acetylene, nitrous oxide, organonitriles, and isocyanides, to look for photochemical reduction.

In conclusion these studies will at worst yield insight into the electronic structure and photochemistry of dinitrogen complexes of Os and may be a vital step in understanding the activation of dinitrogen.

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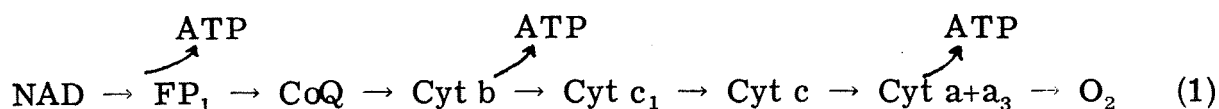
PROPOSITION II

Role of Thioether Groups in Oxidative Phosphorylation
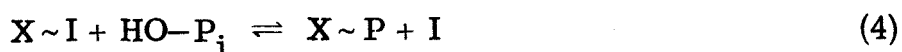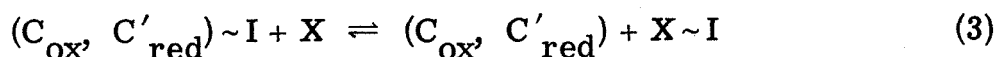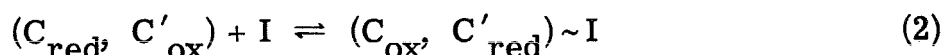
Abstract

It is proposed to test the hypothesis that thioether groups play a role in respiratory chain-linked oxidative phosphorylation.

The mechanism of oxidative phosphorylation (O-P) is still very much a mystery despite intensive investigation.[1] Belitzer and Tzibakova showed phosphorylation of ADP → ATP to be an aerobic process, that is, coupled to respiration rather than to the anaerobic process of glycolysis.[2] Lehninger and Kennedy showed that isolated mitochondria catalyze the process of oxidative phosphorylation coupled to oxidation of tricarboxylic acid cycle intermediates.[3] Lehninger also succeeded in showing that for every 2 electrons transferred from NAD^+ to O_2, 3 molecules of ATP are made.[4] Keilin and Hartree discovered that cytochromes act in series as electron carriers[5] and Warburg discovered that flavoproteins also act to transport electrons.[6] Loomis and Lipmann found that chemical agents, particularly 2,4-dinitrophenol and other halo and nitrophenols, act as uncoupling agents allowing respiration to proceed while inhibiting phosphorylation.[7] Lipmann and others then used these chemical agents to advantage, along with previous discoveries, in determining the overall mechanism of O-P. Process 1 is a sequence of electron-transfer reactions consistent with

existing evidence.[8] Also shown are the probable sites for ATP formation.

$$NAD \to FP_1 \to CoQ \to Cyt\ b \to Cyt\ c_1 \to Cyt\ c \to Cyt\ a+a_3 \to O_2 \qquad (1)$$

with ATP formed at the arrows over FP_1, $Cyt\ b$, and $Cyt\ a+a_3$.

While the sequence in Process 1 is quite certain, the actual mechanism for ATP formation is unknown. Inhibitor studies have led to what is called the chemical-coupling hypothesis. This model[9] is expressed by Reactions 2-5, where ~ represents a chemical bond, C_{red} and C'_{ox}

$$(C_{red},\ C'_{ox}) + I \rightleftharpoons (C_{ox},\ C'_{red}) \sim I \qquad (2)$$

$$(C_{ox},\ C'_{red}) \sim I + X \rightleftharpoons (C_{ox},\ C'_{red}) + X \sim I \qquad (3)$$

$$X \sim I + HO-P_i \rightleftharpoons X \sim P + I \qquad (4)$$

$$X \sim P + ADP \rightleftharpoons X + ATP \qquad (5)$$

are the reduced and the oxidized electron carriers, and I and X are the nonphosphorylated intermediate and phosphate acceptor (both believed to be proteins), respectively. Any progress toward a more detailed mechanism requires an identification of the chemical nature of the two hypothetical entities, I and X.
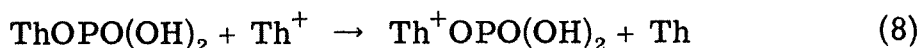
The hypothesis that a high-energy chemical intermediate is formed in mitrochondrial oxidative phosphorylation has inspired several groups to devise model systems in which oxidation is coupled to phosphorylation by such an intermediate. Suggestions have been made, for example, that either NAD[10] or the various quinones[11, 12] (benzo-, naphtho-, and tocopheryl-) known to be present in mitochrondria might function as

phosphate as well as electron carriers (i. e., I = X above). More recently, the suggestion that sulfur containing compounds (mainly thio-ethers) might serve as model systems for oxidative phosphorylation has received some experimental support which looks quite promising.[13-15] Of particular interest is the work by Wilson et al. on thianthrene and 2, 3, 7, 8-tetramethoxythianthrene,[15] which I propose to pursue further.

Studies on thianthrene using cyclic voltammetry[16] showed that this specie undergoes a reversible one electron oxidation process 6 indicating that, in the absence of nucleophiles, the radical cation is stable in
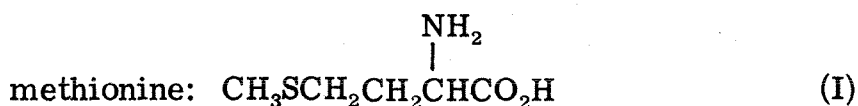
$$\text{(6)}$$
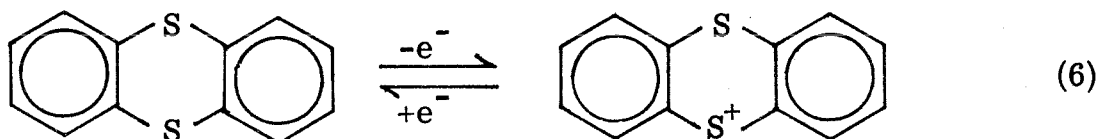
solution. Furthermore, the radical cation was found to effect phosphorylation of AMP in the presence of orthophosphate to give ADP and ATP in 47 and 5% yields, respectively, based on the amount of AMP consumed.[15] The overall reaction mechanism postulated is shown by Reactions 7-9, where Th is thianthrene and ThO is thianthrene sulfoxide.

$$\text{Th}^+ + \text{(HO)}_2\text{PO}_2^- \rightarrow \text{ThOPO(OH)}_2 \qquad (7)$$

$$\text{ThOPO(OH)}_2 + \text{Th}^+ \rightarrow \text{Th}^+\text{OPO(OH)}_2 + \text{Th} \qquad (8)$$

$$\text{Th}^+\text{OPO(OH)}_2 + \text{AMP}^- \rightarrow \text{ADP} + \text{ThO} \qquad (9)$$

Similar results were obtained for the stable dication of 2, 3, 7, 8-tetramethoxythianthrene.[15]
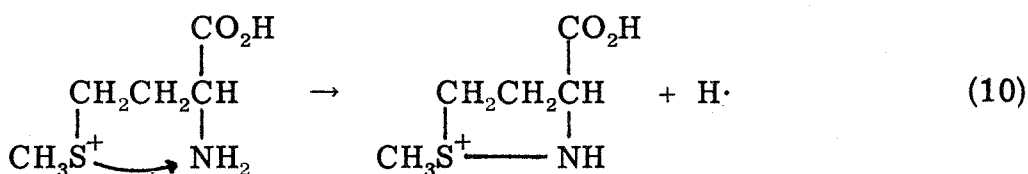
The work reviewed above demonstrates the ability of an aromatic sulfur cation and dication to effect phosphorylation of adenine

nucleotides in the presence of orthophosphate. As a logical extension
of this work, I propose to examine the electrochemistry and phos-
phorylation chemistry of methionine (I) and several of its derivatives (II).

$$\underset{\displaystyle \text{methionine:}}{}\quad \overset{\displaystyle \overset{\textstyle NH_2}{|}}{CH_3SCH_2CH_2CHCO_2H} \qquad (I)$$

$$\underset{\displaystyle \text{methionine derivatives:}}{}\quad \overset{\displaystyle \overset{\textstyle NHR_2}{|}}{R_1SCH_2CH_2CHCOR_3} \qquad (II)$$

These compounds are especially pertinent since (a) they are known to be
oxidized and reduced with relative ease,[14] important for a cyclical bio-
logical process and (b) methionyl residues in proteins, most notably
methionine-80 of cytochrome C, have been postulated as playing im-
portant roles in both electron transport[17] and oxidative phosphory-
lation.[14, 15]

It can be seen that the methionines do not have the capability of
stabilizing a cation or dication intermediate that the π-systems of the
thianthrenes afforded. A reasonable amount of stability can, in theory,
be achieved, however, by the formation of a cyclic structure[18] as shown
for methionine in Process 10.

$$\overset{\displaystyle \overset{\textstyle CO_2H}{|}}{\underset{\underset{\textstyle CH_3S^+ \longrightarrow NH_2}{|}}{CH_2CH_2CH}} \quad \rightarrow \quad \overset{\displaystyle \overset{\textstyle CO_2H}{|}}{\underset{\underset{\textstyle CH_3S^+ \!\!\!-\!\!\!-\!\!\!- NH}{|}}{CH_2CH_2CH}} \quad + \text{ H}\cdot \qquad (10)$$

The presence of this cyclic intermediate could be sought by generating it electrochemically in an ESR and by rapid scan spectrophotometry, assuming that the intermediate had a characteristic spectrum. Various R groups in the methionine derivatives (II), particularly aryl substituents, could be tested for their ability to stabilize the radical cation. Of special interest would be to let R_3 = NHR enabling the formation of a six member, as well as a five member, ring intermediate.

Each compound would be subjected to a logical experimental sequence as outlined here:

(1) Using cyclic voltammetry (CV) study redox of compound. This will show the potential at which oxidation occurs and whether or not the oxidation is reversible. A variable scan speed may determine the lifetime of the intermediate.

(2) If the process is irreversible, i.e., reaction occurs after oxidation, then it would be of interest to conduct an electrolysis, separate and identify products, and run CV on them. Since it is likely that the sulfoxide would be a product, determining redox of the sulfoxide using CV would be important.

(3) Run electrolysis in the presence of water. Separate and analyze products. Again sulfoxide is expected to be the major product.

(4) Run CV studies on the methionine derivative in the presence of AMP and ADP. If cyclic voltammetry shows two distinct peaks, then electrolysis experiments should be carried out at a potential just beyond the first wave and then just beyond the second wave. Each experiment should be analyzed separately for ATP production.

(5) During all of the above studies use a thin cell in conjunction with a fast scan spectrophotometer to look for intermediates.

Materials and Apparatus

1. The derivatives of methionine are readily synthesized.[19] Dried acetonitrile can serve as solvent. $Mg(ClO_4)_2$ is a commonly used electrolyte and will not interfere with identification and work up of products. The disodium salt of ADP is available for use.

2. The usual set up for cyclic voltammetric studies will be used,[20] namely a polarographic analyzer, a triangular wave generator, an x-y recorder, and a cell with the standard $Ag-AgNO_3$, working, and counting electrode. This set-up can be used for electrolysis studies as well.

3. Products will be separated by TLC and analyzed by IR and NMR. ATP will be assayed enzymatically.[21]

It is believed that this study would not only provide significant results in support of a model of oxidative phosphorylation, but also provide interesting information about the electrochemistry of thioethers studied.

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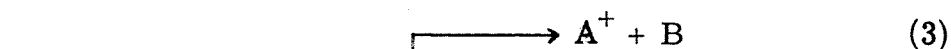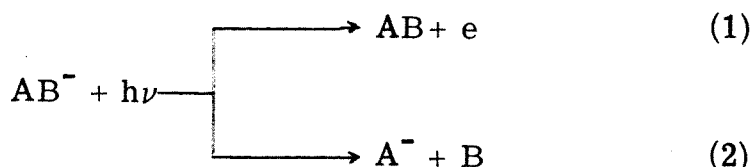893 (1968); (b) E. Bäuerlein and T. Wieland, Chem. Ber., 103,
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PROPOSITION III

Photochemical Investigations of Ions in the Gas Phase
Using Ion Cyclotron Resonance Spectroscopy

Abstract

Several studies in the area of gaseous ionic photochemistry
are proposed based on interesting recent work utilizing ICR
techniques.

ICR ion storage capabilities facilitates the investigation of photo-
physical and photochemical processes involving ions.[1-6] The advan-
tages of the technique involve the ability to generate a wide variety of
interesting ionic species by direct ionization, surface ionization, or
by ion-molecule reactions, and to thermalize these species while they
are trapped in a well defined spatial region. Interactions of photons
with ions are then inferred from observed changes in ion abundance
monitored as a function of time as well as wavelength, enabling the
study of unimolecular and bimolecular reaction kinetics. Processes
amenable to study include electron photodetachment (process 1), ion
photodissociation (processes 2 and 3), and production of excited elec-
tronic states with modified reactivity (process 4) and/or modified
photochemistry (e.g., multiphoton process 5). From these studies
important chemical information can be obtained such as: the absorption
spectra of organic and inorganic ions, acid-base properties of excited
electronic states, shifts in the charge distribution accompanying

$$AB^- + h\nu \longrightarrow \begin{cases} \longrightarrow AB + e & (1) \\ \\ \longrightarrow A^- + B & (2) \end{cases}$$

$$AB^+ + h\nu_1 \rightarrow [AB^+]^* \begin{cases} \longrightarrow A^+ + B & (3) \\ \xrightarrow{\text{neutral}} C^+ + D & (4) \\ \xrightarrow{h\nu_2} A^+ + B & (5) \end{cases}$$

electronic excitation, structural information, and thermochemical information (e. g., electron affinities).

Perhaps the most interesting and least explored area in this field deals with the photoinduced reactions (process 4). To observe this process under the experimental conditions used in ICR, the excited intermediate, $[AB^+]^*$, must have a lifetime on the order of 0.1-1 msec. Our recent study of the photodissociation of benzene cation[2] involves a sequential two photon process as illustrated by 5. In addition to providing the first reported evidence for a long-lived intermediate state, this is the first photodissociation observed to occur below thermodynamic threshold. I am convinced that this unusual reaction can be generalized by selection of systems which should favor long-lived intermediate states. For example, in addition to isomerization and the process of intersystem crossing to an excited state with spin multiplicity differing from the ground state, there is the possibility of internal conversion to a vibrationally excited ground state.[2,3] Further characterization of excited intermediates can be effectively carried out by addition of various collision gases monitoring any photoinduced reaction or, for non-reactive

collisions, determining quenching efficiency. These proposed studies bear an important relationship to energy research, first as a means of achieving high energy excited states by pooling of low energy photons providing a more efficient use of energy from low energy sources and secondly, as a method parallel to well publicized schemes for isotope separation; with sufficient resolution single isotopic species can be selectively excited and then subsequently photodissociated.

Another avenue of research having great potential is the photo-dissociation of weakly bound complexes.[4] In recent years in ours and other laboratories the "synthesis" of a number of complexes has been achieved. For instance, it has been possible to generate complexes of Li^+ with n- and π-donor bases such as Species I.[7] Similar complexes with Na^+, Al^+, Fe^+, Co^+, NO^+, CH_3Hg^+, $C_5H_5Ni^+$ (Species II-VIII) and

I   II   III   IV   V

VI   VII   VIII
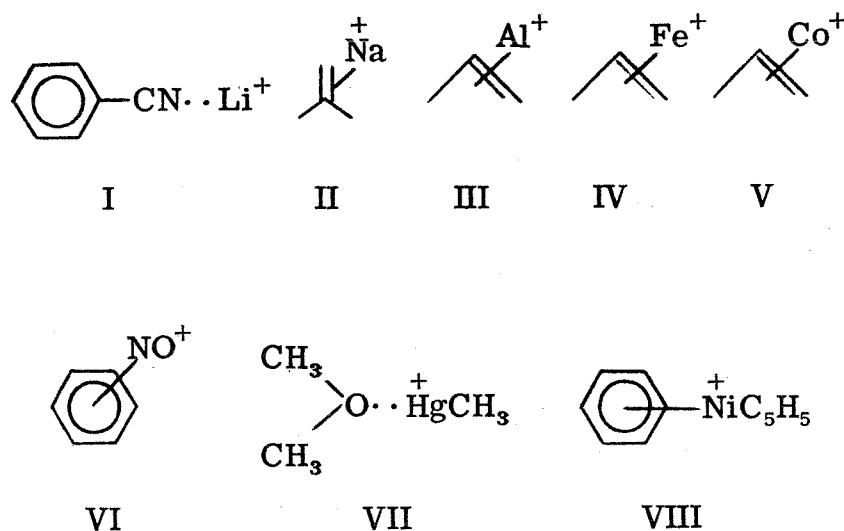
other Lewis acids have also been observed. We reported the photo-dissociation spectra of Li^+ complexes with monosubstituted benzenes

demonstrating that information relating to electron distributions and acid-base properties of molecules in excited electronic states could be derived.[4] These results indicate that this would be an extremely fruitful area of research and I propose to apply these powerful techniques to study the numerous interesting complexes which are evident from a perusal of Species I-VIII. The approach employed will be systematic, investigating complexes in which the ion remains the same while varying the neutral moiety, and vice versa. In the former category, I propose to study the effect of neutrals on the absorption spectra of chromophoric ions. In addition, further work planned utilizing Li^+ will include complexes with organic and inorganic compounds (as a means of delineating excited state properties and charge transfer transitions in these compounds); complexes with species having more than one chromophoric site or where Li^+ is removed from the chromophoric site (as a new method for yielding insight into intramolecular energy transfer); and complexes with species having more than one binding site (as a novel method for determining which site is more basic). From studies keeping the neutral the same and varying the ion, detailed information can be obtained about complex ion structure and the nature of the acid-base bond. For example, we have observed definite effects due to covalent bonding (charge delocalization) of H^+ to cyanobenzene as compared to purely electrostatic bonding when Li^+ is the Lewis acid.[4, 5] Similar studies comparing spectra where the ion is varied from Li^+ to Al^+, Co^+ or Fe^+ may indicate new charge transfer bands having relevance to solution photoredox and organometallic chemistry.

I also propose to investigate the spectroscopy of ionic dimers, including Li^+ and H^+ bound dimers, which we have observed to be formed by bimolecular pathways. Examination of these species would answer how the lowest energy excitations of the monomer and dimer compare, and what is the nature of the energy transfer between components of a complex dimer. Spectroscopy on dimers in which H_2O is one constituent would provide the link between purely gas phase and solution phase absorption spectra and, more generally, the effect of partially solvating an absorbing species with a specific base could be studied. In conjunction with this I also propose to examine the photodissociation of chromophores which have been studied in solution. In this regard we have already examined the photodissociation of perfluoroallyl cation,[1] benzoyl cation,[6] and protonated benzene.[6] The proposed studies will yield absorption spectra free of all effects due to solvent, counterions, and any other neutral or ionic species absorbing in the region of interest and thus provide the standard by which absolute solvent shifts of carbocations can be determined. In addition, these studies will uncover photochemical processes having possible utility in solution.

Finally, because this is an entirely new area of photochemistry, the possibility of unanticipated discoveries is afforded.

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PROPOSITION IV

Mechanistic Study of the Decomposition of Dioxetanes

to Yield Excited State Products

Abstract

Several studies are proposed to probe the mechanism by
which 1,2-dioxetanes decompose to produce excited state
products. Of particular interest are (a) the effect of mo-
lecular structure on the efficiency of excited state pro-
duction and (b) the nature of energy partitioning between
the two carbonyl products.

Electronically excited states of organic molecules are formed in
many chemical reactions.[1] Such chemically produced excited states
are identical to light produced excited states, and undergo the reactions
and transformations expected of such states ("photochemistry without
light"). The excited states can also be used in energy transfer experi-
ments.

One particularly important and interesting family of compounds
receiving a lot of attention in this area are the 1,2-dioxetanes. With-
in only the last ten years have these compounds been synthesized,
studied, and established as precursors in a number of biological chemi-
luminescent reactions. The dioxetane ring was first proposed as a
critical intermediate in the oxygen-dependent chemiluminescent
reactions of the lophines (arylimidazoles),[2] indoles,[3] acridine com-
pounds,[4] peroxalates,[5] and aminoethylenes,[6] largely on the basis of
products formed and the likely pathways for their formation.

Dioxetanes have also been proposed as intermediates in the bioluminescence of the firefly[7] and the crustacean Cypridina hilgendorfii.[8]

In 1968, Kopecky and Mumford[9] synthesized and characterized the first dioxetane, trimethyl-1,2-dioxetane (I). They also established


I
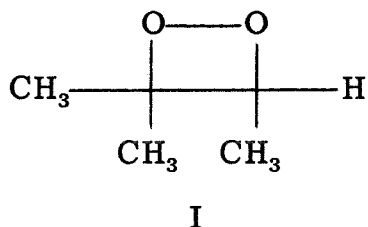
that dioxetanes decompose to give excited states of the carbonyl products formed (eq 1) thus confirming the earlier predictions[10] and proposals.

(1)

hν or photochemical
reactions
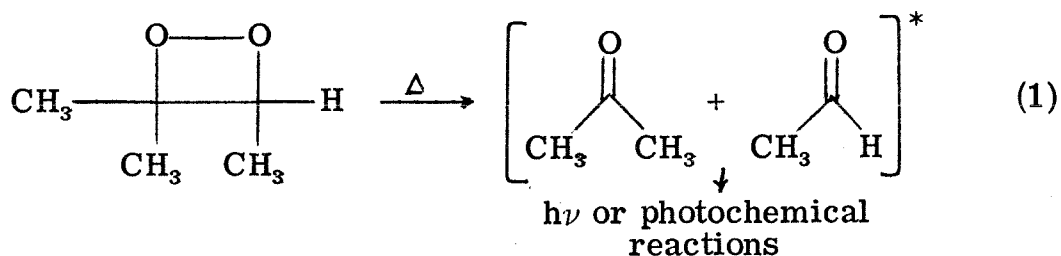
Following Kopecky and Mumford's pioneering work, many papers have appeared concerned with the synthesis and investigation of these high-energy content, small ring compounds.[11] White et al.[12] reported that the decomposition of trimethyl-1,2-dioxetane gave a 5% yield of a triplet carbonyl product. Wilson et al.[13] reported that the decomposition of cis-diethoxy-1,2-dioxetane (II) may yield ethyl formate


II
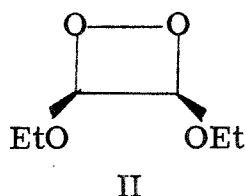
triplets in high, possibly quantitative yield. Güsten et al.[14] suggested that dioxetanedione (III) sensitized reactions with an efficiency
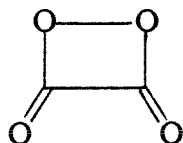

III

approaching 5% in favorable cases. In none of the above papers were the chemelectronically formed excited species unambiguously defined. Turro and co-workers,[15, 16] however, have recently reported a series of elegant experiments in which they chemically titrate the products of thermolysis to determine excited singlet and triplet yields. Using these methods they found, for example, that tetramethyl-1, 2-dioxetane (IV) yields 50% triplet acetone (100% corresponds to one
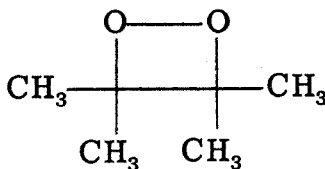

IV

triplet carbonyl per dioxetane) and less than 1% singlet acetone as primary thermolysis products (i.e., triplets are not formed from excited singlet precursors via intersystem crossing).[15] Similar results obtained on trimethyl-1, 2-dioxetane (I) and three other dioxetanes (V-VII) led the investigators to conclude that, in general, the decomposition route greatly favored formation of triplets over

V VI VII
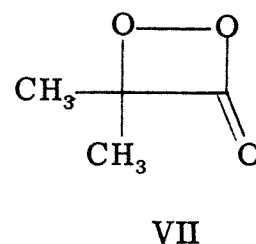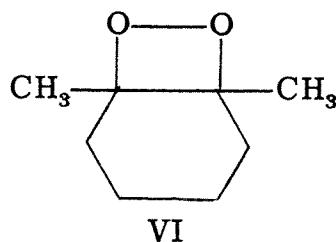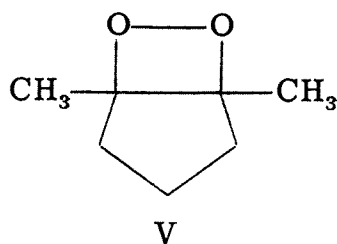
singlets.[16] Contrary to these conclusions, Foote and co-workers[17] reported that the decomposition of 3, 4-dimethyl-3, 4-di-n-butyl-1, 2-dioxetane (VIII) produced nearly equal amounts of singlet and triplet carbonyls.

VIII
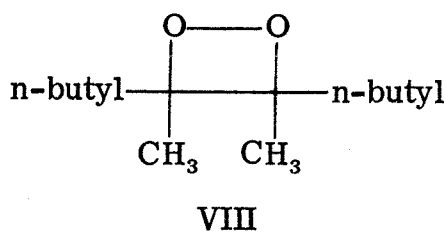
Several explanations have been published attempting to rationalize why 1, 2-dioxetanes decompose thermally to give electronically excited products. The two major mechanisms include a diradical[18] and a concerted mechanism.[19-22] Recent MINDO/3 studies by Dewar et al.[21] on dioxetane (IX) provide evidence that conversion of this

IX
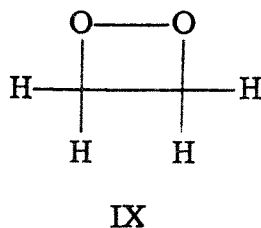
compound to two formaldehydes involves a concerted mechanism with an integral intersystem crossing. The calculated transition state was

bent tortionally (oxygens above and below the plane of the ring) and had an oxygen-oxygen bond too short to be a diradical. Turro et al.[22] present further evidence in support of the concerted mechanism. They argue that the diradical mechanism should exhibit an entropy effect, a negative substituent effect, a solvent effect, and a statistical effect, only the second of which do they observe. They propose a transition state which at some point becomes asymmetric lowering the prohibition to spin interconversion and also suggest that spin-orbit coupling is involved. Other work, however, has been reported in disagreement with their solvent effects.[23]
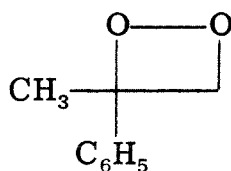
From this brief introduction it is clear that more experimental and theoretical studies are needed for a full understanding of this fascinating and potentially very useful reaction. Some particularly interesting questions which emerge and that I propose to pursue include: (1) What are the factors affecting the quantum yield or quantum efficiency of excited state formation? A complete description of the mechanism requires an understanding of these factors. As stated above, the values of the excitation efficiency obtained for various dioxetanes range from 5% to 100%. The cause of these variations is unknown. (2) How is the energy partitioned in the products, i.e., what determines which carbonyl is excited? No systemmatic study has been reported examining this question, and in fact no examples have been detailed. (3) Does the reaction proceed via a diradical or a concerted mechanism? Can one mechanism explain all of the results? How would the products of a diradical mechanism be expected to differ

from those of a concerted mechanism? (4) How are excited singlet state products formed and what affects their formation efficiency relative to triplet formation? Which mechanism best accounts for singlet formation? One factor of obvious importance in rationalizing any mechanism is the energetics involved. In one of the only thermochemical studies reported on this subject, Lechtken and co-workers[24] found that for tetramethyl-1, 2-dioxetane (IV) there was just enough energy to produce either the singlet or triplet of acetone. Their results also indicated that more energy was available on decomposition in the vapor phase than in solution suggesting a greater singlet yield could be obtained by gas phase decomposition. (5) Are specific vibronic interactions required to promote interconversion of electronic states and, if so, which nuclear motions are most effective?[21] (6) And finally, how will quantum yield vary with the method of decomposition employed (e.g., thermal, photochemical,[17] and sensitized[25] decomposition)?
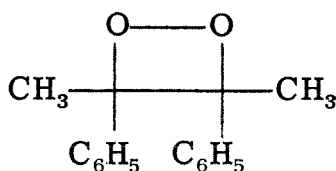
I propose to study the effect of molecular structure on the chemical generation of excited states. This study would include tabulating all of the results to date and observing trends. One problem in doing this appears to be the lack of consistency of results reported from different laboratories. For example, the efficiency of triplet formation from trimethyl-1, 2-dioxetane (I) has been reported to be both 5%[12] and 50%.[22] (Clearly, this suggests a cooperative effort should be

launched to study one compound in several laboratories to establish

uniform methods for quantifying yields !)

The finding that triplet acetophenone from 3-methyl-4-phenyl-

1, 2-dioxetane (X) is formed less efficiently than from 3, 4-dimethyl-

3, 4-diphenyl-1, 2-dioxetane (XI) led White and co-workers[26] to

$$
\underset{\textbf{X}}{\underset{C_6H_5}{CH_3 \overset{\displaystyle O \text{—} O}{\rule{0pt}{1.6em}}}}
\qquad
\underset{\textbf{XI}}{\underset{C_6H_5 \quad C_6H_5}{CH_3 \overset{\displaystyle O \text{—} O}{\rule{0pt}{1.6em}} CH_3}}
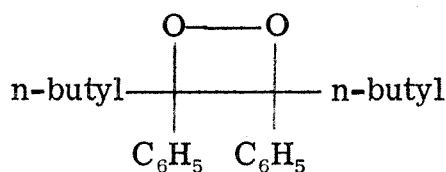$$

suggest that symmetry significantly affects excited state production.

This hypothesis could be readily investigated. It would also be of

interest to test the difference in efficiency of cis- and trans-dioxetanes.

Further work should be performed taking advantage of the extensive

photochemical studies which have been carried out on the Norrish

Type II cleavage and cyclization reactions of carbonyl compounds[17, 27]

and for which quantum yields are understood.[28] For example, the

excited valerophenone expected from the decomposition of 3, 4-di-

n-butyl-3, 4-diphenyl-1, 2-dioxetane (XII) would itself decompose[26] via

$$
\underset{\textbf{XII}}{\underset{C_6H_5 \quad C_6H_5}{n\text{-butyl} \overset{\displaystyle O \text{—} O}{\rule{0pt}{1.6em}} n\text{-butyl}}}
$$

reaction 2 to products which could be quantitated as to yield and

$$C_6H_5\overset{\overset{O^*}{||}}{C}C_4H_9 \rightarrow C_6H_5\overset{\overset{O}{||}}{C}CH_3 + C_3H_6 + \text{(structure)} \tag{2}$$
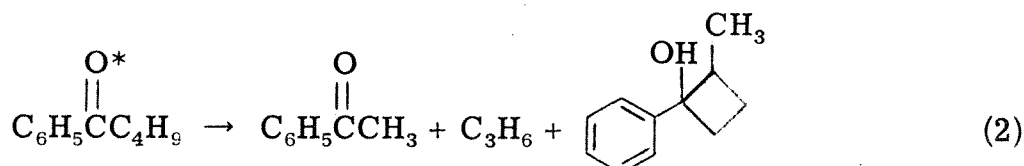
multiplicity of initially generated carbonyl fragments. Phenyl and

n-butyl substituents (electron donating, electron withdrawing, and

heavy atoms) could be systematically tested to see the effect on excited

state production efficiency. In addition, the study of unsymmetrical

derivatives of XII would readily yield information about partitioning

of energy in the two carbonyl products (question 2 above).

There is also an obvious need for more thermodynamic data such

as reported by Lechtken et al.[24] Where possible this data should be

obtained for compounds in solid, gaseous, and solution phases. Singlet

and triplet formation (of gas, liquid, and solid) should be correlated

with the results of these studies.

Solvent effects on the mechanism have not been thoroughly inves-

tigated and as stated above there has been disagreement. These studies

are of obvious importance in distinguishing between a diradical and

concerted mechanism. It would also be of interest to irradiate a

sample with ir light at the energy of the dioxetane's asymmetric stretch

to see if reaction is promoted as implied by Turro's analysis.

Finally, it would be of interest to compare quantum yields

obtained by thermal, photochemical, and sensitized decomposition.

Heavy metals[29] or Xe should, for example, promote reaction if spin-

orbit coupling is important.

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PROPOSITION V

### Sequential Deuterium Exchange Reactions

Abstract

It is proposed to study the sequential deuterium exchange reactions of a range of aromatic compounds including naphthalene, anthracene, and biphenyl, as well as of a variety of other saturated and unsaturated carbonium ions and anions in order to clarify the reaction mechanism of deuterium exchange and provide interesting structural information.

Deuterium exchange has been used in mass spectrometric studies to determine the number of acidic hydrogens in a molecule. Together with knowledge of the heteroatom content from high resolution mass spectrometry, the results afforded by this method aid considerably in functional group identification and hence the elucidation of complex molecular structures.[1,2] Hunt and co-workers have developed a simplified procedure utilizing chemical ionization mass spectrometry (CIMS) with D_2O as the reagent gas.[3] Their findings indicate that hydrogen bonded to heteroatoms in aliphatic alcohols, phenols, carboxylic acids, amines, amides, and mercaptans undergo essentially complete exchange in the ion source prior to protonation by the reagent ions. In addition, they report that unsaturated compounds such as benzene, stilbene, and 3, 3-dimethyl-1-butene fail to exchange, and that the extent of the substitution with ketones, aldehydes, and esters is negligible.

We recently reported[4] preliminary results on a novel deuterium

exchange reaction, observed using ion cyclotron resonance (ICR)

spectroscopy,[5] which had a bearing on the above findings and implica-

tions for further study. In apparent contrast to the results of Hunt

et al., we observed sequential reactions of protonated aromatic com-

pounds with D_2O in the gas phase leading to various degrees of ring

deuteration. For example, in a mixture of benzene and D_2O, it was

found that reactions 1 and 2 lead to the formation of $C_6H_6D^+$ which in

$$D_2O^+ + C_6H_6 \rightarrow C_6H_6D^+ + OD \qquad (1)$$

$$D_3O^+ + C_6H_6 \rightarrow C_6H_6D^+ + D_2O \qquad (2)$$
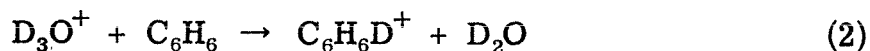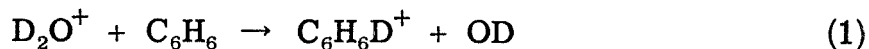
further reaction with D_2O undergoes rapid stepwise exchange of H for

D (reaction 3).[6] By monitoring reaction 3 it was possible to determine

$$C_6H_{7-n}D_n^+ + D_2O \rightarrow C_6H_{6-n}D_{n+1}^+ + HDO \quad (n = 1\text{-}6) \qquad (3)$$
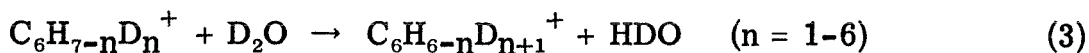
the number of deuteriums exchanged and qualitatively assess the

kinetic parameters describing the first exchange. Table I, taken from

this paper, summarizes the results and demonstrates a number of

important features. It is apparent from the table that deuterium

exchange varies significantly for different structural isomers. Thus

while o- and p-difluorobenzene exchange all hydrogens rapidly, the

meta isomer slowly exchanges only a single hydrogen. A similar com-

parison can be made for the xylenes and trisubstituted benzenes. This

result was especially significant since the mass spectra of these

isomeric compounds are in general indistinguishable.[7,8] Species
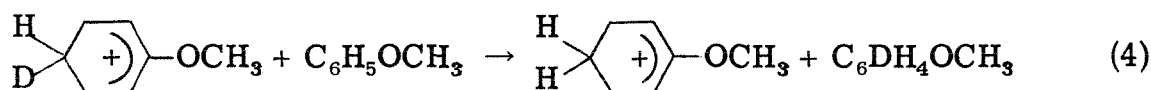
Table I. Summary of Cationic Deuterium Exchange Results[4]

Compounds	No. of Exchangeable Hydrogens	Max. No. of Hydrogens Exchanged Starting with Deuterated Parent Ion[a]	Relative Rate of First Exchange[b]	Site of Protonation[c]
Benzene	6	6	f	R
Fluorobenzene	5	5	f	R
o-Difluorobenzene	4	4	f	R
m-Difluorobenzene	4	1	m	R
p-Difluorobenzene	4	4	f	R
1,3,5-Trifluorobenzene	3	0	-	R
1,2,4-Trifluorobenzene	3	3	f	R
Toluene	8	5	m	R
o-Xylene	10	4	m	R
m-Xylene	10	1	s	R
p-Xylene	10	4	m	R
Mesitylene	12	0	-	R
Anisole	8	0	-	R
Benzonitrile	5	0	-	S
Benzaldehyde	6	0	-	S
Acetophenone	8	0	-	S

[a] - indicates exchange not observed.

[b] The symbols f, m, and s indicate, respectively, fast ($1-5 \times 10^{-10}$ $cm^3 mol^{-1} sec^{-1}$), medium ($10^{-11} - 10^{-10}$ $cm^3 mol^{-1} sec^{-1}$), and slow ($\leq 10^{-11}$ $cm^3 mol^{-1} sec^{-1}$) reaction rates.

[c] R and S indicate that evidence was obtained for the favored site of protonation being on the ring and substituent, respectively. With sufficiently acidic donors both sites may be protonated.

such as the benzoyl cation, radical cations, and $C_7H_7^+$ derived from

toluene and cycloheptatriene were found not to undergo exchange.

Finally, it was concluded that ring protonation is a necessary, but

not sufficient, condition to observe exchange. Demonstrating this

last point it was found that while anisole does not undergo exchange

it does react by thermoneutral proton transfer (reaction 4), the

$$\underset{D}{\overset{H}{>}}\hspace{-2pt}\left\langle\!\!\!\overbrace{+}\!\!\!\right\rangle\!\!-OCH_3 + C_6H_5OCH_3 \rightarrow \underset{H}{\overset{H}{>}}\hspace{-2pt}\left\langle\!\!\!\overbrace{+}\!\!\!\right\rangle\!\!-OCH_3 + C_6DH_4OCH_3 \qquad (4)$$

latter indicative of ring protonation.

Martinsen and Buttrill[9] corroborated these results using chem-

ical ionization mass spectrometry. In addition, they reported that

lack of exchange coupled with the formation of cluster ions (the

association of the protonated species with one or more D_2O molecules[10])

in the CIMS spectra is evidence of protonation on the substituent rather

than the ring and concluded, for example, that bromobenzene and iodo-

benzene protonate on the ring while diaminobenzenes and dihydroxy-

benzenes protonate on the substituent.

Bierbaum et al.,[11] using flowing afterglow techniques, reported

that carbanions also undergo deuterium exchange. Their results

(Table II) showed, for example, that CH_2CN^- exchanges both its hydro-

gens by reaction 5. They also found that $C_7H_7^-$ from toluene exchanges

$$CH_2CN^- \xrightarrow{\;D_2O\;} CHDCN^- \xrightarrow{\;D_2O\;} CD_2CN^- \qquad (5)$$
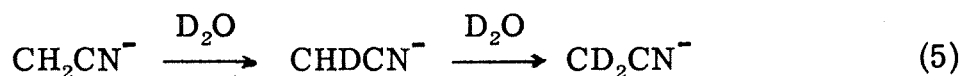
two hydrogens illustrating quite elegantly that this ion has a non-

scrambling benzyl structure.

Table II. Summary of Anionic Deuterium Exchange Results[11]

Neutral (HA) which Produced Anion (A⁻)	Number of H-Atoms Present in A⁻	Max. No. of H-Atoms in A⁻ which Exchange
Propylene	5	4
cis-2-Butene	7	7
trans-2-Butene	7	7
cis-2-Pentene	9	9
2-Butyne	5	2
Acetonitrile	2	2
Glycol Aldehyde	3	1
Acetaldehyde	3	0
Acetic Acid	3	0
Ethylene Glycol	5	1
Methanol	3	0
Toluene	7	2

At least three mechanisms can be proposed for the deuterium exchange reactions of protonated benzenes. First, the reaction might be concerted with D_2O simultaneously donating a deuterium and abstracting a proton (I and II). Alternatively, the chemically activated
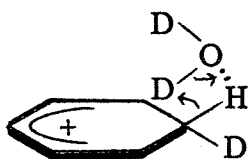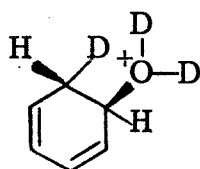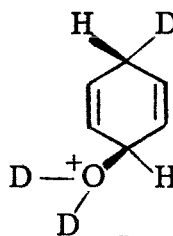

I
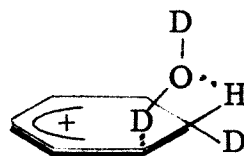
II

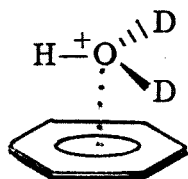intermediates III and IV may be formed (adduct formation) with


III

IV

sufficient internal excitation for a variety of exchange processes to occur before dissociation to regenerate the reactants. Finally a reaction complex V could be formed leaving isotopically exchanged

V

products after dissociation. Similar mechanisms can be suggested for the anion reactions. An intermediate VI analogous to V, for example, would be a possibility.

$$B \cdots {}^-OD$$
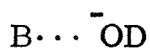
VI

This proposal addresses itself both to gaining further insight into the reaction mechanism and to answering a variety of interesting structural questions.

(1) While qualitative information about the rate of the first exchange was given in the ICR study,[4] it is important that quantitative information be obtained for all of the rates of exchange in order to determine, for example, whether the rate is statistical. Trapped ion data together with computer programs available[12] make this problem tractable.

(2) In order for complex V to be formed, the energy of complexation must be equivalent or greater than the difference between the proton affinities of water and benzene (or in general, the neutral which undergoes exchange) suggesting, for example, that anisole does not exchange (Table I) because its proton affinity is too high.[13] Deuterium exchange reactions with various fluorosubstituted anisoles would be of interest, since fluorine would be expected to lower the basicity of anisole. Similarly, for complex VI to be formed, the energy of complexation must be equivalent or greater than the difference between the proton affinities of ^-OD and the organic anion. This predicts that the lower the proton affinity of the organic anion, the less likely it is for deuterium exchange to occur. This hypothesis could be tested by observing the extent of deuteration of, for example, $C_5H_9^-$ from cis-2-pentene (Table II) and its fluorinated derivatives, the flourines lowering the proton affinity. Coinciding with these experiments, deuterium exchange using the reagents CH_3OD and C_2H_5OD would be instructive. (DCl, DCN, D_2S, CH_3SD, etc., should be tried).

(3) It would be of interest to investigate a range of protonated higher aromatic compounds including protonated naphthalene, anthracene, biphenyl and their derivatives to determine the extent of deuteration. The results from these studies would yield structural information about protonation site, as well as indicate whether carbons without hydrogens hinder reaction.

(4) To test the generality of the reaction, exchange with a wide variety of other unsaturated and saturated carbonium ions would be tested. For example, it would be interesting to study the conjugate acids of species VII-XIII, as well as allyl cations and so forth.


| VII | VIII | IX | X | XI | XII | XIII |
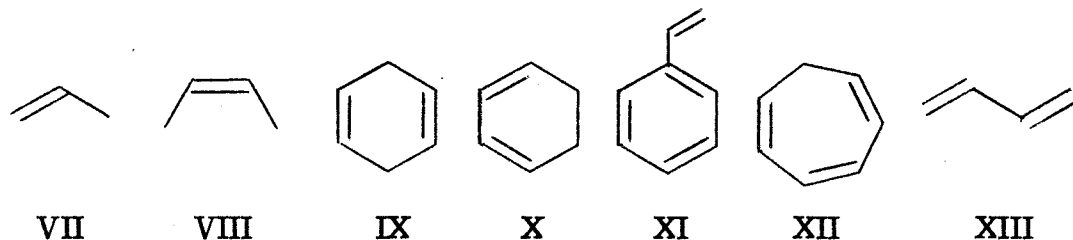
(5) The rate of exchange of C_6D_6 with H_2O should be measured to determine isotope effects if any.

(6) Finally, it is proposed to study $C_7H_7^-$ anions produced from cycloheptatriene and norbornadiene to distinguish isomeric structures (compared to $C_7H_7^-$ from toluene), as well as investigate a variety of other anionic species such as those formed by proton abstraction from species XIV-XIX.

| XIV | XV | XVI | XVII |

CH_3X (X = NO_2, ONO, halogens) $(CH_3)_3B$
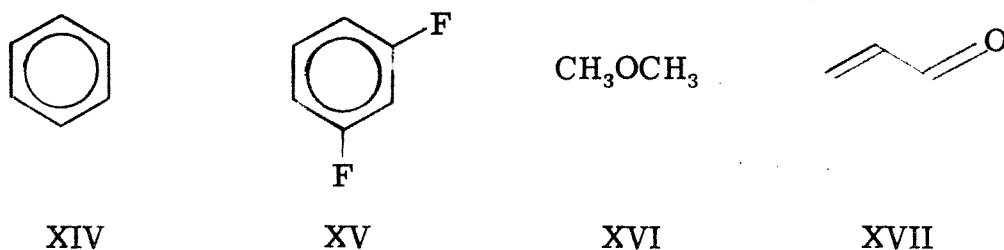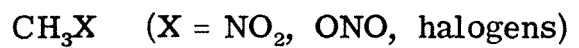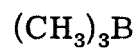
XVIII   XIX

The studies outlined above give some indication of the variety of experiments possible.

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