

INFRARED PHOTOCHEMISTRY

Thesis by
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Dedicated to Professor Josiah Carberry of Brown University

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ABSTRACT

Three types of photochemical processes are observed resulting from relatively low power ($< 100 \text{ W cm}^{-2}$) cw laser irradiation. Multiphoton excitation and dissociation of gas phase polyatomic ions is described in Chapters II, III and V. Ions are produced, stored, trapped for irradiation and analyzed using techniques of ion cyclotron resonance (ICR) spectroscopy. The effect of isotopic substitution on infrared multiphoton excitation of $(\text{CH}_3)_2\text{Cl}^+$, $(\text{CH}_3)\text{Cl}^+(\text{CD}_3)$ and $(\text{CD}_3)_2\text{Cl}^+$ is the topic of Chapter II. Infrared photodissociation spectra are used to probe ion structures. For example, the wavelength dependence of perfluorocyclopropane parent ion is identical to that of perfluoropropylene ion indicating isomerization of the former to the latter. Measurement of dissociation kinetics indicates 100% of the ions isomerize. Thermochemical data on the $\text{C}_3\text{F}_6^+/\text{C}_3\text{F}_6$ system obtained by photoionization mass spectroscopy are discussed.

Low power multiphoton excitation guarantees that target molecules decompose along the lowest energy pathway. This result is used to single out the lowest energy process in a series of reactions for which activation energies are unknown. Infrared photochemistry of alcohol proton bound dimers is used to demonstrate the utility of this technique (Chapter V). Additional thermochemical data on these species are provided in Chapter IV.

Infrared excitation also leads to an increase of more than three orders of magnitude in a bimolecular reaction rate (Chapter VI). Gas phase ions are the reacting species. Excitation is very selective as only one ion in a complex chemical system is perturbed by the infrared

radiation. The bimolecular process is competitive with multiphoton dissociation of the reacting ion.

Single photon infrared photodissociation is explored in a study of van der Waals molecules (Chapters VII and VIII). Clusters containing ethylene are formed in a molecular beam and detected mass spectrometrically. Photodissociation spectra show homogeneous lines dominated by lifetime broadening. Derivation of a lineshape equation is described. For each ethylene-containing cluster a band maximum, predissociative lifetime and transition moment are determined. Vibrational mode selectivity is explored by studying C_2D_4 clusters. Results are compared with theoretical treatment of triatomic van der Waals molecule predissociation.

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CHAPTER I

INTRODUCTION

INTRODUCTION

Chemists have long recognized that light is more than just a spectroscopist's tool.¹ Photons can also be used as reagents. Molecules in excited electronic states often show drastically different reactivity compared to the same species in the ground state.² In some cases excitation leads to unimolecular decomposition.¹ However, the range of both chemical bond energies and electronic energy levels of isolable molecules dictates that visible or ultraviolet radiation is necessary for photochemistry to occur. Single photon infrared excitation does not impart sufficient energy to the target molecule to allow photodissociation. In principle vibrational excitation of one reagent could alter bimolecular reaction rates but few successes have been reported (see below).³⁻⁷

The genesis of infrared photochemistry followed development of high-power ($>1 \text{ MW cm}^{-2}$) CO_2 lasers and the observation that the high-intensity laser radiation can induce multiphoton infrared excitation.⁸ Isolated molecules in the gas phase can absorb sufficient infrared energy to allow bond breaking even when > 20 photons are required.⁹ Although high-power lasers were used to discover infrared multiphoton processes, a key experiment revealed that total energy input, not peak power, is the major factor in determining photodissociation yields.¹⁰ Thus, multiphoton excitation could be achieved using a low-power (several W cm^{-2}) CW source if molecules were irradiated under nearly collision-free conditions for times up to several seconds. This hypothesis was proven correct by experiments performed in our laboratory.¹¹

Low-power infrared multiphoton dissociation experiments use gas phase polyatomic ions as the target molecules.¹¹ These species are formed, stored and detected using the techniques of ion-cyclotron resonance (ICR) spectroscopy.¹² Initial research aimed to understand the slow, multiphoton excitation process. Variation of photo-dissociation rates with laser wavelength, laser power, ion-molecule collision frequency, isotopic substitution (Chapter II) and ion internal energy were all examined in detail. Specific chemical systems were chosen for study such that laser-induced reactions could be compared quantitatively with known thermal reactions. Thus ion-molecule chemistry was used as a probe of multiphoton excitation dynamics.

After a reasonable description of low-power multiphoton dissociation was developed, it became possible to employ infrared photochemistry as a probe of ion-molecule system. Chapter III of this thesis describes using infrared photodissociation spectroscopy to compare structures of $C_3F_6^+$ obtained by electron impact ionization of two isomeric compounds, perfluoropropylene and perfluorocyclopropane. The results demonstrate that infrared laser-driven dissociation can help solve a problem that often plagues mass spectroscopy: how to distinguish among isomeric ions?

Slow multiphoton excitation results in unimolecular decomposition along the lowest energy route.¹¹ Thus in cases where thermochemical information is not complete. Infrared activation can be used to single out the lowest energy pathway from several plausible reaction schemes. This technique has been applied to a study of potential energy surfaces for reactions between protonated alcohols and neutral alcohols.

The results are described in Chapter V. Additional thermochemistry of protonated alcohols is given in Chapter IV.

As mentioned in the first paragraph, use of vibrational excitation to change bimolecular reaction rates has met with limited success.³⁻⁷ Most of the positive results come from studies of atom-diatom systems such as $K + HCl$ ($\nu = 1$)³ or $Ba + HF$ ($\nu = 1$).⁴ Extensive work has been devoted to understanding the dynamics of the $NO + O_3$ (001) reaction.⁵ Bimolecular decomposition of vibrationally excited $H_3B \cdot PF_3$ has been reported also.⁶ We observe that relatively low-power (34 W cm^{-2}) CW infrared laser radiation increases selectively the rate constant of a single bimolecular reaction by three orders of magnitude in a complex system (Chapter V).⁷ Although the reacting ions absorb less energy than is needed for unimolecular decomposition, the average ion absorbs ~ 4 infrared photons prior to bimolecular reaction.

Finally, the realm of single-photon infrared photochemistry is reached in the study of van der Waals molecules.¹³ These species are formed in a supersonic molecular beam. Irradiation by a cw CO_2 laser effects fission of the van der Waals bond. Chapters VII and VIII describe infrared photochemistry of van der Waals molecules containing ethylene. Dissociation spectra are dominated by lifetime broadening characteristics of lifetimes 10^{-13} - 10^{-12} s. Variations of spectral linewidths and cross sections with cluster composition are presented along with a detailed analysis of the photodissociation lineshape.

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CHAPTER II

ISOTOPIC SELECTIVITY IN INFRARED MULTIPHOTON
DISSOCIATION USING LOW-INTENSITY CW LASER
RADIATION. INFRARED PHOTOCHEMISTRY OF GAS
PHASE $(\text{CH}_3)_2\text{Cl}^+$, $(\text{CH}_3)\text{Cl}^+(\text{CD}_3)$, and $(\text{CD}_3)_2\text{Cl}^+$.

ISOTOPIC SELECTIVITY IN INFRARED MULTIPHOTON DISSOCIATION
USING LOW-INTENSITY CW LASER RADIATION. INFRARED PHOTO-
CHEMISTRY OF GAS PHASE $(\text{CH}_3)_2\text{Cl}^+$, $(\text{CH}_3)\text{Cl}^+(\text{CD})_3$ and $(\text{CD}_3)_2\text{Cl}^+$.

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Abstract

Isotope effects on slow infrared multiphoton dissociation of gas phase ions are described. Of the three species $(\text{CH}_3)_2\text{Cl}^+$, $(\text{CH}_3)\text{Cl}^+(\text{CD}_3)$ and $(\text{CD}_3)_2\text{Cl}^+$ only $(\text{CD}_3)_2\text{Cl}^+$ dissociates following irradiation by a relatively low power ($< 100 \text{ W cm}^{-2}$) cw CO_2 laser. No chlorine isotope shift is detected. Wavelength dependence of $(\text{CD}_3)_2\text{Cl}^+$ multiphoton dissociation over the $925\text{-}1080 \text{ cm}^{-1}$ tuning range of the laser is reported. Observed isotopic selectivity is discussed by comparison with infrared absorption spectra of an isoelectronic molecule, dimethyl sulfide, and its deuterium substituted variants. Also detailed are possible isotope effects on the mechanism of multiphoton excitation as well as the evidence for mode selective chemistry in dimethylchloronium. Infrared photodissociation of $\text{C}_2\text{H}_5\text{ClH}^+$ is mentioned briefly. Techniques of cyclotron resonance (ICR) spectroscopy are used to generate, store and detect the gas phase ions.

I. Introduction

Recently we demonstrated infrared multiphoton dissociation of gas phase ions using low intensity ($< 100 \text{ W cm}^{-2}$) cw laser radiation (1-5). One key result obtained is that photodissociation spectra show linewidths comparable to those observed in infrared absorption spectra of corresponding neutrals (4, 5). In contrast, it is known that high power ($> 1 \text{ MW cm}^{-2}$) pulsed laser radiation yields photodissociation spectra which are broadened and shifted to longer wavelengths relative to infrared absorption spectra of the target molecules (6). Thus, it was inferred that the wavelength dependence of low intensity multiphoton dissociation is selective with respect to both isotopic substitution and variations in molecular structure (4, 5).

We wish to report observation of a large isotope shift in the gas phase infrared photochemistry of $(\text{CD}_3)_2\text{Cl}^+$, $(\text{CH}_3)\text{Cl}^+(\text{CD}_3)$ and $(\text{CH}_3)_2\text{Cl}^+$. Comparisons with infrared absorption spectra of the isoelectronic dimethyl sulfide analogues are made in an attempt to distinguish between isotope effects manifest as changes in ion absorption spectra and those which alter the rate of intramolecular energy transfer.

In addition, use of infrared multiphoton dissociation to distinguish between isomeric ions $(\text{CH}_3)_2\text{Cl}^+$ and $\text{CH}_3\text{CH}_2\text{ClH}^+$ is described.

II. Experimental

Ion cyclotron resonance (ICR) techniques have been described in detail in the literature (7, 8). Ions formed by electron impact ionization are stored in crossed electric and magnetic fields for times up to 2s and then mass analyzed. Neutral pressures are varied from 1×10^{-7} to 5×10^{-6} Torr. The instrument used in this study was built in the Caltech shops and is of standard design utilizing a 23.4 kG electromagnet and

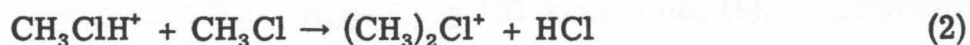
a marginal oscillator detector. Pressures are measured using a Schulz-Phelps type ionization gauge calibrated against an MKS Baratron Model 90H1-E capacitance manometer. It is estimated that absolute pressure determinations are within $\pm 20\%$.

ICR modifications for infrared photochemistry are described elsewhere (2). Briefly, unfocused output from a grating tuned Apollo 550A cw CO₂ laser is directed into the ICR cell through a 92% transmittance mesh (in place of the front source drift plate). The beam reflects off the mirror finish on the back source plate and exits the ICR cell after a second pass through the ion storage region. Ions can be irradiated during any portion of the ion storage period and irradiation is controlled by an electronically gated mechanical shutter.

All reagents were obtained from commercial sources and were used without further purification except for freeze-pump-thaw cycles to remove of non-condensable gases. No impurities were detected by mass spectrometry. CD₃Cl (Mallinckrodt Nuclear) was measured to be > 99 atom percent pure.

III. Results

Ion-molecule chemistry of CH₃Cl is described in detail elsewhere (9). Briefly, dimethylchloronium ion, (CH₃)₂Cl⁺, is formed in a two-step sequence, reactions 1 and 2. (CH₃)₂Cl⁺ is unreactive



towards methyl chloride at the pressures and trapping times used in these experiments. Ionization of a 1:1 mixture of CH₃Cl and CD₃Cl yields statistical amounts of (CH₃)₂³⁵Cl⁺, (CH₃)₂³⁷Cl⁺

$(\text{CH}_3)^{35}\text{Cl}^+(\text{CD}_3)$, $(\text{CH}_3)^{37}\text{Cl}^+(\text{CD}_3)$, $(\text{CD}_3)_2^{35}\text{Cl}^+$ and $(\text{CD}_3)_2^{37}\text{Cl}^+$. No deuterium scrambling among methyl groups is observed. The upper trace of Figure 1 shows a partial mass spectrum of a 1:1 $\text{CH}_3\text{Cl}:\text{CD}_3\text{Cl}$ mixture (total pressure = 1.9×10^{-7} Torr) at 2s of ICR trapping time. All six isotopic variants of dimethylchloronium are clearly visible. Results of an experiment in which the ions were continuously irradiated by the infrared laser during the ion trapping period are shown in the lower mass spectrum in Figure 1. Intensities of $(\text{CD}_3)_2^{35}\text{Cl}^+$ and $(\text{CD}_3)_2^{37}\text{Cl}^+$ are reduced by $\sim 75\%$ while the other four ions are unperturbed. Repeating this experiment at different laser wavelengths and with added N_2 buffer pressures up to 5×10^{-6} Torr indicates only $(\text{CD}_3)_2^{35}\text{Cl}^+$ and $(\text{CD}_3)_2^{37}\text{Cl}^+$ undergo multiphoton dissociation in the $925\text{--}1080\text{ cm}^{-1}$ region covered by the CO_2 laser.

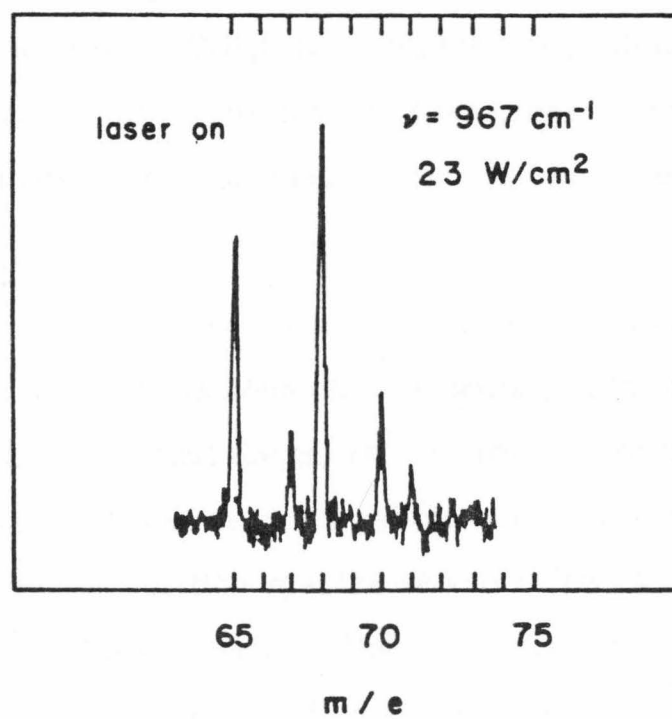
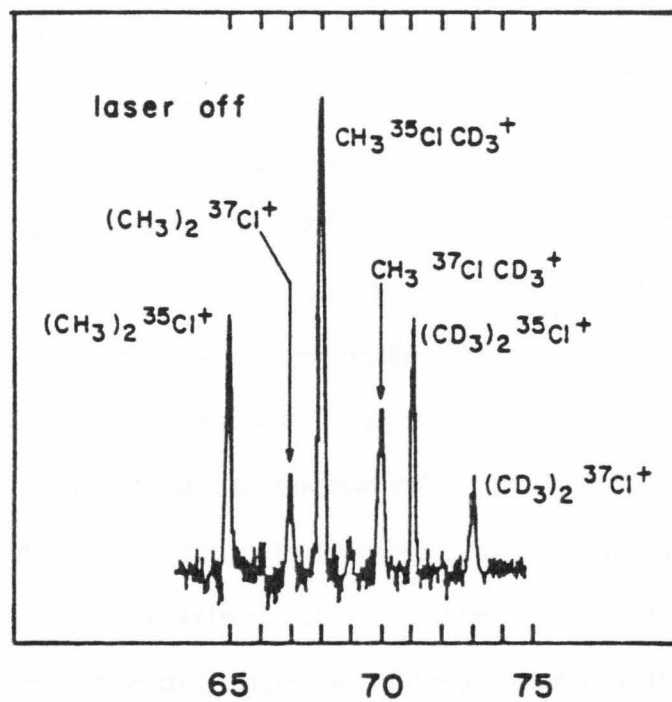
Laser induced decomposition of $(\text{CD}_3)_2\text{Cl}^+$ yields $\text{CD}_2\text{Cl}^+ + \text{CD}_4$, reaction 3. Process 3 is confirmed both by



direct observation of the ionic product and by ICR double resonance; no further reaction of CD_2Cl^+ is detected. Insufficient data are available to determine the energetics of reaction 3. Estimates of ΔH_f (CH_2Cl^+) based on comparisons with known thermochemistry of related ions vary over a 50 kcal/mole range depending on choice of model system. Similarly, only an upper bound to the heat of formation of $(\text{CH}_3)_2\text{Cl}^+$ is reported; $\Delta H_f[(\text{CH}_3)_2\text{Cl}^+] \leq 191\text{ kcal/mole}$ (9). However all estimates agree that the multiphoton dissociation reaction, equation 3, is at least 50 kcal/mole endothermic, corresponding to absorption of a minimum of 18 infrared photons.

FIGURE 1. Upper trace is 2s time delay mass spectrum of 1:1 $\text{CH}_3\text{Cl}:\text{CD}_3\text{Cl}$. Ionization is by 50 ms pulse of 14 eV electrons. Total pressure is 1.9×10^{-7} Torr. Lower trace shows same mass region for experiment on which ions undergo 2 s continuous infrared laser irradiation (23 W cm^{-2} at 967 cm^{-1}).

Signal Intensity



All other ions in this system including the reactants in processes 1 and 2 (as well as their deuterated analogues) are unaffected by laser irradiation. A check of the temporal variation of $(\text{CD}_3)_2^{35}\text{Cl}^+$ decomposition indicates the multiphoton dissociation reaction is first order in $(\text{CD}_3)_2^{35}\text{Cl}^+$ and the ion population is characterized by one dissociation rate constant (for fixed laser power and wavelength).

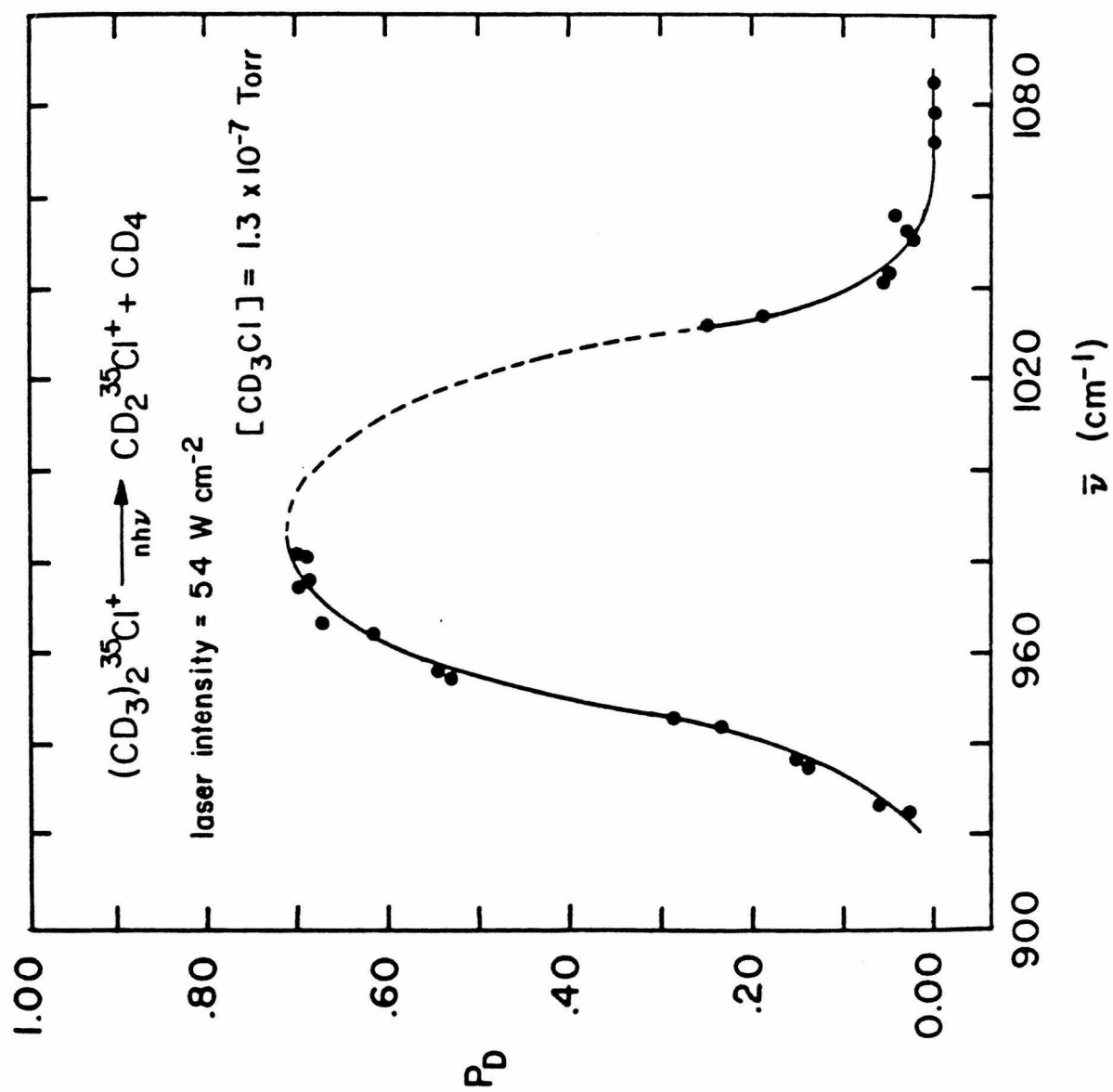
Figure 2 shows the variation with laser wavelength of $(\text{CD}_3)_2^{35}\text{Cl}^+$ photodissociation yield, P_D . In this case, P_D is defined as the fractional change in ion intensity resulting from 2s continuous laser irradiation at 51 W cm^{-2} . The band maximum is at $\sim 980 \text{ cm}^{-1}$ and its width is $\sim 70 \text{ cm}^{-1}$. No chlorine isotope effect is observed; the $(\text{CD}_3)_2^{37}\text{Cl}^+$ photodissociation spectrum is identical to that shown in Figure 2.

To examine the effects of structural variation in addition to the effects of isotopic substitution an attempt was made to study infrared photochemistry of $\text{C}_2\text{H}_5\text{ClH}^+$, an isomer of dimethylchloronium. Multiphoton dissociation of $\text{C}_2\text{H}_5\text{ClH}^+$ (prepared by protonation of ethyl chloride) was observed but details of the laser induced chemistry could not be elucidated due to several competing ion-molecule reactions (9).

IV. Discussion

Slow, infrared multiphoton dissociation of dimethylchloronium ion shows a dramatic isotope effect resulting from deuterium substitution. It is assumed that the initial vibrational excitation of a ground state ion is by a resonant single photon absorption (4, 5, 10). Thus infrared photodissociation spectra should reflect a shift in frequencies of the fundamental vibrations. Unfortunately, there are no reported infrared absorption spectra of gas phase $(\text{CH}_3)_2\text{Cl}^+$ to allow comparison with results shown in Figure 2. Olah (11) prepared $(\text{CH}_3)_2\text{Cl}^+$ in super

FIGURE 2. Infrared photodissociation spectrum of $(\text{CD}_3)_2^{35}\text{Cl}^+$.
 CD_3Cl pressure is 1.3×10^{-7} Torr. Ionization as in Figure 1.
Laser power is 54 W cm^{-2} . P_D denotes fraction of ions dissociated
during 2s continuous laser irradiation.



acid solution and lists Raman band positions for C-Cl-C deformation (392 cm^{-1}), C-Cl stretch (610 cm^{-1}) and C-H stretch (2865 , 2950 , 2980 and 3080 cm^{-1}). The full Raman spectrum, including the 900 - 1100 cm^{-1} region, is not reported, nor were deuterated demethyl-chloronium ions studied.

Assuming deuterium substitution alters photodissociation band positions but not lineshapes, a shift of $\geq 160\text{ cm}^{-1}$ to higher energy is necessary to move the peak shown in Figure 2 out of the CO_2 laser wavelength region. Dimethyl sulfide is isoelectronic with dimethyl-chloronium ion. Table 1 lists the fundamental vibrations of $(\text{CH}_3)_2\text{S}$, $(\text{CH}_3)\text{S}(\text{CD}_3)$ and $(\text{CD}_3)_2\text{S}$ observed by Ypenburg (12, 13). Five of the vibrational frequencies (ν_3 , ν_4 , ν_{10} , ν_{11} and ν_{15}) show isotope shifts well in excess of 160 cm^{-1} . However, none of the molecules listed in Table 1 is completely transparent between 900 and 1100 cm^{-1} . Although the identity of the infrared active modes in dimethyl sulfide- d_0 , $-\text{d}_3$ and $-\text{d}_6$ may differ, each species has at least three vibrations resonant with CO_2 laser radiation.

Comparison of $(\text{CH}_3)_2\text{S}$ vibrations (Table 1) with reported Raman bands of solution phase $(\text{CH}_3)_2\text{Cl}^+$ shows only fair agreement as mentioned by Olah (11). In particular the C-Cl-C deformation in dimethyl-chloronium (392 cm^{-1}) corresponds to $\nu_7 = 281\text{ cm}^{-1}$ in $(\text{CH}_3)_2\text{S}$ and the C-Cl stretch in the ion (610 cm^{-1}) correlates with $\nu_8 = 692\text{ cm}^{-1}$ in the isoelectronic neutral. One does not expect exact agreement among other fundamentals in $(\text{CH}_3)_2\text{S}$ and $(\text{CH}_3)_2\text{Cl}^+$, yet even variations of $\sim 100\text{ cm}^{-1}$ are not sufficient to predict both $(\text{CH}_3)_2\text{Cl}^+$ and $(\text{CH}_3)\text{Cl}^+(\text{CD}_3)$ to be inactive to infrared laser radiation. Furthermore, the laser power used is sufficient to saturate even weak transitions.

Table 1: VIBRATIONAL FREQUENCIES OF DIMETHYL SULFIDE AND ITS DEUTERIUM SUBSTITUTED ANALOGUES.^a

	(CH ₃) ₂ S		(CH ₃)S(CD ₃)		(CD ₃) ₂ S	
	symmetry	frequency (cm ⁻¹)	symmetry	frequency (cm ⁻¹)	symmetry	frequency (cm ⁻¹)
ν_1	A ₁	3000	A'	3002	A ₁	2248
ν_2		2932		2934		2138
ν_3		~1445		2254		1057
ν_4		1333		2137		1023
ν_5		1029		1447		828
ν_6		692		1328		643
ν_7		281		1058		241
ν_8	B ₁	3000		1021	B ₁	2248
ν_9		2932		985		2138
ν_{10}		~1445		880		1057
ν_{11}		1316		743		1013
ν_{12}		1029		659		828
ν_{13}		743		263		705
ν_{14}	B ₂	2974	A''	2977	B ₂	2233
ν_{15}		1429		2237		1051
ν_{16}		973		1433		745
ν_{17}		182		1047		135
ν_{18}	A ₂	3000 ^b		960	A ₂	2237 ^b
ν_{19}		1449 ^b		728		1051 ^b
ν_{20}		969 ^b		180		720 ^b
ν_{21}		176 ^b		134		126 ^b

^aReferences 12 and 13.

^bCalculated from force constants (13).

Thus, it is interesting to note that for dimethylchloronium ion, slow multiphoton dissociation may be mode selective. This result is consistent with the proposed mechanism for the multiphoton excitation process (10). A vibrational mode in resonance with the laser field is pumped and then depopulated by intramolecular energy transfer. When the resonant mode returns to the ground state it is free to absorb another photon. This process is repeated until the quasi-continuum of vibrational states is reached, then absorption occurs within the quasi-continuum. Observed selectivity results from a high probability of intramolecular energy transfer out of the pumped mode in $(\text{CD}_3)_2\text{Cl}^+$ in contrast to inefficient energy transfer from modes excited in $(\text{CH}_3)\text{Cl}^+(\text{CD}_3)$ and $(\text{CH}_3)_2\text{Cl}^+$. However, variations in intramolecular energy transfer rates among the three dimethylchloronium ions may be due to differences in densities of vibrational states (14) instead of resulting from the properties of selected vibrational modes. The perdeuterated ion possesses lower frequency vibrations, so its density of vibrational states increases most rapidly with increasing energy. The two possibilities could be distinguished if it were possible to extend the wavelength range of the experiment to higher photon energies. Observation of multiphoton dissociation of $(\text{CH}_3)\text{Cl}^+(\text{CD}_3)$ and $(\text{CH}_3)_2\text{Cl}^+$ occurring at shorter wavelength would support the inference of mode-selective excitation.

V. Conclusions

Deuterium substitution leads to a dramatic change in infrared multiphoton dissociation probabilities of gas phase dimethylchloronium ion. $(\text{CD}_3)_2\text{Cl}^+$ undergoes dissociation when irradiated by a low power cw CO_2 laser while $(\text{CH}_3)_2\text{Cl}^+$ and $(\text{CH}_3)\text{Cl}^+(\text{CD}_3)$ are unaffected. Com-

parison with reported vibrational spectra of the isoelectronic species, dimethylsulfide and its deuterated analogs, indicates shifts in fundamental vibration frequencies in excess of 160 cm^{-1} are plausible (12, 13). However, it appears likely that all three ions have at least one infrared active vibrational mode within the tuning range of the laser. Thus the isotope effect results, in part, from shifts in intramolecular energy transfer rates. The uniqueness of $(\text{CD}_3)_2\text{Cl}^+$ reflects either properties of a specific vibrational mode in $(\text{CD}_3)_2\text{Cl}^+$ or its relatively large density of states. The latter property leads to large statistical factors favoring facile energy transfer.

Additional spectroscopic data on super acid solutions of $(\text{CH}_3)_2\text{Cl}^+$, $(\text{CH}_3)\text{Cl}^+(\text{CD}_3)$ and $(\text{CD}_3)_2\text{Cl}^+$ would aid interpretation of results obtained in this study.

Although it is not possible to examine in detail infrared photochemistry of $\text{CH}_3\text{CH}_2\text{ClH}^+$, the observation of multiphoton dissociation of this species indicates isomeric ions can be distinguished using infrared laser excitation. Inability to identify ion structures is a problem which frequently plagues mass spectrometric studies (15-17). Infrared photodissociation spectroscopy represents a powerful technique for ion structure analysis.

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CHAPTER III

ENERGETICS OF THE REARRANGEMENT OF NEUTRAL
AND IONIZED PERFLUOROCYCLOPROPANE TO PER-
FLUOROPROPYLENE. USE OF INFRARED MULTIPHOTON
DISSOCIATION SPECTRA TO IDENTIFY STRUCTURAL
ISOMERS OF MOLECULAR IONS.

Energetics of the Rearrangement of Neutral and Ionized
Perfluorocyclopropane to Perfluoropropylene. Use of
Infrared Multiphoton Dissociation Spectra to Identify
Structural Isomers of Molecular Ions.

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Infrared photodissociation spectroscopy is used to compare the structure of gas phase $C_3F_6^+$ ions obtained by electron impact ionization of two isomeric precursors: perfluoropropylene and perfluorocyclopropane. Photodissociation spectra are obtained by observing the extent of multiphoton dissociation as the CO_2 laser is tuned across the $925\text{--}1080\text{ cm}^{-1}$ wavelength range. Ions are formed, stored and detected using techniques of ion cyclotron resonance (ICR) spectroscopy. Infrared multiphoton excitation is effected using low power, cw laser radiation. The "fingerprint" spectrum of the molecular ion of perfluorocyclopropane is identical to that obtained from perfluoropropylene, indicating rearrangement of the former to the latter. Photodissociation kinetics indicate that the entire perfluorocyclopropane molecular ion population isomerizes to the more stable perfluoropropylene structure. Thermochemistry of C_3F_6 and $C_3F_6^+$ isomers is discussed. Comparisons are made with the analogous $C_3H_6/C_3H_6^+$ system. Photo-ionization mass spectroscopy (PIMS) results yield $\Delta H_f(\text{cyclo-}C_3F_6) = -224\text{ kcal/mole}$.

Introduction

Mass spec-mass spec techniques have been developed recently to analyze minute quantities of complex chemical mixtures.²⁻⁸ Typically, electron impact ionization or chemical ionization of the mixture is followed by collision induced dissociation of a mass selected ion. These ions are characterized using the fragmentation pattern generated by the collision. Two mass spectrometers in sequence obviate the need for separation of the mixture by gas chromatography or similar technique and reduces the minimum sample size required. The scope of this method could be greatly increased if it were also possible to obtain infrared spectra of ions. This would facilitate ion structure determination hence amplify the usefulness of mass spectroscopy as an analytic tool.

Unfortunately, it is nearly impossible to achieve sufficient ion number density to permit conventional light absorption measurements. Most knowledge of ion spectroscopic states has been obtained using photodissociation.⁹⁻¹³ Energies required for typical bond cleavage processes necessitate visible or uv radiation for single photon events. We have observed that relatively low power ($< 100 \text{ W cm}^{-1}$) cw CO_2 laser irradiation induces multiphoton infrared excitation and dissociation of gas phase ions.¹⁴⁻¹⁷ Low laser power avoids power broadening and sharply peaked infrared photodissociation spectra can be obtained.¹⁶ Furthermore, it is inferred that infrared photodissociation spectra mimic absorption spectra over the same wavelength region. In the present study slow multiphoton dissociation is used to compare parent ions of two isomers of C_3F_6 .

Gas phase ions are formed, stored and mass analyzed using the

techniques of ion cyclotron resonance (ICR) spectroscopy.

Experimental

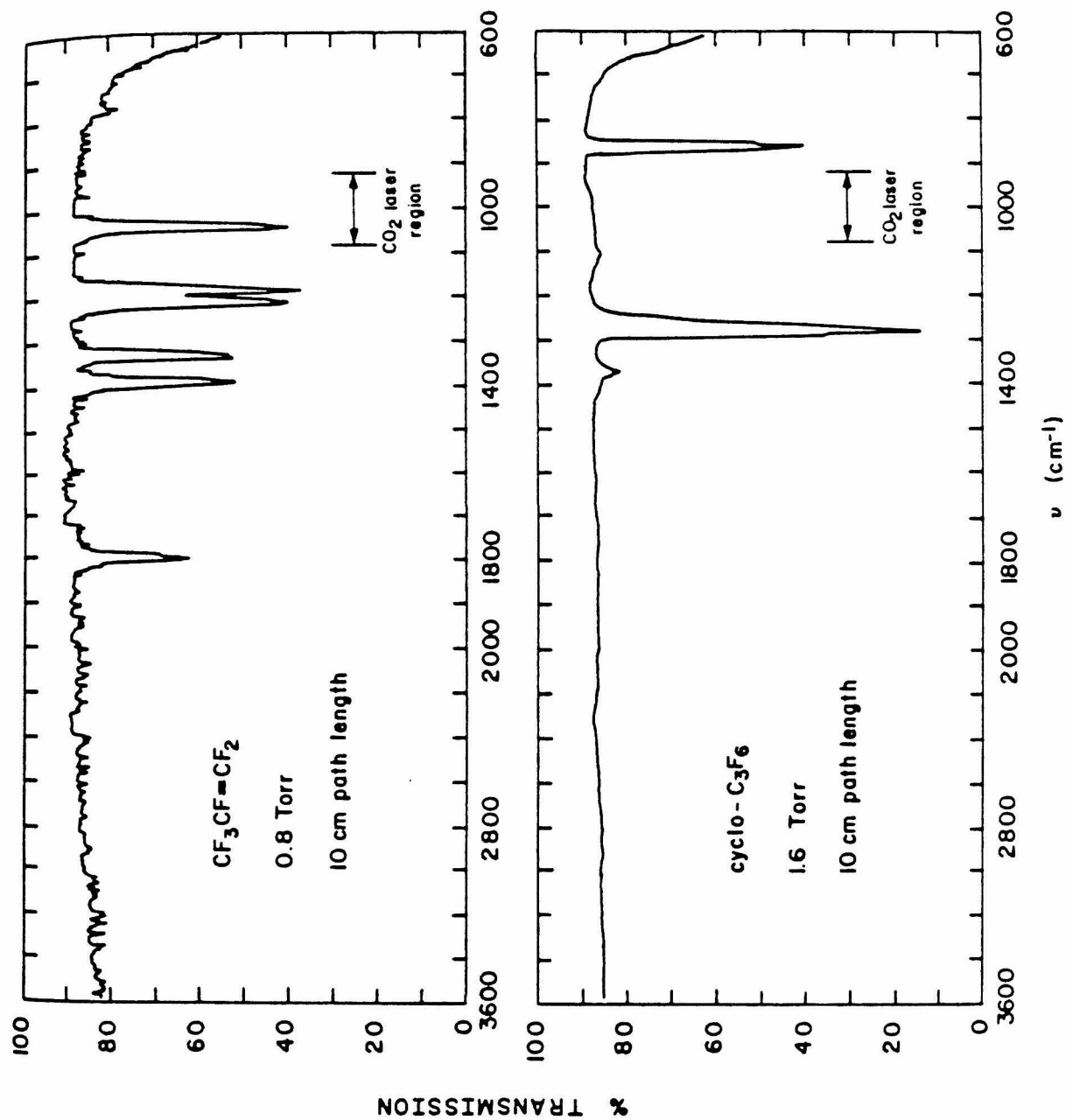
Ion cyclotron resonance (ICR) techniques have been described in detail in the literature.¹⁸⁻¹⁹ Ions formed by electron impact ionization are stored in crossed electric and magnetic fields for times up to 2s and then mass analyzed. Neutral pressures are varied from 10^{-8} to 10^{-6} Torr. The instrument used in this study was built in the Caltech shops and is of standard design utilizing a 23.4 kG electromagnet and a marginal oscillator detector. Pressures are measured using a Schulz-Phelps type ionization gauge calibrated against an MKS Baratron Model 90H1-E capacitance manometer. It is estimated that absolute pressure determinations are within $\pm 20\%$.

ICR modifications for infrared photochemistry are described elsewhere.¹⁵ Briefly, unfocused output from a grating tuned Apollo 550A cw CO₂ laser is directed into the ICR cell through a 92% transmittance mesh (in place of the front source drift plate). The beam reflects off the mirror finish on the back source plate and exits the ICR cell after a second pass through the ion storage region. Ions can be irradiated during any portion of the ion storage period and irradiation is controlled by an electronically gated mechanical shutter.

Infrared absorption spectra of neutrals were recorded with a Beckman IR-12 spectrometer. Samples were held in a 10 cm path length cell equipped with NaCl windows.

The photoionization mass spectrometer (PIMS) used in this study has also been described in detail.²⁰ The hydrogen many-line spectrum and the Hopfield continuum in helium were employed as light sources. Monochromator resolution was set for 1.5 Å resolution and data obtained

FIGURE 1. Gas phase infrared absorption spectra of perfluoropropylene (top) and perfluorocyclopropane (bottom). See experimental section for details.



at 0.4 Å intervals. Sample pressures were 5×10^{-4} Torr for perfluoropropylene and 8×10^{-4} Torr for perfluorocyclopropane. The repeller voltage was maintained at +0.2 V with respect to the ionization chamber yielding ion residence times $\sim 10 \mu\text{s}$.

Perfluoropropylene was purchased from PCR, Inc. Perfluorocyclopropane was a gift from Professor J. D. Roberts. Chemicals were used without further purification except for freeze-pump-thaw cycles to remove non-condensable gases. No impurities were detected by mass spectrometry.

Results and Discussion

Infrared Spectra of C_3F_6 Isomers. Figure 1 shows gas phase infrared absorption spectra of two isomers of C_3F_6 , perfluoropropylene (top) and perfluorocyclopropane (bottom). Spectrometer resolution is $\sim 2 \text{ cm}^{-1}$. The same samples are also used for the ion multiphoton dissociation experiments discussed in a later section.

Infrared absorption bands of perfluoropropylene (Figure 1, top) have been assigned and are reported in the literature.²¹ The peak at 1037 cm^{-1} is the only feature which lies in the CO_2 laser wavelength region. It has been identified as a C-F stretch of A' symmetry. Comparison with other fluorinated species suggest that this vibrational mode involves only the CF_3 group. Since the lowest energy ionization process in perfluoropropylene entails removing an electron from the C-C double bond, this particular vibrational frequency is unperturbed in going from the neutral to the cation. We have observed the multiphoton dissociation spectrum of perfluoropropylene parent cation exhibits a single maximum at 1047 cm^{-1} .¹⁶

There are only three absorption bands in the infrared spectrum of

perfluorocyclopropane shown in Figure 1. The small peak at 1369 cm^{-1} is assigned as a C-F stretch of A_2'' symmetry.²² Strong absorptions at 1278 cm^{-1} and 865 cm^{-1} are a C-F stretch and C-C ring stretch respectively, both of E' symmetry.²² No vibrational bands including infrared inactive modes of perfluorocyclopropane fall within the CO_2 laser wavelength range. In fact, only four perfluorocyclopropane fundamental vibrations have energies exceeding 1100 cm^{-1} .²² In addition to the pair of degenerate modes already mentioned there is a C-C stretch (A_1' symmetry; Raman active) at 1557 cm^{-1} and another degenerate C-F stretch (E'' symmetry, Raman active) at 1280 cm^{-1} .

Thermochemistry and Mass Spectrometry of Cyclo- C_3F_6 . Table 1

lists thermochemical data obtained by photoionization mass spectrometry (PIMS) of perfluorocyclopropane. Also included is the cyclo- C_3F_6 adiabatic ionization potential measured by photoelectron spectroscopy. By analogy to the Walsh molecular orbital analysis of cyclopropane²³ the highest occupied molecular orbital (HOMO) in cyclo- C_3F_6 is an in-plane, ring bonding orbital of e' symmetry. Energies of fluorine non-bonding orbitals²⁴⁻²⁵ (typically $< -15\text{ eV}$) are considerably below the HOMO energy (-11.17 eV). Thus, there should be little contribution of the fluorine lone pairs to the perfluorocyclopropane HOMO. This bonding analysis predicts ionization should weaken C-C bonds and only perturb slightly C-F bond strengths.

Data from Table 1 are used to construct reaction coordinate diagrams for isomers of C_3F_6 and C_3F_6^+ .²⁶⁻²⁷ These are shown in Figure 2 along with corresponding diagrams depicting reaction energetics in the $\text{C}_3\text{H}_6/\text{C}_3\text{H}_6^+$ system.²⁶ Note that for neutral cyclo- C_3F_6 thermolysis does not result in isomerization to perfluoropropylene.²⁸ Instead the

TABLE 1. Heats of Formation of Neutral Molecules and Ions
Pertinent to this Study

M	$\Delta H_f(M)$ (kcal/mole)	IP(M) (eV)	$\Delta H_f(M^+)$ (kcal/mole)
$CF_3-CF=CF_2$	-268.9 ^a	10.595 ^b (10.62 ^c)	-14.6
cyclo- C_3F_6	-224 ^b	11.17 ^b (11.20 ^c)	39
C_2F_4	-157.4 ^d	10.12 ^e	85.2
CF_2	-43.5 ^b	--	--

a) W. M. D. Bryant, J. Polym. Sci., 56, 277 (1962).

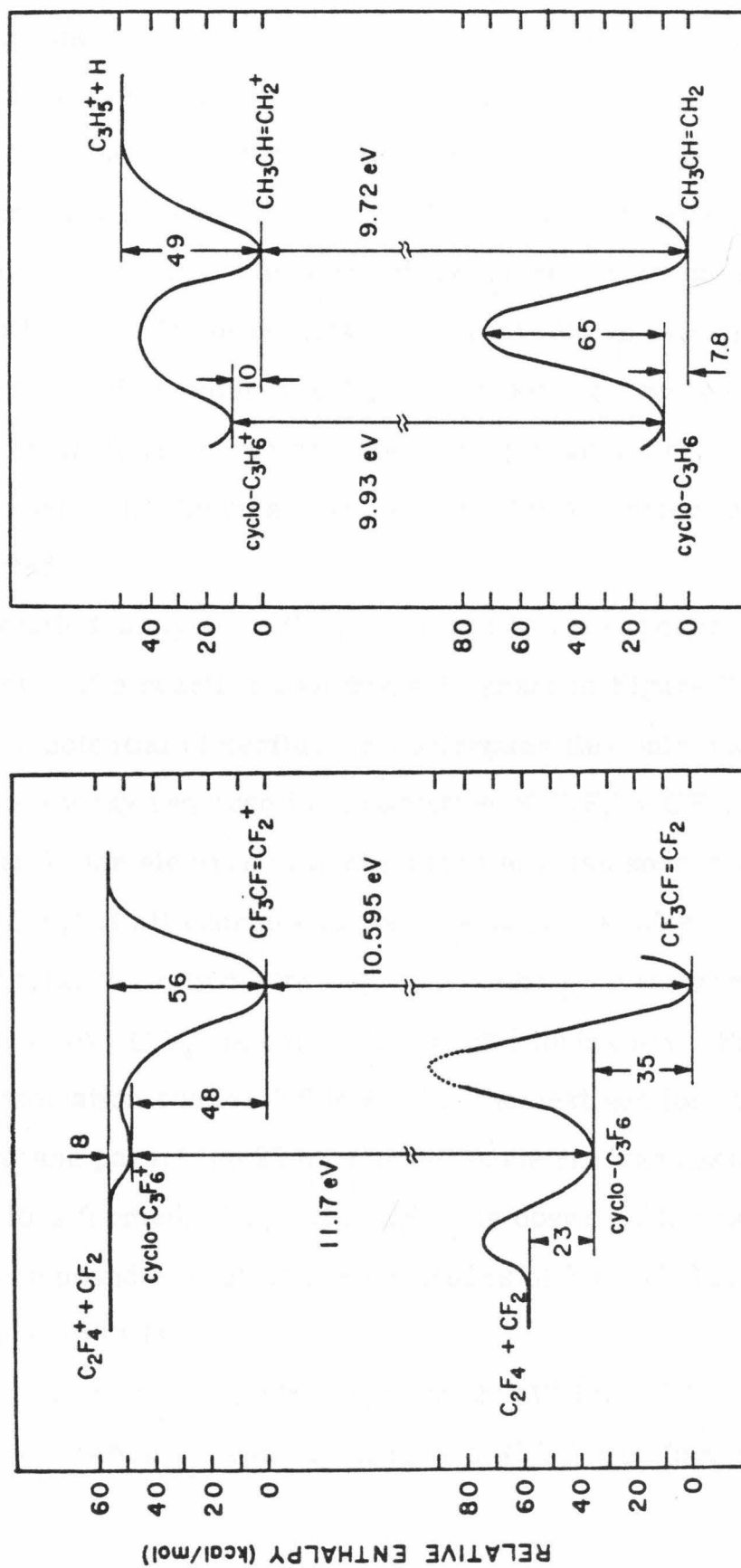
b) Result of photo-ionization mass spec (PIMS) study.

c) Adiabatic IP from photoelectron spectrum.

d) J. R. Locker and H. A. Skinner, J. Chem. Soc. A, 1034 (1968).

e) Ref. 26.

FIGURE 2. Reaction coordinate diagram for C_3F_6 and C_3F_6^+ (at left) and for C_3H_6 and C_3H_6^+ (at right). Data compiled from Table 1 and reference 26.



observed pyrolysis reaction is CF_2 elimination. The barrier to unimolecular isomerization must exceed the measured 38 kcal/mole activation energy for the observed decomposition reaction.²⁸

Magnitudes of barriers to ion (both C_3F_6^+ and C_3H_6^+) isomerization have not been measured. Ausloos reports²⁹ photoionization of cyclopropane yields two forms of C_3H_6^+ and the relative fractions vary with ionization energy. Ions are distinguished by their different reactivity with NH_3 . These results are interpreted as evidence for existence of a stable cyclic isomer of C_3H_6^+ but do not rigorously exclude the possibility of high-energy and low-energy reaction regimes of a single ring-opened C_3H_6^+ species. No estimate for a barrier to isomerization is reported.

Detailed analysis of C_3F_6^+ isomers has not appeared previous to this study. The reaction coordinate diagram in Figure 2 indicates the ionization potential of perfluorocyclopropane lies only 8 kcal/mole below the energy required for production of $\text{C}_2\text{F}_4^+ + \text{CF}_2$. Thus the base peak in the electron impact ionization mass spectrum of cyclo- C_3F_6 is C_2F_4^+ at all energies above threshold. At 20 eV, the parent ion is 4% of total ionization with C_2F_4^+ accounting for the remaining 96%. At 70 eV, C_3F_6^+ is only 0.8% of total ionization. For infrared photodissociation studies (discussed in the next section) of perfluorocyclopropane parent ion 20 eV ionization energy was used. Neither of the two ions formed, C_3F_6^+ and C_2F_4^+ , is observed to react with the parent compound at neutral gas pressures of 5×10^{-6} Torr and ion trapping times up to 1s.

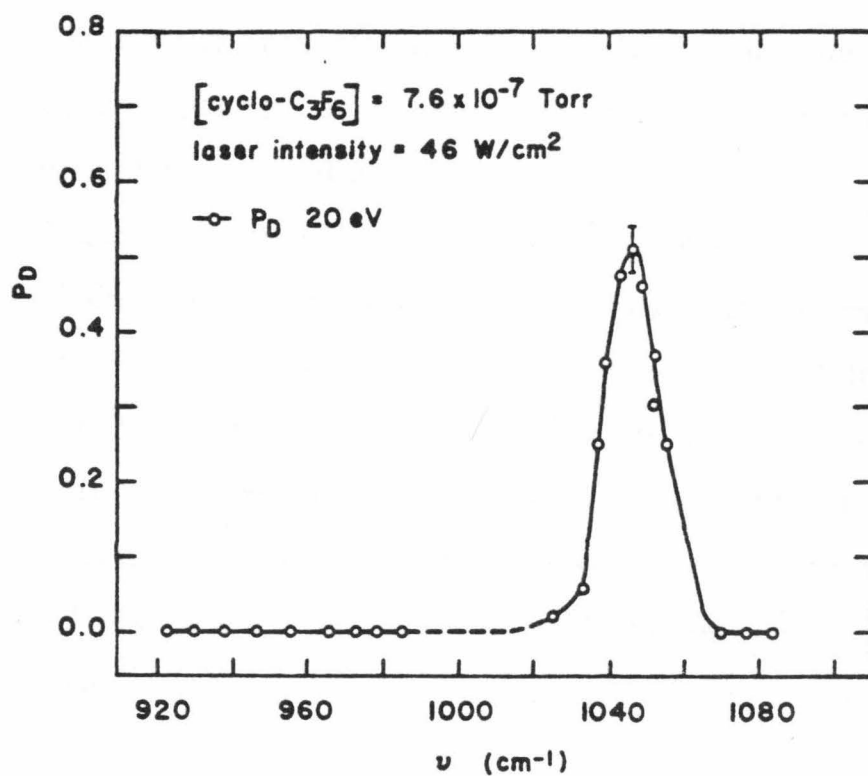
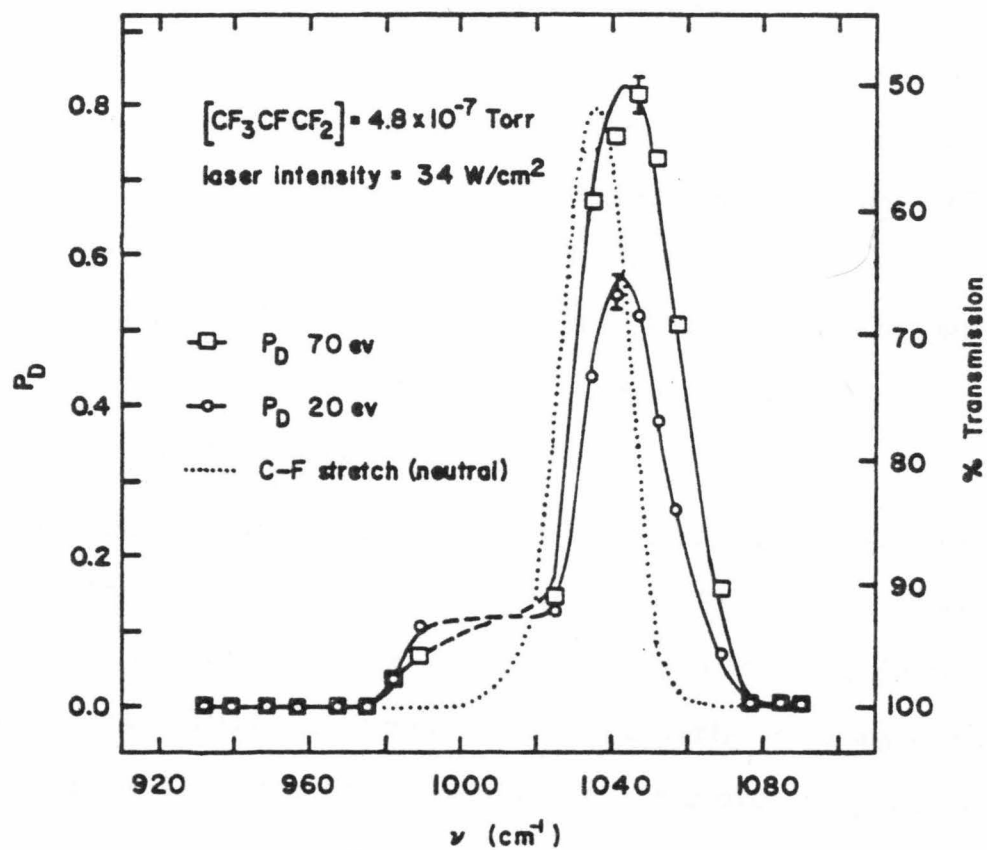
At the optimum electron energy (20 eV) for production of cyclo- C_3F_6 parent cation the number density of C_2F_4^+ also formed by electron

impact ionization of perfluorocyclopropane results in significant ion-ion repulsion and concomitant loss of ICR trapping efficiency. To offset this problem during trapped ion studies of $C_3F_6^+$, ICR double resonance³⁰ is used to eject selectively $C_2F_4^+$.

Infrared Photochemistry. Figure 3 shows the infrared photodissociation spectra of $C_3F_6^+$ derived from perfluoropropylene (top) and of $C_3F_6^+$ obtained by ionization of cyclo- C_3F_6 (bottom). In the upper spectrum there are two sets of photodissociation data points corresponding to electron impact ionization energies of 20 eV and 70 eV. Also shown in the upper spectrum is the infrared absorption spectrum of neutral perfluoropropylene over the CO_2 laser wavelength region. A single $CF_3CF=CF_2$ absorption band at 1037 cm^{-1} also seen in Figure 1 is the only discernible feature although a combination band at 978 cm^{-1} is detected at higher sensitivity.²¹

The infrared photodissociation spectrum of $C_3F_6^+$ derived from perfluorocyclopropane (Figure 3, bottom) shows only a single band and its maximum ($\bar{\nu} = 1047\text{ cm}^{-1}$) coincides exactly with the maximum in the photodissociation spectrum of perfluoropropylene cation. Absolute intensities of the two spectra are not directly comparable. In the upper spectrum the photodissociation yield, P_D , is a measure of the fraction of $C_3F_6^+$ decomposed following 2s continuous laser irradiation at 34 W cm^{-2} . In the results shown for cyclo- C_3F_6 cation P_D corresponds to photodissociation yield following 0.45s irradiation at 46 W cm^{-2} . Differences in experimental conditions are dictated by the fragmentation pattern of the two C_3F_6 isomers under electron impact ionization. The experimental sequence for the perfluorocyclopropane system includes double resonance ejection of $C_2F_4^+$ during the initial 300 ms of trapping

FIGURE 3. Photodissociation spectra of $C_3F_8^+$ isomers over the CO_2 laser spectral range. Upper spectrum is for perfluoropropylene parent ion. Left ordinate is fraction of $C_3F_8^+$ dissociated after two seconds of irradiation at 34 W cm^{-2} . The two solid curves are for ionization energies of 70 eV ($\square$) and 20 eV ($\circ$). Perfluoropropylene pressure is 4.8×10^{-7} Torr. Dotted line is infrared absorption spectrum of perfluoropropylene at 0.8 Torr in a 10 cm path length cell. Lower spectrum is perfluorocyclopropane parent ion. Data points are fraction of $C_3F_8^+$ dissociated following 450 ms irradiation at 46 W cm^{-2} . Perfluorocyclopropane pressure is 7.6×10^{-7} Torr.



time. Laser irradiation begins at 500 ms trapping time and continues until the ions are detected at 950 ms. Increasing the laser power to 46 W cm^{-2} for perfluorocyclopropane, compared to 34 W cm^{-2} for $\text{CF}_3\text{CF}=\text{CF}_2$, compensates for the shorter irradiation time yet limits the number of usable CO_2 laser lines. Any small feature in the lower spectrum in Figure 3 comparable to the shoulder at $\sim 1000 \text{ cm}^{-1}$ in the upper spectrum is below the limit of detectability.

Infrared multiphoton dissociation of C_3F_6^+ yields the same products, reaction 1, irrespective of C_3F_6^+ neutral precursor.

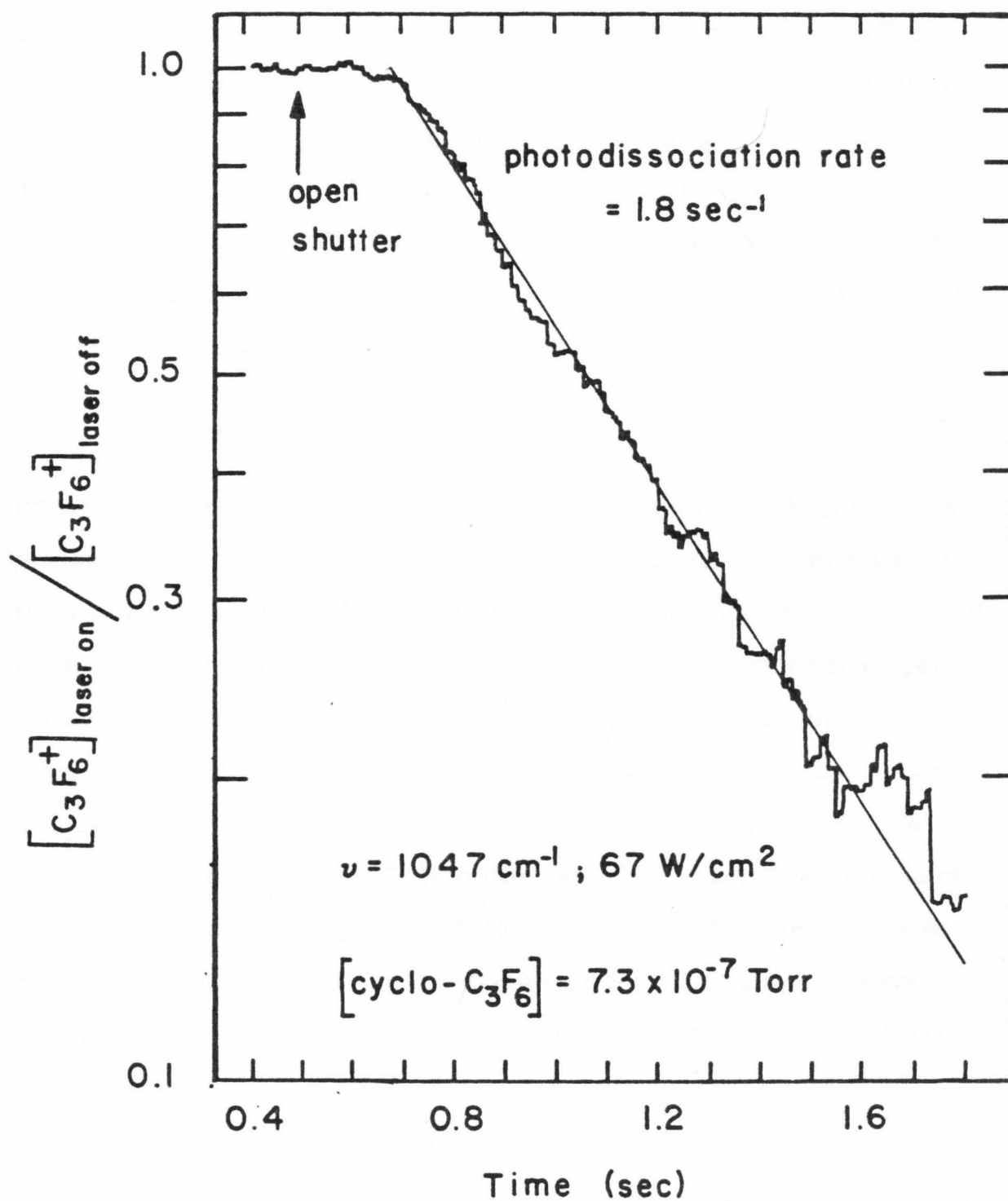


Process 1 is confirmed both by direct observation of product C_2F_4^+ and by ICR double resonance. As can be seen in Figure 2 this reaction is the lowest enthalpy process for C_3F_6^+ decomposition. It is 56 kcal/mole (19 photons at 1047 cm^{-1}) endothermic for perfluoropropylene ion and 8 kcal/mole (3 photons) endothermic for perfluorocyclopropane ion. No other infrared laser induced reactions are observed.

The results presented indicate electron impact ionization of perfluorocyclopropane produces an ion identical in structure to the perfluoropropylene molecular ion.

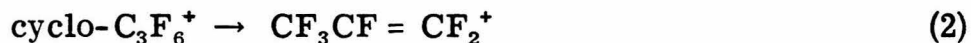
Figure 4 shows the temporal behavior of multiphoton dissociation of C_3F_6^+ derived from perfluorocyclopropane. The normalized ion signal (C_3F_6^+ intensity during irradiation divided by C_3F_6^+ intensity without irradiation) is plotted on a logarithmic scale as a function of trapping time. After the start of laser irradiation at 0.5s trapping time there is an induction period of $\sim 180 \text{ ms}$ followed by an exponential decay of the C_3F_6^+ population. It appears possible to dissociate 100% of the ions and the entire C_3F_6^+ population is characterized by a single photodisso-

FIGURE 4. Temporal dependence of perfluorocyclopropane cation photodissociation. Ordinate is normalized ("laser on" divided by "laser off") ion signal intensity plotted on a logarithmic scale. Irradiation (67 W cm^{-2} at 1047 cm^{-2}) begins at 500 ms trapping time. Perfluoropropylene pressure is 7.3×10^{-7} Torr.



ciation rate constant. Unlike reported results for cyclopropane,²⁹ electron impact ionization of cyclo- C_3F_6 yields a single isomer of C_3F_6^+ which is the ring opened species.

For perfluoropropylene the population of vibrationally excited C_3F_6^+ is greater when formed with 70 eV electrons than with 20 eV electrons. The increase in photodissociation yield (Figure 3, top) at 70 eV compared to 20 eV is attributed to an increased facility for multiphoton dissociation of vibrationally excited species. There is no detectable shift in band maximum and only a small change in bandwidth for the two sets of perfluoropropylene data points. Data from Table 1 and Figure 2 indicate the ring opening reaction, process 2,



imparts 48 kcal/mole internal energy to the product ion. In light of the perfluoropropylene result, the initial vibrational excitation might alter the absolute magnitude of the photodissociation yield but should not affect the form of the wavelength dependence. Also, C_3F_6^+ formed from perfluorocyclopropane undergoes ~ 6 ion-molecule collisions prior to the start of laser irradiation. Collisional deactivation might remove some internal energy; however, nonresonant collisional energy transfer is known to be inefficient.³¹⁻³² Recently reported³² radiative lifetime of vibrationally excited CF_3O^- is 0.05 s. A comparable lifetime for excited C_3F_6^+ predicts $>99\%$ of the ions would thermalize by radiative emission during the 0.5 s trapping time before laser irradiation commences.

Conclusions

Infrared photodissociation spectroscopy is an effective method for

obtaining structural information of gas phase ions. Even when limited to a relatively small portion of the infrared spectrum it is possible to "fingerprint" ions for direct comparison of isomeric species. Measured photodissociation wavelength dependence and kinetics establish unambiguously that electron impact ionization of perfluorocyclopropane yields a ring opened ion identical to perfluoropropylene parent cation.

Other commercially available infrared lasers can be used to extend the available wavelength range. Multiphoton dissociation using high power pulsed lasers³²⁻³³ is suitable for more conventional mass spectrometers in which ion-residence times are on the $\sim 10^{-6}$ s. Thus infrared photodissociation can be developed as a complementary technique to collisional activation for ion structure analysis. In particular, infrared excitation may be better suited to distinguish isomeric species because collision induced dissociation of isomers often yields fragment ions in ratios that vary only slightly with structure of the precursor ion.^{2, 34}

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CHAPTER IV

THERMOCHEMISTRY AND PROTON BOND ENERGIES
OF GAS PHASE PROTON BOUND DIMERS OF
ALIPHATIC ALCOHOLS.

Thermochemistry and Proton Bond Energies of Gas
Phase Proton Bound Dimers of Aliphatic Alcohols

D. S. Bomse¹ and J. L. Beauchamp*

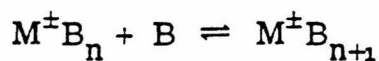
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Abstract

Ion cyclotron resonance (ICR) spectroscopy is used to measure equilibrium constants for exchange reactions $B' + BH^+B \rightleftharpoons B'H^+B + B$ where B' , B are oxygen-containing bases ethanol, isopropanol, 2-butanol, t-butanol and dimethyl ether. Thermochemical results indicate the dimer dissociation energies $D(BH^+-B)$ all lie between 30 and 33 kcal/mole. This agrees very well with Kebarle's measurements of $D(BH^+-B)$ value for oxygen-containing bases B = dimethyl ether, water, methanol, acetone and dimethyl sulfoxide. Results are analyzed by comparison with a qualitative potential energy surface for proton bond formation. Comparison is also made with energetics of the negative ion species $RO^- \cdots HOR$. New estimates for proton affinities of isopropanol and 2-butanol are reported.

INTRODUCTION

A prominent application of gas phase ion chemistry is the determination of intrinsic acidities and basicities of molecules free from complicating solvent effects.²⁻⁴ Now that a substantial body of thermodynamic information on simple acid-base interactions has been acquired, the scope of this work has been expanded to studies of cluster formation.⁵⁻⁷ Quantitative measurements of clustering reactions, generalized in equation 1, provide a detailed description of



solvation energetics and help bridge the gap between gas and condensed phases. Typically $M^{\pm}$ is a simple monotomic ion such as H^+ , Li^+ , Na^+ , K^+ , F^- , Cl^- , Br^- , I^- and $B = H_2O$, NH_3 , etc.⁵⁻⁷

One surprising result obtained by Kebarle is that for all oxygen-containing bases B studied, enthalpy changes for the association reaction $BH^+ + B \rightarrow B_2H^+$ lie in the range $\Delta H = -31 \pm 2$ kcal/mole.^{5,8-10} Only one alcohol, $B = CH_3OH$, is among the compounds studied.⁹

Previous work in our laboratory has focused on the chemical consequences of strong hydrogen bonding in the gas phase.¹¹⁻¹⁴ In particular, ion-molecule chemistry of secondary and tertiary alcohols is dominated by reactions which proceed through proton-bound intermediates.^{11,12,14} Exchange reactions of proton-bound alcohol dimers were studied to verify the reversibility of cluster formation.¹⁴ Mechanisms for cluster formation at low pressures were postulated.^{12,14} To understand better the dynamics of protonated alcohols and to test

the generalization implied by Kebarle's results we have measured heats of formation and dissociation energies of proton-bound dimers of several aliphatic alcohols. These values are obtained using the technique of ion cyclotron resonance (ICR) spectroscopy from equilibrium constants of exchange reactions, process 2, where B



and B' represent Lewis bases.

McIver¹⁵ has studied energetics of the analogous hydrogen-bonded negative ions, $RO^- \cdot HOR$. Results of this study are compared with his reports of alkoxide cluster thermochemistry.

Also, new estimates for proton affinities of some secondary alcohols are presented.

EXPERIMENTAL

The theory, techniques and instrumentation of trapped ion ICR spectroscopy have been described in detail.^{16,17} The spectrometer used in this study was built at Caltech and incorporates a 15-inch electromagnet capable of 23.4 kG. A three-section flat ICR cell equipped for ion trapping is used.

All ICR experiments were carried out in the range 10^{-7} - 10^{-5} Torr, corresponding to neutral particle densities of 3×10^9 - 3×10^{11} molecules cm^{-3} . Pressure is measured with a Schulz-Phelps-type ionization gauge calibrated against an MKS Instruments Baratron Model 90HI-E capacitance manometer. It is expected that absolute pressure determinations are within $\pm 20\%$ using this method, with pressure ratios being somewhat more accurate. Sample mixtures are prepared directly in the instrument using three sample inlets and the Schulz-Phelps gauge.

Typically, alcohol pressure ratios were adjusted so that two of three proton-bound dimers (i.e., $(R_1OH)H^+(R_2OH)$ and $(R_1OH)_2H^+$) were in equilibrium while minimizing concentration of the third dimer ion, $(R_2OH)_2H^+$. Equilibrium constants were obtained both by determination of product to reactant ratios as well as by direct measurement of forward and reverse reaction rates.

All reagents were obtained from commercial suppliers and were used without further purification except for freeze-pump-thaw cycles to remove non-condensable gases. Mass spectrometry revealed no detectable impurities. Some dehydration of t-butanol occurs in the

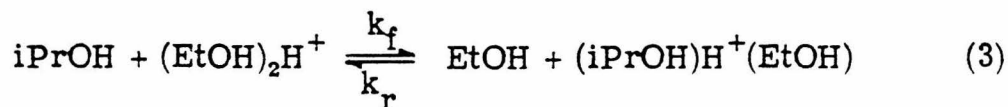
stainless steel inlet system yielding isobutene. This problem was minimized by conditioning the inlet system overnight with the alcohol.

All experiments were performed at ambient instrument temperature, $\sim 30^{\circ}$.

RESULTS AND DISCUSSION

Proton-bound dimer formation occurs by one or more sequences of ion-molecule reactions following ionization of secondary or tertiary alcohols. These reactions are described in detail elsewhere.^{11,12,14} Briefly, ions which contain labile protons (such as protonated alcohols or α -cleavage ions) induce ionic dehydration of the neutral alcohol to form hydrated ions, such as $(\text{ROH})\text{H}^+(\text{OH}_2)$. Displacement of water by alcohol yields proton-bound alcohol dimers. Proton-bound dimers of ethanol (which does not undergo ionic dehydration) were formed by exchange reactions (i.e., equation 2) in mixtures with isopropanol.

Equilibrium constants for exchange reactions, equation 2, were measured for Lewis bases ethanol, isopropanol, s-butanol, t-butanol and dimethyl ether. Results for one equilibrium, reaction 3, are

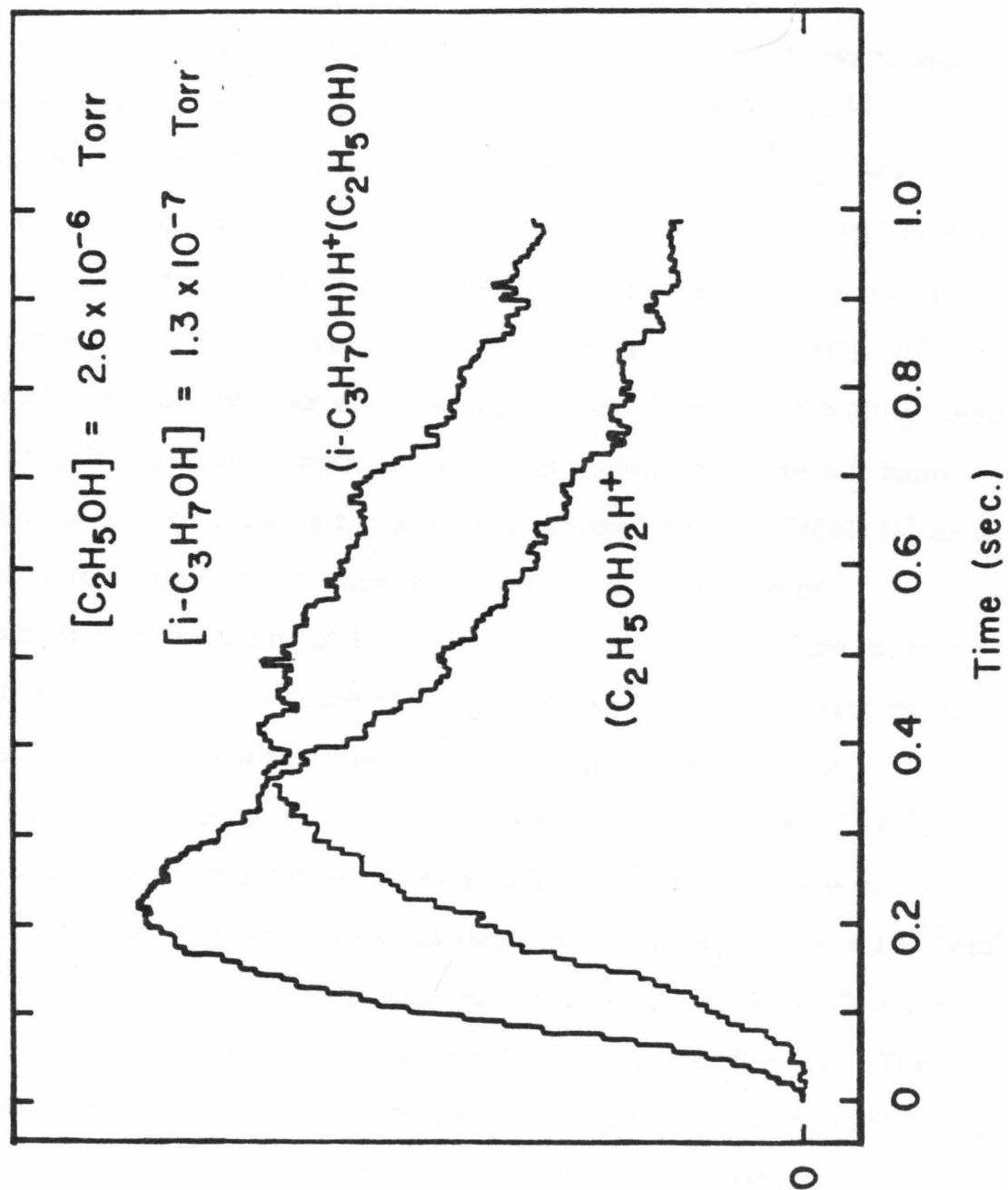


presented in Figures 1 and 2. EtOH and iPrOH represent ethanol and isopropanol, respectively. Figure 1 shows ICR trapped ion data for the two proton-bound species in reaction 2. After ~ 0.5 s trapping time the ratio of ion intensities reaches a constant value.

$\{[(\text{iPrOH})\text{H}^+(\text{EtOH})]/[(\text{EtOH})_2\text{H}^+] = 1.55 \pm 0.05\}$ as equilibrium is established. The ratio of neutral alcohol pressures is $[\text{EtOH}]/[\text{iPrOH}] = 20$, yielding an equilibrium constant for reaction 3 of $K = 31 \pm 6$ and $\Delta G = -2.0 \pm 0.2$ kcal/mole.

In Figure 1, the decrease in proton-bound dimer intensities is

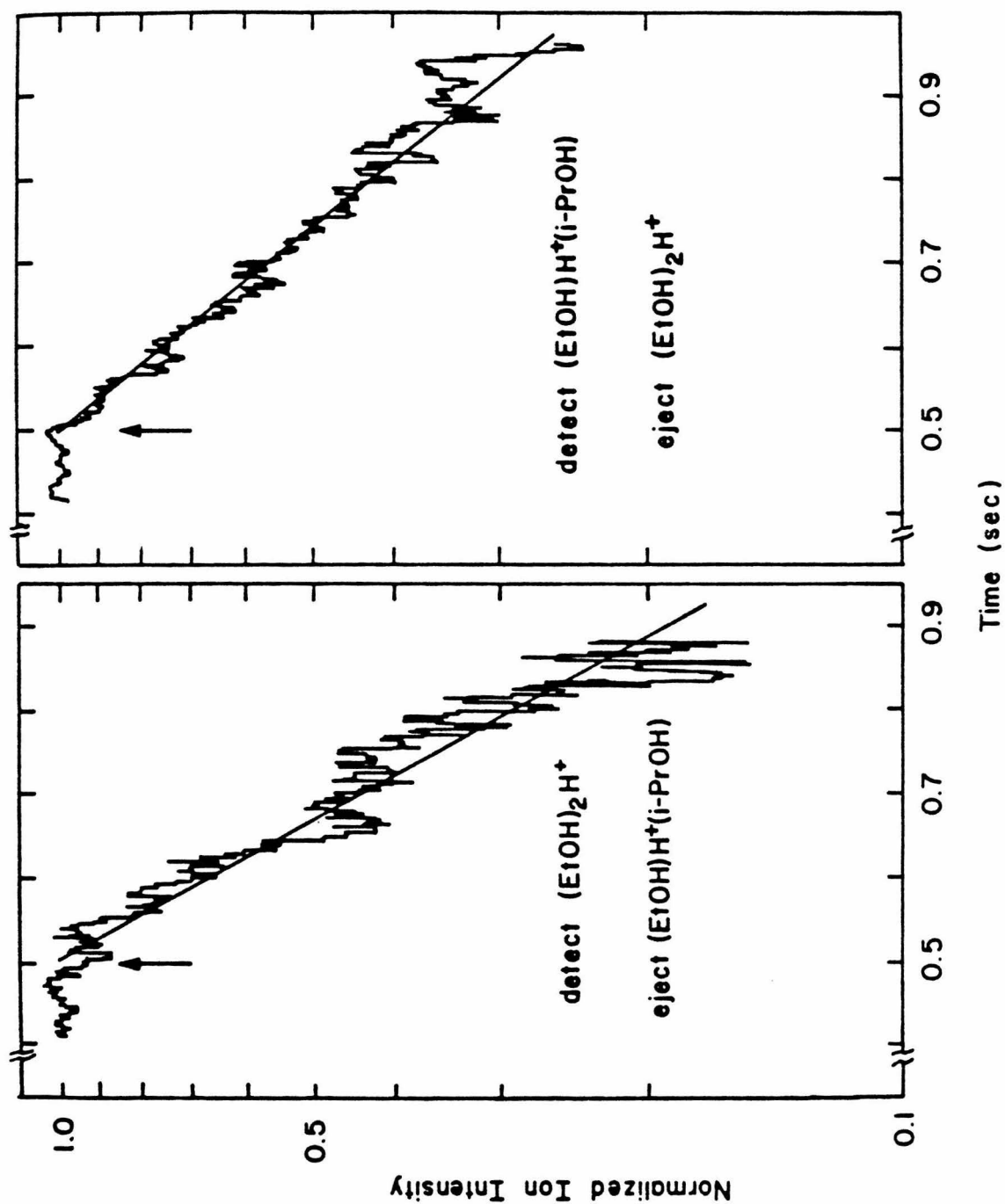
FIGURE 1. Ion intensities as a function of trapping time for $(\text{EtOH})_2\text{H}^+$ and $(\text{i-PrOH})\text{H}^+(\text{EtOH})$ formed by ion-molecule reactions 2.6×10^{-6} Torr EtOH plus 1.2×10^{-7} Torr i-PrOH. Ion intensities must be divided by ion mass to correct for differences in ICR sensitivity. Ionization is by a 10 ms pulse of 70 eV electrons.



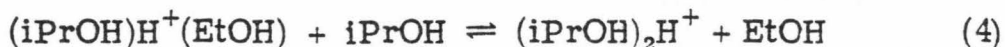
due primarily to ion loss from the trapping cell. At the low iPrOH pressure used, formation of $(\text{iPrOH})_2\text{H}^+$ is very slow and does not reach equilibrium concentration during the time scale of the experiment shown in Figure 1. The intensity of $(\text{iPrOH})_2\text{H}^+$ does not exceed 30% of the total proton-bound alcohol dimer population.

Figure 2 shows data for a direct measure of both forward and reverse reaction rates of process 2. ICR double resonance^{16,17} ejection of $(\text{iPrOH})\text{H}^+(\text{EtOH})$ results in an exponential decay of the $(\text{EtOH})_2\text{H}^+$ population as the latter ion reacts to form $(\text{iPrOH})\text{H}^+(\text{EtOH})$ and is ejected from the cell. Double resonance ejection occurs during alternate ICR trapping cycles allowing measurement of $(\text{EtOH})_2\text{H}^+$ intensity with and without ejection of $(\text{EtOH})\text{H}^+(\text{iPrOH})$. Dividing these two signals yields a normalized $(\text{EtOH})_2\text{H}^+$ intensity. The left hand portion of Figure 2 shows the normalized population of $(\text{EtOH})_2\text{H}^+$ as a function of trapping time when double resonance ejection of $(\text{iPrOH})\text{H}^+(\text{EtOH})$ begins at 0.5 s. The ordinate scale is logarithmic and the negative of the slope of the line is the forward reaction rate, 4.2 s^{-1} . Combined with a measured isopropanol pressure of $1.3 \times 10^{-7} \text{ Torr}$, this result yields $k_f = 9.97 \times 10^{-9} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Data shown in the right-hand portion of Figure 2 yield a rate of 3.4 s^{-1} for the reverse process in reaction 3 and $k_r = 4.04 \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Combined results in Figure 2 give $K = k_f/k_r = 23.5 \pm 5$ corresponding to $\Delta G = -1.9 \pm 0.2 \text{ kcal/mole}$ for reaction 3. The two methods (Figures 1 and 2) for measuring the free energy change of the exchange reaction agree within experimental uncertainty.

FIGURE 2. Data for direct measurement of forward and reverse rates of reaction 2. Plot at left shows exponential decay of normalized $(\text{EtOH})_2\text{H}^+$ intensity following the start of double resonance ejection of $(\text{EtOH})\text{H}^+(\text{i-PrOH})$ at 500 ms (vertical arrow). Slope of the semi-log plot indicates forward reaction rate is 4.2 s^{-1} . Data at right show decay of normalized $(\text{EtOH})\text{H}^+(\text{i-PrOH})$ signal resulting from double resonance ejection of $(\text{EtOH})_2\text{H}^+$. Reverse reaction rate is 3.4 s^{-1} . Reagent pressures and ionization conditions identical to those of Figure 1.



A different mixture of EtOH and iPrOH ($[\text{EtOH}]/[\text{iPrOH}] = 5.3$) was used to evaluate the equilibrium constant for an exchange reaction involving $(\text{iPrOH})_2\text{H}^+$, reaction 4. Under these conditions the concen-



tration of $(\text{EtOH})_2\text{H}^+$ is nearly zero once equilibrium is established.

Results of all measured equilibria are presented in Table 1. Listed are ΔG , ΔS_{calc} , and ΔH_{ex} for the exchange reactions. Entropy changes, ΔS_{calc} , are calculated from ratios of symmetry numbers of reactants and products.³ It is assumed that proton-bound species undergo free internal rotation about the oxygen-proton bond, thus the symmetry number of a given Lewis base is invariant whether or not the molecule is bound in a complex. Symmetrically substituted proton-bound dimers such as $(\text{EtOH})_2\text{H}^+$ possess a two-fold rotational symmetry not present in asymmetric dimers such as $(\text{EtOH})\text{H}^+(\text{iPrOH})$. Thus for reaction 3, $T\Delta S_{\text{calc}} = RT \ln 2 = 0.41$ kcal/mole. In Table 1 ΔG and ΔH_{ex} values are computed relative to reaction with $[(\text{CH}_3)_2\text{O}]_2\text{H}^+$, process 5. Also listed are absolute proton affinities of the bases used



in this study. Note that proton affinities of some alcohols are not experimentally determined and must be estimated. These estimates are discussed in the appendix.

Cluster dissociation energies, $D(\text{B}'\text{H}^+-\text{B})$, are calculated from the thermodynamic cycle shown in Scheme I. Kebarle's value of

Table I. Energetics of Proton-Bound Dimer Exchange Reactions

B'	B	ΔG^a (kcal/mole)	$T\Delta S_{\text{calc}}^a$ (kcal/mole)	ΔH_{ex}^a (kcal/mole)	PA(B') ^b (kcal/mole)
C ₂ H ₅ OH	C ₂ H ₅ OH	2.3	0	2.3	191.4 ^c
C ₂ H ₅ OH	i-C ₃ H ₇ OH	0.5	0.4	0.9	-
i-C ₃ H ₇ OH	i-C ₃ H ₇ OH	-0.3	0	-0.3	194.4 ± 0.5 ^d
i-C ₃ H ₇ OH	s-C ₄ H ₉ OH	-1.6	0.4	-1.2	-
s-C ₄ H ₉ OH	s-C ₄ H ₉ OH	-1.8	0	-1.8	194.9 ± 0.5 ^d
i-C ₃ H ₇ OH	t-C ₄ H ₉ OH	-1.8	0.4	-1.4	-
t-C ₄ H ₉ OH	t-C ₄ H ₉ OH	-2.5	0	-2.5	196.6 ^e
(CH ₃) ₂ O	i-C ₃ H ₇ OH	-0.7	0.4	-0.3	-
(CH ₃) ₂ O	(CH ₃) ₂ O	0	0	0	194.8 ^c

a) Relative to [(CH₃)₂O]₂H⁺ as indicated by reaction 5. Uncertainties are ± 0.3 kcal/mole.

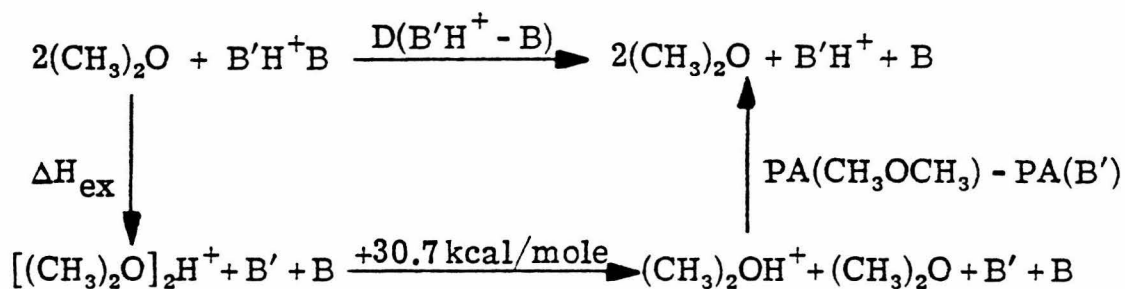
b) Assumes PA(NH)₃ = 207.0 kcal/mole.

c) Reference 3.

d) Estimated, see Appendix.

e) Reference 21.

Scheme I



30.7 kcal/mole is used for the dissociation energy of the $(\text{CH}_3)_2\text{O}$ proton-bound dimer.⁹ Experimentally determined values of $\Delta\text{H}_{\text{ex}}$ are taken from Table 1. The data obtained for the alcohol proton-bound dimers has been augmented by cluster dissociation energies reported for other oxygen-containing bases^{1,9,10} and the combined set of $\text{D}(\text{B}'\text{H}^+ - \text{B})$ values are presented in matrix form in Table II. For asymmetric ions, $\text{B}'\text{H}^+\text{B}$, dissociation yields $\text{B}'\text{H}^+ + \text{B}$, not $\text{B}' + \text{H}^+\text{B}$.

A striking result is observed by reading the entries along the main diagonal of Table II. All measured dissociation energies of symmetrically substituted proton-bound dimers lie between 30 and 33 kcal/mole for oxygen containing bases. The 3 kcal/mole variation among measured energies $\text{D}(\text{BH}^+ - \text{B})$ is minute compared to the 38 kcal/mole range in proton affinities encompassed by the Lewis bases listed. In fact, differences in proton-bound alcohol dimer dissociation energies reflect the uncertainties in alcohol proton affinities more than any systematic variation with physical properties of the alcohols. The similarity in proton bond strengths can be understood by examining Scheme I.^{8,18} Consider the case $\text{B}' = \text{B} \equiv \text{B}$, increasing the proton affinity of B results in a large endothermic

TABLE II. Hydrogen Bond Strengths in Proton-Bound Dimers of Oxygen Bases.^a

B' \ B	H ₂ O	CH ₃ OH	C ₂ H ₅ OH	(CH ₃) ₂ O	i-C ₃ H ₇ OH	s-C ₄ H ₉ OH	(CH ₃) ₂ CO	t-C ₄ H ₉ OH	(CH ₃) ₂ SO
H ₂ O	32 ^b	36 ^c	40.5 ^d	42.5 ^c	42 ^c	42.5 ^c	44.5 ^c	42 ^c	53 ^c
CH ₃ OH	25 ^c	33.1 ^b							
C ₂ H ₅ OH	24 ^d		31.7 ^e		36 ^e				
(CH ₃) ₂ O	22.5 ^c			30.7 ^b	31.4 ^e				
i-C ₃ H ₇ OH	22.5 ^c		32.0 ^e	31.0 ^e	31.4 ^e	32.4 ^e		30.7 ^e	
s-C ₄ H ₉ OH	22.5 ^c				32.9 ^e	32.4 ^e			
(CH ₃) ₂ CO	21.0 ^c						30 ^f		
t-C ₄ H ₉ OH	20.5 ^c				28.5 ^e			29.6 ^e	
(CH ₃) ₂ SO	15 ^c								31 ^f

a) Bond energies $D(B'H^+-B)$ in kcal/mole.

b) Reference 9.

c) Estimated using empirical method of Ref. 23.

d) Reference 5.

e) This work. Uncertainties are ± 0.3 kcal/mole plus uncertainty in proton affinity measurement (see Table 1).

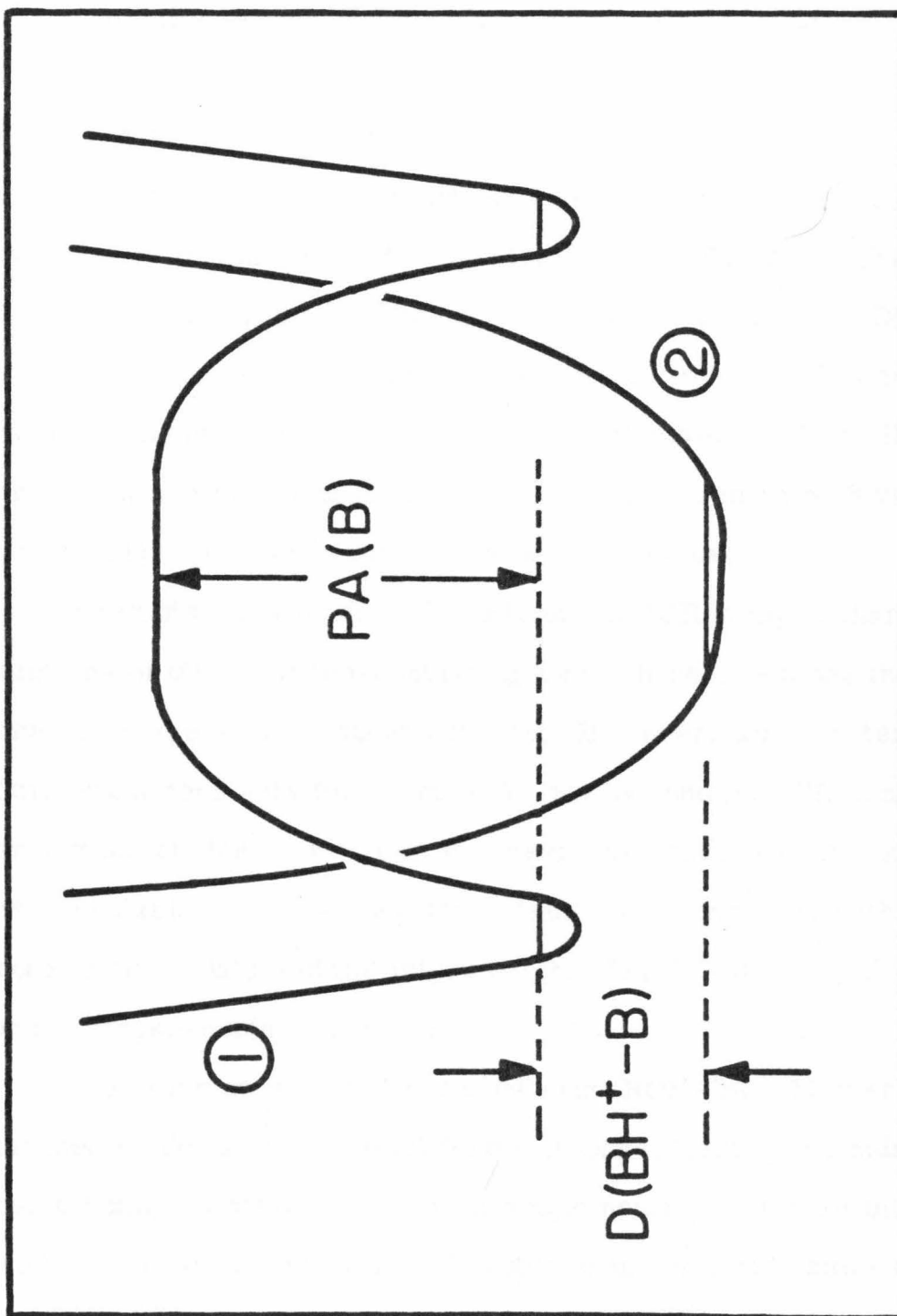
f) Reference 8.

ΔH_{ex} (see Table 1) and an equally large but exothermic proton affinity difference relative to $(\text{CH}_3)_2\text{O}$. The effects nearly cancel to yield a dimer dissociation energy of 31 ± 2 kcal/mole. Similar results have been reported for proton-bound dimers of aliphatic amines in which the symmetric species yield $D(\text{BH}^+ - \text{B})$ values between 21 and 25 kcal/mole for $\text{B} = \text{NH}_3$, CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$.¹⁸

A qualitative potential energy surface for $\text{B} + \text{B} + \text{H}^+$ is shown in Figure 3. Curve 1 depicts the system when the two oxygen-containing bases are at "infinite" separation. The wells represent BH^+ formation with the well depth equal to the proton affinity of B. No interaction between bases occurs. Increasing the base strength of B results in greater delocalization of charge in the $\text{O}-\text{H}^+$ bond and increased electron density on the proton. As the second base approaches BH^+ a new proton bond is formed. However at short O-O separation, interaction across the proton between basic lone pairs on the two oxygen atoms are repulsive and result in a weakening of the first proton bond. Curve 2 in Figure 3 shows the potential energy curve for the proton-bound dimer. The two oxygen atoms generate a symmetric bonding well for the proton (there may or may not be a double well) with the O-O distance determined by opposing effects of the acid-base interaction and repulsive orbital overlap. In asymmetrically substituted dimers bonding strength of the second base decreases as the difference in proton affinities increases.^{5, 18, 19} A limiting case is reached where the second bond is purely electrostatic with virtually no electron donation by the weaker base to the proton. This explains the decrease in $D(\text{B}'\text{H}^+ - \text{OH}_2)$ values as one

FIGURE 3. Qualitative potential energy surfaces for symmetric proton-bound dimer BH^+B . B represents an oxygen-containing Lewis base. Surface 1 is for "infinite" oxygen-oxygen separation. Surface 2 represents oxygen-oxygen separation in lowest energy configuration of BH^+B . Vertical energy scales of curves 1 and 2 are not directly comparable.

Enthalpy



$O \cdots H^+ \cdots O$ Coordinate

reads down the first column in Table II.

Typical experimental and theoretical values for oxygen-oxygen separations in $(\text{H}_2\text{O})_2\text{H}^+$ are 2.4-2.6 Å.²⁰ Assuming this distance to be correct for oxygen-containing ions $\text{B}'\text{H}^+\text{B}$, it is apparent that steric interactions are not very important in determining energetics of proton bound dimer formation for the species listed in Table II. The one possible exception is the bulkiest base studied, t-butanol. $D(\text{BH}^+-\text{B}) = 29.6$ kcal/mole for $\text{B} = \text{t-butanol}$ is the lowest measured dimer dissociation energy (Table II). However, the steric effect, if any, is very slight and no discernible change in bond strength with variation in molecular bulk exists among the other alcohols.

Attempts were made to include in this ICR study exchange reactions of other oxygen-containing Lewis bases. Among these compounds are several dialkyl ethers. However, ambient temperature equilibrium constants for reaction 1 are beyond the ICR dynamic range when choice of one base was restricted to those compounds listed in Table 1. These negative results are consistent with measured proton affinity data and the inference that $D(\text{BH}^+-\text{B}) = 31 \pm 2$ kcal/mole for all oxygen-containing bases.

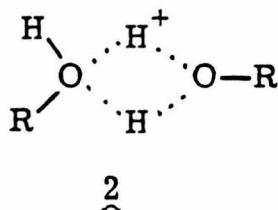
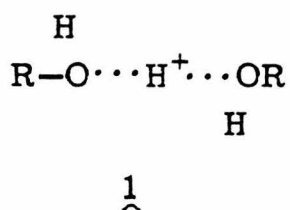
In a study of solvated alkoxide ions ($\text{ROH}-\text{OR}^-$) McIver observed that methoxide (a strong base) forms stronger hydrogen bonds than does ethoxide (a weaker base) to a single neutral methanol molecule.¹⁵ Thus the solvation energetics of proton-bound alkoxide anions is qualitatively similar to those of protonated alcohols. Although absolute values for $D(\text{RO}^--\text{HOR})$ are not reported, the difference in energies between the case $\text{R} = \text{CH}_3$ and the case $\text{R} = \text{C}_2\text{H}_5$ is only 0.3 kcal/mole

with $\text{CH}_3\text{O}^- \cdot \text{HOCH}_3$ possessing the stronger bond. In comparison, CH_3O^- is more basic than $\text{C}_2\text{H}_5\text{O}^-$ by 1.9 kcal/mole. Thus, the reported results are not inconsistent with the possibility of similar dissociation energies for all complexes $\text{RO}^- \cdot \text{HOR}$. Definitive conclusions cannot be drawn from this limited amount of information.

CONCLUSIONS

Dissociation energies, $D(\text{BH}^+-\text{B})$, of proton-bound dimers are nearly identical for all oxygen-containing bases examined to date. Combining results of this study with Kebarle's^{5,9,10,18,19} data, the dimer dissociation energies all lie between 30 and 33 kcal/mole for bases containing σ -bonded or π -bonded oxygen atoms. The thermodynamic cycle shown in Scheme 1 illustrates that increasing the base strength of B stabilizes both ions BH^+ and BH^+B by nearly the same amount, leaving $D(\text{BH}^+-\text{B})$ invariant. This result is understood in terms of a potential energy diagram, Figure 3, and consideration of oxygen-oxygen repulsive interactions as well as attractive oxygen-proton bonding.

Nearly identical bond strengths for all symmetrically substituted dimers listed in Table II is evidence for a simple hydrogen bond structure, 1, common to all ions BH^+B . Complex interactions, such as the four-center bond shown in 2, are not possible for species without

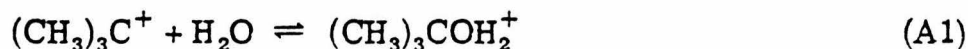


extra, labile hydrogens (i.e., $(\text{CH}_3)_2\text{O}$ and acetone) hence only structure 1 is available to all bases. Furthermore, calculations have shown 1 ($\text{R}=\text{H}$) is the most stable geometry for $(\text{H}_2\text{O})_2\text{H}^+$ with species 2 being higher in energy.²⁰ Similar arguments can be used to exclude 3 as geometry of the acetone proton-bound dimer.



APPENDIX

Proton transfer equilibria are not observed among ion-molecule reactions of most secondary and tertiary alcohols. Instead, the protonated alcohols react rapidly with neutral alcohols yielding dehydration products.^{11,12,14} Thus, accurate proton affinities (usually determined by proton transfer equilibria) have not been determined for these alcohols. One exception is *t*-butanol for which the heat of formation of the protonated species $\Delta H_f(\underline{t}\text{-C}_4\text{H}_9\text{OH}_2^+) = 93.9$ kcal/mole is obtained from equilibrium A1.²¹ This predicts $\text{PA}(\underline{t}\text{-C}_4\text{H}_9\text{OH}) = 196.6$ kcal/mol. The proton affinity of *t*-butanol is



tied to the standard proton affinity scale [relative to $\text{PA}(\text{NH}_3)$] by the heat of formation of $(\text{CH}_3)_3\text{C}^+$ which is calculated from the proton affinity of isobutene.

Proton affinities of isopropanol and 2-butanol are estimated by comparison with substituent effects shown by other Lewis bases. For example, differences in proton affinities between aliphatic alcohols ROH and the corresponding amines RNH_2 approaches a value of 26.7 kcal/mole as the size of the unbranched alkyl chain increases.³ Using the reported value of $\text{PA}(\underline{i}\text{-C}_3\text{H}_7\text{NH}_2) = 221.2$ kcal/mole (relative to the proton affinity of NH_3) predicts $\text{PA}(\underline{i}\text{-C}_3\text{H}_7\text{OH}) = 194.5$ kcal/mole. Similarly, proton affinity differences between RCHO and ROH are ~ 1.0 kcal/mole for R groups larger than CH_3 .³ A value of 195.3 kcal/mole is reported for $\text{PA}(\underline{i}\text{-C}_3\text{H}_7\text{CHO})$ which yields an estimate of $\text{PA}(\underline{i}\text{-C}_3\text{H}_7\text{OH}) = 194.3$. The two estimates agree well

and their average is listed in Table 1. The error limits on the estimate fall within the limits placed on the proton affinity of isopropanol by the experimental study of Long and Munson.²²

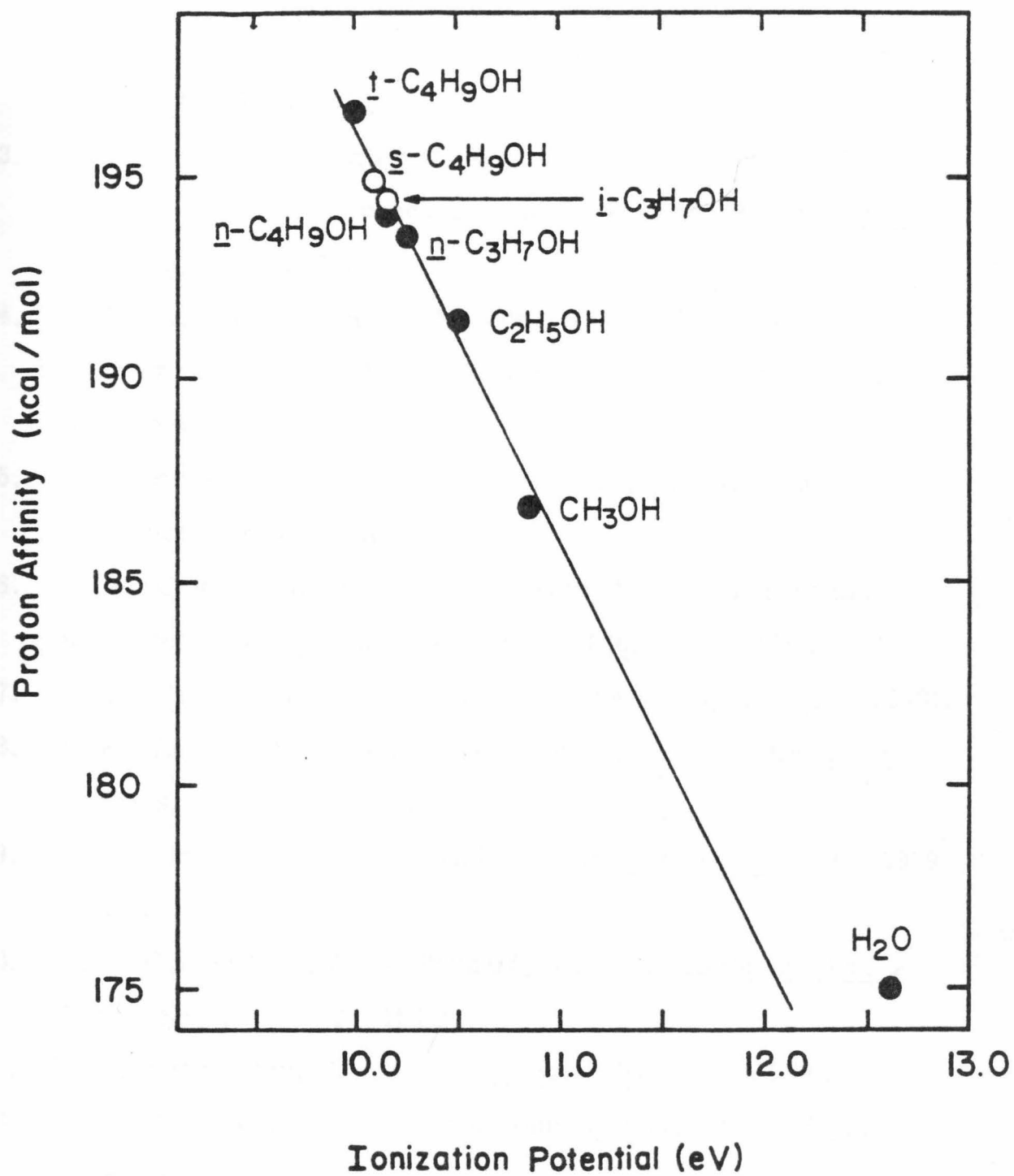
There are no reference compounds available which contain s-butyl groups. Instead, the s-butanol proton affinity is estimated by assuming comparable increases in basicity in going from n-propanol to isopropanol as between n-butanol and s-butanol. Thus an estimate of $PA(\underline{s}\text{-C}_4\text{H}_9\text{OH}) = 194.9 \text{ kcal/mole}$ is obtained.

There is, in general, an inverse correlation between the ionization potential of a compound and its proton affinity.¹⁴ Figure 4 is a plot of proton affinities vs. ionization potentials for water and alcohols pertinent to this study. Both experimentally determined (filled circles) and estimated (open circles) proton affinities are grouped close to the straight line drawn in the figure. This result gives additional credence to the estimate.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy. We are grateful to Professor Kebarle for communicating his results prior to publication.

FIGURE 4. Plot of proton affinities vs. ionization potentials for water and alcohols used in this study. Experimentally determined proton affinities are represented by filled circles whereas estimated values are open circles. Proton affinity data from Ref. 3 and assumes $PA(NH_3) = 207.0$ kcal/mole. Ionization potentials from Ref. 24.



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CHAPTER V

SLOW MULTIPHOTON EXCITATION AS A PROBE OF
BIMOLECULAR REACTION ENERGISTICS. MULTI-
PHOTON DISSOCIATION OF PROTON BOUND ALCOHOL
DIMERS.

Slow Multiphoton Excitation as a Probe of Bimolecular
Reaction Energetics. Multiphoton Dissociation of
Proton Bound Alcohol Dimers.

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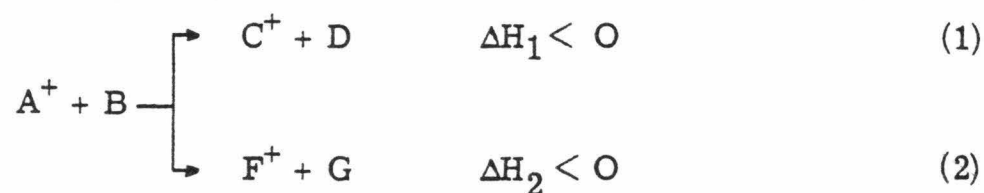
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Abstract

Low intensity infrared CW laser induced multiphoton dissociation of gas phase ions is used to identify lowest energy decomposition pathways. The target molecules are proton bound dimers of simple aliphatic alcohols $(R_1OH)H^+(R_2OH)$ where $R_1, R_2 = CH_3, C_2H_5, i-C_3H_7, n-C_3H_7, s-C_4H_9, t-C_4H_9$ and $t-C_5H_{11}$. By identifying the lowest energy route to dissociation it is possible to construct a qualitative potential energy surface for ion-molecule processes involving reactants $R_1OH_2^+$ and R_2OH . For each proton bound dimer studied experimental results are consistent with formation of an ion-molecule complex as an intermediate in the dissociation reaction. Isomeric ions are distinguished by formation of different sets of decomposition products. Use of infrared multiphoton excitation as a complementary technique to collisional activation of ions in mass spec-mass spec instrumentation is discussed. For this study, ions are formed, stored and detected using techniques of ion cyclotron resonance (ICR) spectroscopy.

Introduction

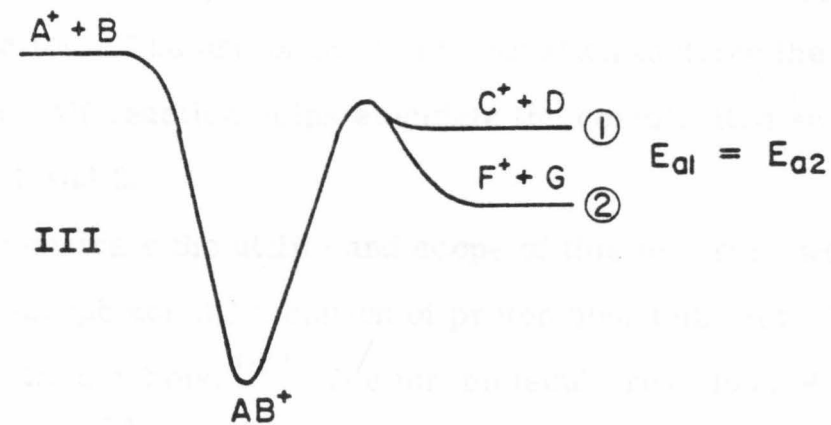
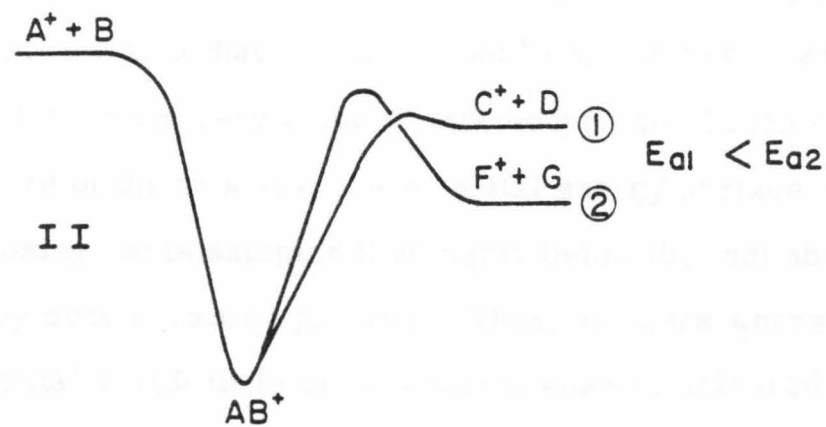
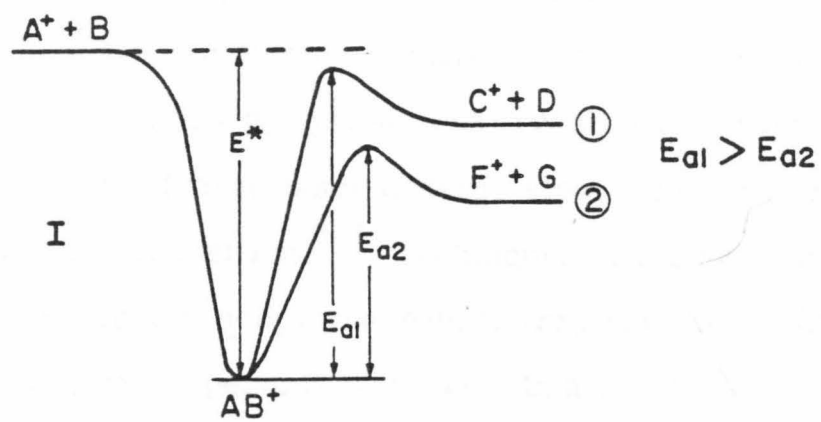
In complex chemical systems where multiple sets of products result from a bimolecular encounter, reaction coordinate diagrams have proven extremely useful for visualizing reaction energetics. Consider, for example, the hypothetical ion-molecule reaction between A^+ and B which has two exothermic reaction channels, reactions 1 and 2. Figure 1 depicts three possible sets of reaction coordinates for this system.



(Although this example is an ion-molecule reaction, the considerations are general.) Typically, ΔH_1 and ΔH_2 are well known. AB^+ may represent a cluster or another stable species whose thermochemistry is well characterized. For most ion-molecule systems the values of activation energies E_{a1} and E_{a2} are not known. When reaction of A^+ with B yields both C^+ and F^+ all that can be inferred is that no point along paths followed on the potential energy surface from reactants to products exceeds the energy E^* available to the reactive intermediate AB^+ . No information is available to distinguish among cases I, II and III in Figure 1.

Several experimental techniques have been developed to probe details of a reaction potential energy surface.¹ These typically involve measuring branching ratios as a function of E^* .¹ One commonly used method is to form AB^+ from different sets of reactants (such as

FIGURE 1. Three possible potential energy surface for the exothermic ion-molecule reaction of $A^+ + B$ leading to products $C^+ + D$ and $F^+ + G$.

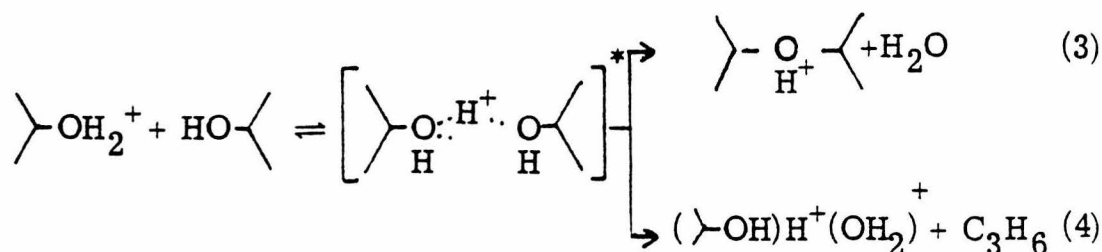


$A + B^+$).² Varying reactant translational energy also changes the value of E^* .³ Formation of stable (i. e., vibrationally "cold") AB^+ followed by collisional excitation provides information on activation energies and the nature of the reaction coordinate in the exit channel.⁴

We have shown that gas phase ions irradiated by a low power ($< 100 \text{ W cm}^{-2}$) cw infrared laser undergo slow, sequential multiphoton absorption and decomposition.⁵⁻⁷ Techniques of ion cyclotron resonance (ICR) spectroscopy are used to trap ions in a spatially well-defined region for periods up to 2s. In a previous study⁷ a dramatic isotope effect observed in an intramolecular competition experiment demonstrates that ions activated by CW infrared laser radiation decompose at energies very close to thermodynamic threshold. Due to the slow nature of the process, the potential energy surface available to a decomposing ion is sampled thoroughly below (but not above) the lowest energy decomposition pathway. Thus, in cases where AB^+ can be formed initially with little or no internal energy, infrared laser excitation and dissociation of AB^+ identifies the lowest energy decomposition reaction. The use of infrared activation to drive the ion-molecule half reaction helps elucidate the complicated energetics of reactions 1 and 2.

To demonstrate the utility and scope of this process, we have studied the multiphoton dissociation of proton bound dimers of some simple aliphatic alcohols.⁸⁻¹⁴ The ion-molecule reactions of the protonated alcohols⁹⁻¹⁴ have been studied in great detail and much of the pertinent thermochemistry is available.¹⁵ Thus they represent well characterized reactions which can be used to test infrared multiphoton activation. For example, reaction of protonated isopropyl alcohol,

$i\text{-C}_3\text{H}_7\text{OH}_2^+$ with the neutral alcohol $i\text{-C}_3\text{H}_7\text{OH}$ initially forms a chemically activated intermediate $(i\text{-C}_3\text{H}_7\text{OH})_2\text{H}^+$.¹² This is analogous to $A^+ + B \rightarrow AB^+ (E = E^*)$ shown in Figure 1. As shown below, the activated proton bound alcohol dimer can dissociate back to reactants, or eliminate H_2O to form a protonated ether $(i\text{-C}_3\text{H}_7)_2\text{OH}^+$, reaction 3, or lose propylene to yield $(i\text{-C}_3\text{H}_7\text{OH})\text{H}^+(\text{OH}_2)$, reaction 4.



Both reactions 3 and 4 are observed at room temperature¹² but exact details of the reaction energetics are not known. Similarly for the other alcohols studied,⁸⁻¹⁴ the proton bound dimer $(\text{ROH})\text{H}^+(\text{R}'\text{OH})$ where $\text{R}, \text{R}' = \text{CH}_3, \text{C}_2\text{H}_5, n\text{-C}_3\text{H}_7, i\text{-C}_3\text{H}_7, s\text{-C}_4\text{H}_9, t\text{-C}_4\text{H}_9$ and $t\text{-C}_5\text{H}_{11}$, has three plausible routes to decomposition (except for $\text{R}, \text{R}' = \text{CH}_3$). Reaction enthalpies lie within a < 20 kcal/mole range;¹⁵ however, for all processes except direct proton bond cleavage the activation energies are unknown. Multiphoton dissociation of the proton bound dimer singles out the lowest energy process. Effects of alcohol structure on the reaction pathway are explored.

Experimental Section

The theory, techniques, and instrumentation of trapped ion ICR spectroscopy have been previously described in detail.^{16, 17} The spectrometer used in this study was built at Caltech and incorporates a

15-in. electromagnet capable of 23.4 kG. A flat ICR cell is utilized, in which the upper source plate is replaced with a 92% transmittance mesh to allow irradiation of trapped ions.

All ICR experiments were carried out in the range 5×10^{-7} - 5×10^{-6} Torr, corresponding to neutral particle densities of 1.5×10^{10} - 1.5×10^{11} molecules cm^{-3} . Pressure is measured with a Schulz-Phelps type ionization gauge calibrated against an MKS Instruments Baratron Model 90H1-E capacitance manometer. It is expected that absolute pressure determinations are within $\pm 20\%$ using this method, with pressure ratios being somewhat more accurate. Sample mixtures are prepared directly in the instrument using three sample inlets and the Schulz-Phelps gauge.

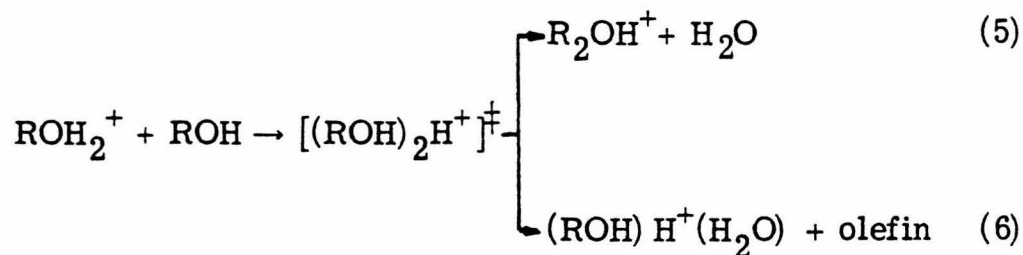
Proton bound methanol dimers are formed by ion-molecule reactions in a mixture of CH_3OH , H_2O and Br_2CHCH_3 .⁸ Proton bound ethanol dimers are produced in a mixture of $\text{C}_2\text{H}_5\text{OH}$ and CH_3F .¹¹ All other proton bound alcohol dimers form rapidly following ionization of the parent alcohol.¹²⁻¹⁵ All reagents except H_2O were obtained from commercial suppliers. Samples were degassed by repeated freeze-pump-thaw cycles.

ICR spectrometer modifications and details of the experimental arrangement used for infrared laser photochemistry studies are published elsewhere.⁷ In a typical experiment ions are formed by a 10 ms pulse of electrons (70 eV except for the ethanol system for which the electron energy is 14 eV). During the first 0.5s of trapping time ion-molecule reactions go to completion, forming proton bound alcohol dimers. Laser irradiation occurs during the next 0.5s and ion abun-

dances are measured at ~ 1.0 s of trapping time. Laser intensity is adjusted ($15\text{--}50\text{ W cm}^{-2}$) so that $\sim 60\%$ of the dimer ions are dissociated. This insures sufficient formation of product ions for ICR double resonance¹⁶ analysis while minimizing the extent of subsequent product ion photolysis. (Double resonance is the selective ejection from the ICR cell of ions of a particular charge to mass ratio allowing positive identification of reaction pathways.¹⁶). For each system the temporal variation of ion population during laser irradiation is also measured. In each case photodissociation is found to be first order (in ion population) and it is possible to dissociate 100% of the ions. The laser wavelength is 944 cm^{-1} (P(20) line of the $10.6\text{ }\mu\text{m}$ branch) except where noted.

Results and Discussion

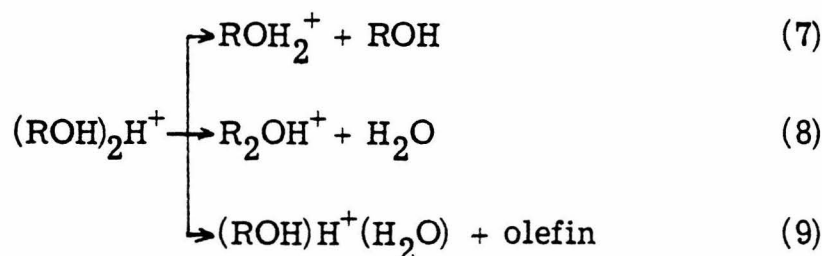
For the aliphatic alcohols the ion-molecule reactions, generalized by processes 1 and 2 and shown specifically for isopropanol by 3 and 4, are the reactions of the protonated alcohol ROH_2^+ with neutral alcohol ROH, equations 5 and 6.⁹⁻¹⁴



In these reactions the proton bound alcohol dimer $(\text{ROH})_2\text{H}^+$ is equivalent to the hypothetical intermediate AB^+ shown in Figure 1. Reaction 5 is observed for all the alcohols used in this study, whereas ionic dehydration, equation 6, occurs only for $\text{R} = \text{n-C}_3\text{H}_7$, $\text{i-C}_3\text{H}_7$, $\text{s-C}_4\text{H}_9$,

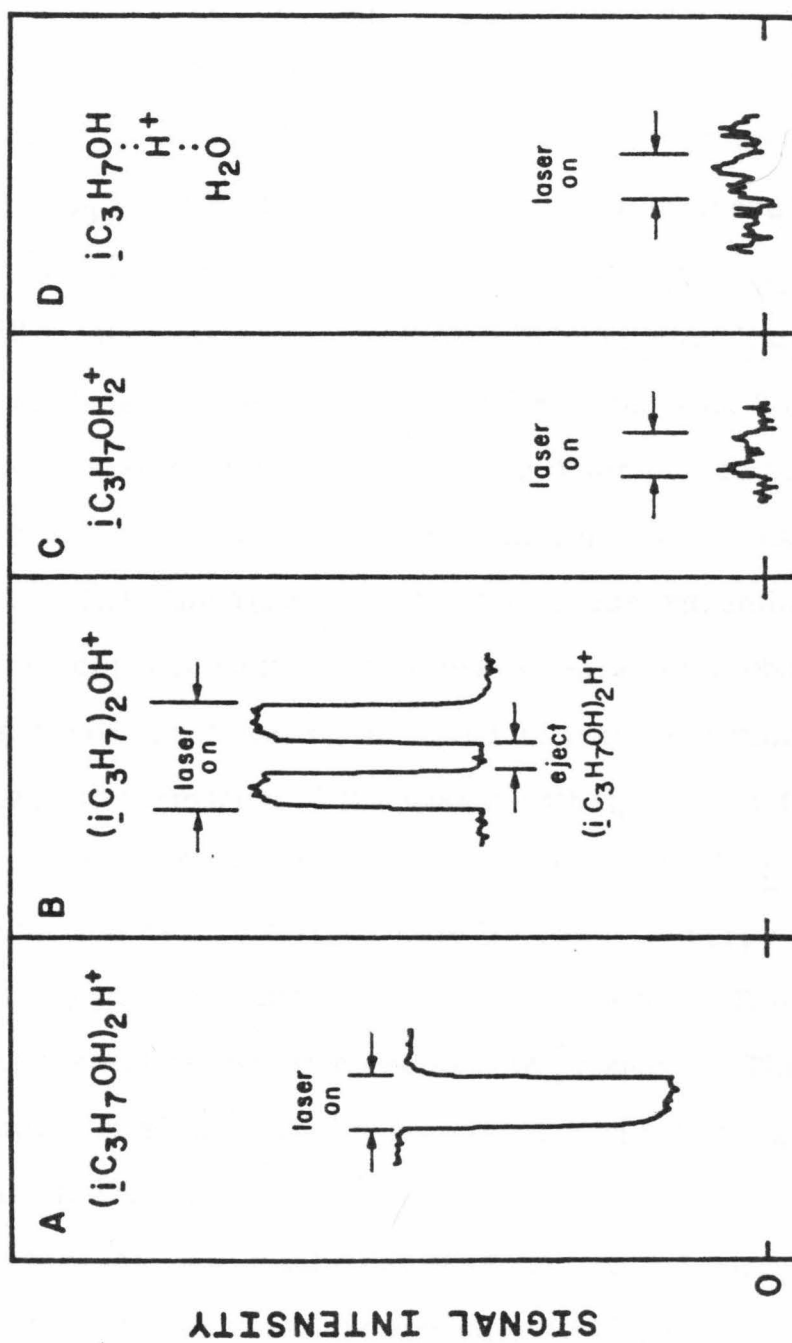
$t\text{-C}_4\text{H}_9$ and $t\text{-C}_5\text{H}_{11}$. At the pressures ($< 5 \times 10^{-6}$ Torr) used in these experiments, formation of proton bound dimer by direct bimolecular clustering of ROH_2^+ and ROH occurs only for the n-propanol case. Full details of alcohol ion-molecule chemistry including reaction sequences leading to $(\text{ROH})_2\text{H}^+$ formation⁸⁻¹⁴ and pertinent thermochemistry are published elsewhere.¹⁵

Infrared laser irradiation leads to multiphoton dissociation of each proton bound alcohol dimer investigated. By analogy to the general case shown in Figure 1 and equations 5 and 6, there are three plausible routes to decomposition of $(\text{ROH})_2\text{H}^+$, equations 7 - 9



Typical experimental results for $\text{R} = i\text{-C}_3\text{H}_7$ are shown in Figure 2. Data indicate ICR signal intensities of four ions measured at 950 ms of trapping time. Intensities of different ions are not directly comparable¹⁶ but should be multiplied by 1.00, 1.17, 0.13 and 0.29, respectively, (reading left to right). Scan A, at the far left in Figure 2, shows the decrease in proton bound alcohol dimer, $(i\text{-C}_3\text{H}_7\text{OH})_2\text{H}^+$, population caused by infrared laser irradiation (33 W cm^{-2} beginning at 500 ms of trapping time). Part B shows increase in $(i\text{-C}_3\text{H}_7)_2\text{OH}^+$ due to laser irradiation. When corrected for variations in ICR sensitivity the increase in $(i\text{-C}_3\text{H}_7)_2\text{OH}^+$ accounts for 99% of the decrease in $(i\text{-C}_3\text{H}_7\text{OH})_2\text{H}^+$. All of the laser-induced signal enhancement

FIGURE 2. ICR signal intensities measured at 950 ms of trapping time of four ions generated following 70 eV electron impact ionization of 3.1×10^{-7} Torr *i*-C₃H₇OH. Intensities should be multiplied by 1.00, 1.17, 0.13, and 0.29 for A, B, C, and D, respectively, to allow direct comparison. Laser irradiation (33 W cm^{-2}) begins at 500 ms trapping time as does double resonance ejection, where noted. Ions A, B, C, and D are identified in the Figure.



in B is eliminated by double resonance ejection (also beginning at 500 ms) of $(i\text{-C}_3\text{H}_7\text{OH})_2\text{H}^+$. This identifies reaction 8 ($R = i\text{-C}_3\text{H}_7$) as a multiphoton dissociation pathway. In Figure 2, part C shows a very slight increase in protonated alcohol resulting from laser irradiation. Double resonance (not shown) establishes this increase results from dissociation of $(i\text{-C}_3\text{H}_7)_2\text{OH}^+$. Finally, part D shows no measurable change in $(i\text{-C}_3\text{H}_7\text{OH})\text{H}^+(\text{OH}_2)$ intensity with laser irradiation. Consideration of ICR detection limits indicates no more than 2% of $(i\text{-C}_3\text{H}_7\text{OH})_2\text{H}^+$ dissociates to give a product ion other than $(i\text{-C}_3\text{H}_7)_2\text{OH}^+$. Thus we conclude that neither reaction 7 nor reaction 9 occurs for $R = i\text{-C}_3\text{H}_7$. Experimental results for the other proton bound dimers show comparable uncertainties in determining "null" reaction pathways.

Table 1 lists the alcohol proton bound dimers, enthalpy changes for reactions corresponding to processes 7-9 and the observed multiphoton dissociation pathways. Infrared activation of dimers 1, 2, 4, 7 and 9 leads to formation of the lowest enthalpy products; type I potential energy surfaces (Figure 1). $(t\text{-C}_5\text{H}_{11}\text{OH})_2\text{H}^+$, 8, is the one example which is described by a type II potential energy surface.¹⁸ The remaining proton bound alcohol dimers listed in Table 1 (3, 5 and 6) dissociate yielding two or more sets of products. These are the first examples of slow multiphoton dissociation following more than one reaction pathway.

Note that low power infrared laser activation does not open up any additional reaction channels available to $(\text{ROH})_2\text{H}^+$. Products of multiphoton dissociation of $(\text{ROH})_2\text{H}^+$, equations 5 and 6, are the same products generated by exothermic reaction of ROH_2^+ and ROH,

Table I: UNIMOLECULAR DECOMPOSITION REACTIONS OF PROTON BOUND ALCOHOL DIMERS. CIRCLED NUMBERS DENOTE OBSERVED IR LASER-DRIVEN REACTIONS.^a

dimer ion (R ₁ OH) H ⁺ (R ₂ OH)	ΔH (kcal mol ⁻¹) reaction 5	ΔH reaction 6	ΔH reaction 7	ΔH reaction 7'
1 $\underline{\sim}$ R ₁ =R ₂ =CH ₃ ^b	31	(18)	89	-
2 $\underline{\sim}$ R ₁ =R ₂ =C ₂ H ₅	32	(15)	19	-
3 $\underline{\sim}$ R ₁ =R ₂ = <u>n</u> -C ₃ H ₇	(33)	(17)	(19)	-
4 $\underline{\sim}$ R ₁ =R ₂ = <u>i</u> -C ₃ H ₇	31	(19)	22	-
5 $\underline{\sim}$ R ₁ =R ₂ = <u>s</u> -C ₄ H ₉	32	(15)	(20)	-
6 $\underline{\sim}$ R ₁ = <u>i</u> -C ₃ H ₇ ; R ₂ = <u>s</u> -C ₄ H ₉	33 ^c	(19)	(18) ^d	(24) ^e
7 $\underline{\sim}$ R ₁ =R ₂ = <u>t</u> -C ₄ H ₉	31	(20)	23	-
8 $\underline{\sim}$ R ₁ =R ₂ = <u>t</u> -C ₅ H ₁₁	31	19	(22)	-
9 $\underline{\sim}$ R ₁ = <u>i</u> -C ₃ H ₇ ; R ₂ = <u>t</u> -C ₄ H ₉	30 ^c	(13)	22 ^f	23 ^g

a) Reference 15.

b) Reference 29.

c) Assumes more basic alcohol is protonated.

d) Products are (i-C₃H₇OH)H⁺(OH₂) + trans-CH₃CH = CHCH₃.

e) Products are (s-C₄H₉OH) H⁺(OH₂) + CH₃CH = CH₂

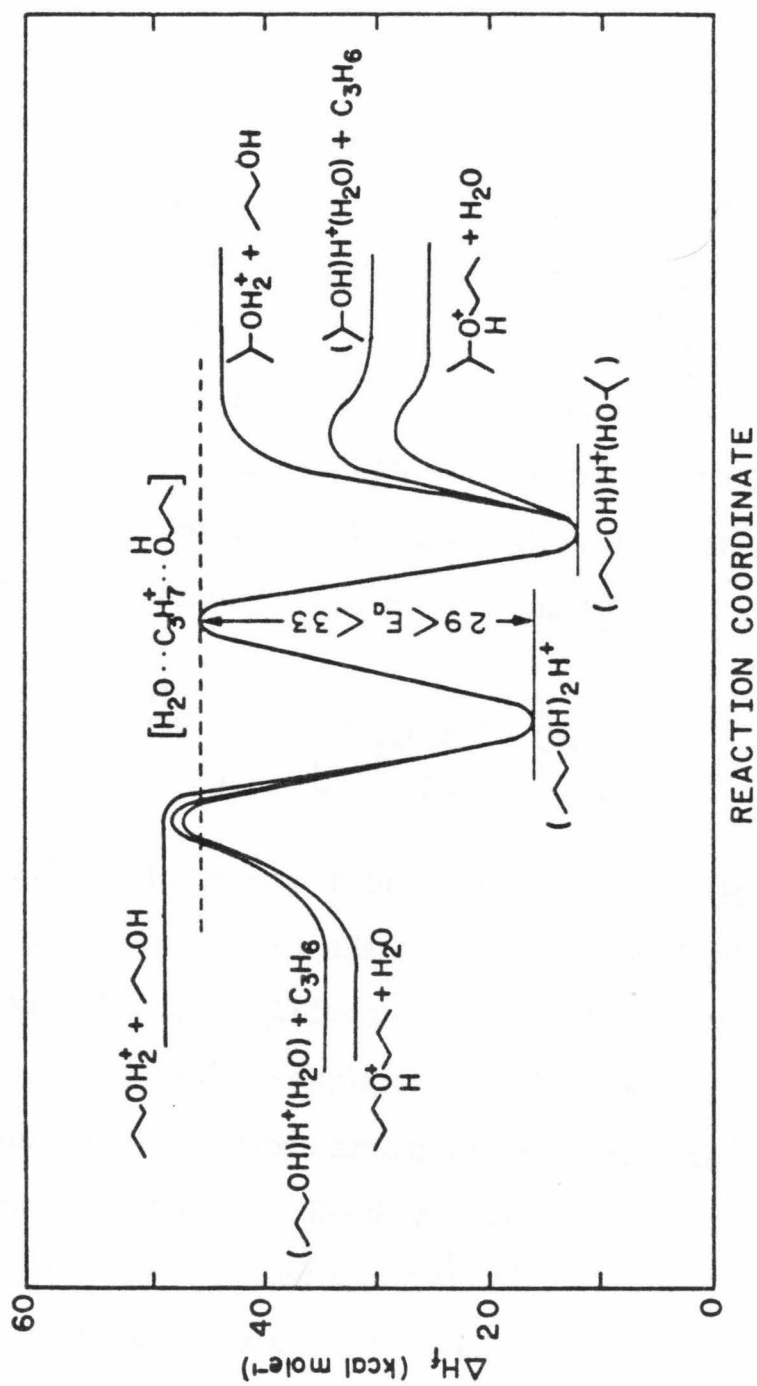
f) Products are (t-C₄H₉OH) H⁺(OH₂) + CH₃CH = CH₂

g) Products are (i-C₃H₇OH)H⁺(OH₂) + H₂C = C(CH₃)₂

equations 8 and 9. The only difference is that laser activation is more selective. For example, multiphoton dissociation of $(\text{C}_2\text{H}_5\text{OH})_2\text{H}^+$ yields exclusively $(\text{C}_2\text{H}_5)_2\text{OH}^+ + \text{H}_2\text{O}$ (Table 1) which is also the only set of products formed at pressures $< 10^{-5}$ Torr by exothermic ion-molecule reaction of $\text{C}_2\text{H}_5\text{OH}_2^+$ and $\text{C}_2\text{H}_5\text{OH}$ ^{9, 11}. This result can be understood as follows: Although the exact energy requirements for reactions 8 and 9 are unknown, the energy required for reaction 7 is well defined because simple hydrogen bond cleavage does not have an activation energy in excess of reaction endothermicity. Thus the enthalpy change (E^* in Figure 1) for dissociation of $(\text{ROH})_2\text{H}^+$ to ROH_2^+ and ROH, reaction 7, determines an upper bound to the level of infrared excitation in $(\text{ROH})_2\text{H}^+$ since decomposition is faster than continued excitation at energies above reaction threshold. No process which is endothermic relative to ROH_2^+ and ROH can be achieved by slow multiphoton dissociation of $(\text{ROH})_2\text{H}^+$. Furthermore, any exothermic reaction of ROH_2^+ and ROH (equations 5 and 6) must follow a pathway that is always lower in energy than the reactants. Such a pathway is a low energy route to decomposition of $(\text{ROH})_2\text{H}^+$ whether the activated proton bound dimer is prepared by collision of ROH_2^+ and ROH or by infrared laser excitation.

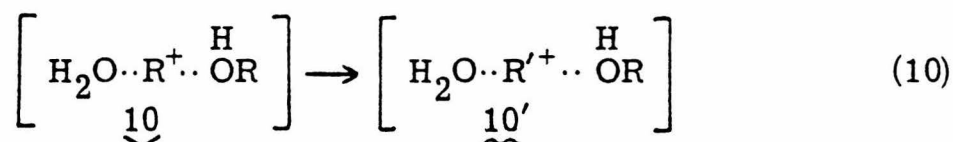
Proton bound alcohol dimers 3, 5 and 6 each yield more than one set of products from slow multiphoton dissociation (Table 1). The measured branching ratios are invariant to changes in laser wavelength ($942 - 1079 \text{ cm}^{-1}$) or laser power ($27 \text{ to } 63 \text{ W cm}^{-2}$). Dimers 3, 5 and 6 contain n-propanol or 2-butanol. Of the alcohols used in this study, only those two can isomerize to more stable alcohols. We infer that

FIGURE 3. Reaction coordinate diagram for isomerization and decomposition of the proton bound dimer of n-propanol. Thermochemical data from reference 15.



more than one set of dissociation products is formed because an isomerization which occurs in the transition state releases sufficient energy to make accessible two or three reaction channels. This corresponds to case III in Figure 1. Results of a previous study indicate slow multiphoton dissociation is extremely sensitive to small differences in activation energies implying more than one set of products can arise from different transition states only if the corresponding activation energies are almost identical. It is highly unlikely that an accidental degeneracy exists in three different proton bound dimers.

A candidate for the transition state involving alkyl isomerization entails a complex^{19, 20} formed by an alkyl cation R^+ , water and alcohol ROH, in which R^+ isomerizes to R'^+ ($\underline{10}$ and $\underline{10'}$).

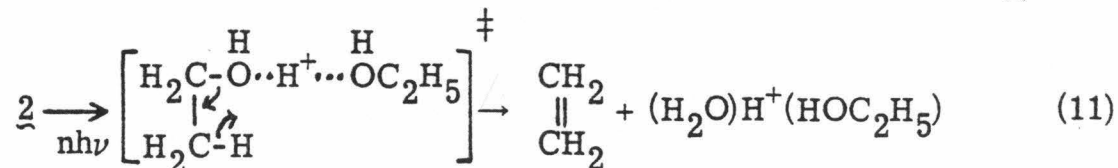


Loss of H_2O results in formation of protonated ether $(\text{R})(\text{R}')\text{OH}^+$. Alternatively deprotonation of R'^+ leads to $(\text{R}'\text{OH})\text{H}^+(\text{OH}_2)$ plus an olefin or recombination of R'^+ and H_2O forms $\text{R}'\text{OH}_2^+ + \text{ROH}$. Ion-molecule complexes have been invoked to explain isotopic label exchange processes¹⁹ and isomer distributions among neutral products²⁰ of several ion-molecule reaction systems. Bonding between the ion and neutral components is electrostatic not covalent.^{19, 20}

Thermochemical constraints composed on the isomerization and decomposition of $(\underline{n}\text{-C}_3\text{H}_7\text{OH})_2\text{H}^+$, $\underline{3}$, are shown in Figure 3. ΔH_f for the transition state must be < 49 kcal/mol, otherwise direct dissociation to $\underline{n}\text{-C}_3\text{H}_7\text{OH}_2^+$ and $\underline{n}\text{-C}_3\text{H}_7\text{OH}$ (reaction 7) would occur. As-

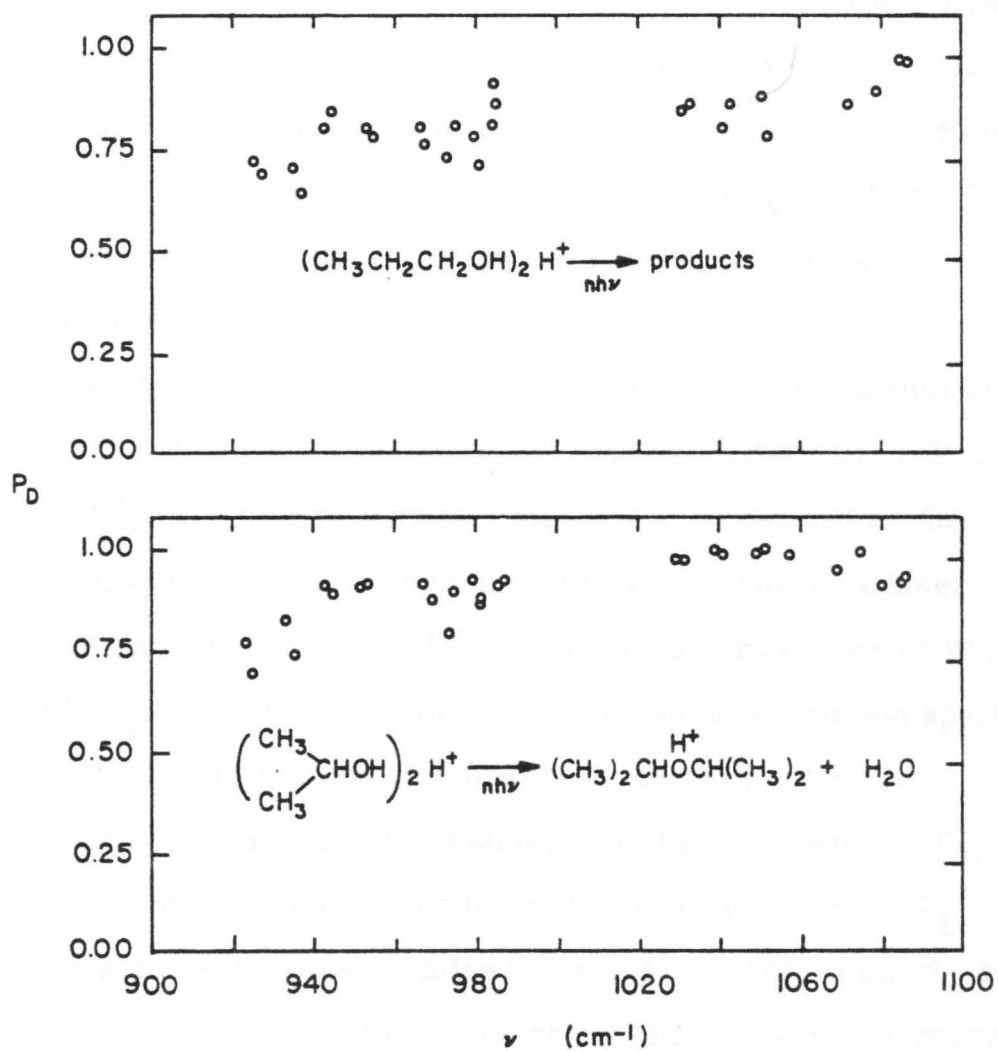
suming only one alkyl group isomerizes²¹ the transition state heat of formation must be >44.5 kcal/mol to allow formation of $\underline{i}\text{-C}_3\text{H}_7\text{OH}_2^+$ and $\text{C}_3\text{H}_7\text{OH}$. The activation barrier for reaction is determined to be $29 < E_a < 33$ kcal/mol. Furthermore, as seen at the left side of Figure 3, enthalpies of transition states leading directly to $(\underline{n}\text{-C}_3\text{H}_7)_2\text{OH}^+ + \text{H}_2\text{O}$ (reaction 5) and to $(\underline{n}\text{-C}_3\text{H}_7\text{OH})\text{H}^+(\text{OH}_2) + \text{C}_3\text{H}_6$ (reaction 6) must both be above ΔH_f of the isomerization transition state. This places the former two values very close in energy to $\underline{n}\text{-C}_3\text{H}_7\text{OH}_2^+ + \text{C}_3\text{H}_7\text{OH}$. Such a requirement is consistent with the observation that for $\text{R} = \underline{n}\text{-C}_3\text{H}_7$ reactions 5 and 6 occur at rates comparable to each other and to the direct clustering reaction rate. Analysis similar to that shown in Figure 3 for the isomerization reaction of dimer 5 brackets the activation energy between 13 and 26 kcal/mole.²²

Of the three plausible dimer decomposition reactions, equations 7-9, process 8 entails the most extensive rearrangement yet is the most prevalent reaction. There is no obvious direct mechanism for the dehydration reaction. Most likely the dissociation proceeds through an ion-molecule complex such as 10. In contrast, one can imagine* a simple four-center intermediate²³ available to all dimers (except 1) leading directly to olefin elimination, reaction 9. This intermediate is shown below for the ethanol proton bound dimer, 2.



However, only ion 8 dissociates exclusively via pathway 9. The slight

FIGURE 4. Infrared photodissociation spectra of isomeric ions (n-C₃H₇OH)₂H⁺ (top) and (i-C₃H₇OH)₂H⁺ (bottom). For upper spectrum laser power is 34 W cm⁻² and n-C₃H₇OH pressure is 4.1×10⁻⁷ Torr. In lower spectrum, laser power is 17 W cm⁻² and i-C₃H₇OH pressure is 4.4×10⁻⁷ Torr. In both spectra ions are formed by a 70 eV 10 ms pulse of electrons, laser irradiation begins at 500 ms trapping time and ions are detected at 1.0 s trapping time.



difference in structure between t-butanol and t-amyl alcohol does not seem sufficient to explain a preference for the four-center intermediate in decomposition of 8 compared to reaction of (t-C₄H₉OH)₂H⁺, 7. In fact, reactions proceeding through four-center intermediates such as shown in equation 11 while not formally "forbidden"²³ by orbital symmetry consideration usually show sizable activation barriers.²⁴ Thus, it appears that all ions (ROH)₂H⁺ dissociate through an ion-molecule intermediate²⁵ 10 and the selectivity demonstrated by 1, 2, 4 and 7-9 reflects differences in activation energies for the various pathways to decomposition of 10.

Figure 4 shows the variation in photodissociation yield with laser wavelength (925-1080 cm⁻¹) for isomeric ions (n-C₃H₇OH)₂H⁺, 3, and (i-C₃H₇OH)₂H⁺, 4. Photodissociation yield, P_D, is defined as the fraction of ions decomposed by 500 ms laser irradiation at a laser power of 34 W cm⁻² for (n-C₃H₇OH)₂H⁺, upper spectrum, and 17 W cm⁻² for (i-C₃H₇OH)₂H⁺, lower spectrum. Neither photodissociation spectrum has any distinct, readily identified features. Instead, both are characterized by a continuous band showing a slight increase in P_D with increasing photon energy. At lower laser powers, where P_D values are not as close to "saturation" (i. e., P_D = 1.00), a check of several laser wavelengths indicates no change in the overall appearance of the photodissociation spectra of 3 and 4. Although both spectra in Figure 4 show similar P_D values at each wavelength, the laser powers used differ by a factor of two. Previous studies indicate apparent multiphoton photodissociation cross sections to be a very sensitive function of the ion-molecule collision rate.⁶⁻⁷ Data for both spectra

in Figure 4 were obtained at nearly identical pressure (4.1×10^{-7} Torr $n\text{-C}_3\text{H}_7\text{OH}$ for the upper spectrum compared with 4.4×10^{-7} Torr $i\text{-C}_3\text{H}_7\text{OH}$ for the lower spectrum). Thus, these results indicate $(i\text{-C}_3\text{H}_7\text{OH})_2\text{H}^+$ has a much larger photodissociation cross section at each wavelength studied than does $(n\text{-C}_3\text{H}_7\text{OH})_2\text{H}^+$.⁵⁻⁷

Conclusions

Slow multiphoton dissociation represents a sensitive probe of reaction potential energy surfaces. Products of multiphoton dissociation of proton bound dimer $(\text{ROH})_2\text{H}^+$ are also products of an exothermic reaction of $\text{ROH}_2^+ + \text{ROH}$. Under special circumstances accurate quantitative determinations of activation energies for $(\text{ROH})_2\text{H}^+$ decomposition are possible. All observed alcohol dimer decompositions, including those giving multiple sets of products, are consistent with the formation of an electrostatically bound complex intermediate.

Multiphoton dissociation reaction can be used to distinguish structural isomers of ions. Proton bound dimers 3 and 4 have identical charge-to-mass ratios, and even identical infrared photodissociation spectra yet the isomers yield different characteristic sets of products from multiphoton dissociation. Similarly isomers 5 and 7 form distinguishable sets of products following infrared laser radiation. Although the sample of photodissociation spectra shown in Figure 4 represents a negative result, other systems should demonstrate greater wavelength selectivity.

In light of current interest in mass spec-mass spec techniques²⁶ used to analyze complicated mixtures and to "fingerprint" ions by their secondary fragmentation patterns, infrared multiphoton excitation

represents a novel method for ion decomposition. Although low power ($< 100 \text{ W cm}^{-2}$) infrared radiation leads to decomposition exclusively by the lowest energy pathway,⁵⁻⁷ pulsed laser irradiation at high peak powers ($\geq 1 \text{ MW cm}^{-2}$) is known to make multiple reaction channels energetically accessible.^{27, 28} The only requirement is that infrared absorption rates exceed unimolecular decomposition rates of the irradiated molecule. Appropriate choice of laser power selects for either the case in which only the lowest energy decomposition occurs, or the regime in which multiple fragmentations are possible.

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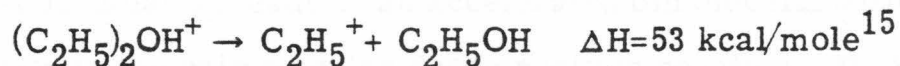
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CHAPTER VI

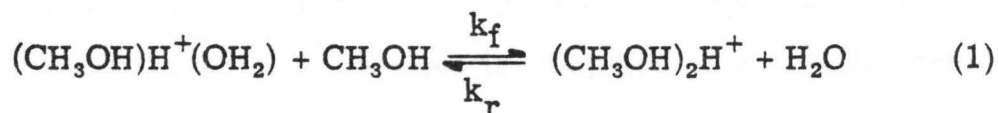
SELECTIVE ENHANCEMENT OF BIMOLECULAR RE-
ACTION RATES BY OVER THREE ORDERS OF MAG-
NITUDE USING LOW INTENSITY CW INFRARED
LASER RADIATION.

Selective Enhancement of Bimolecular Reaction Rates by Over Three Orders of Magnitude Using Low-Intensity CW Infrared Laser Radiation.

Sir:

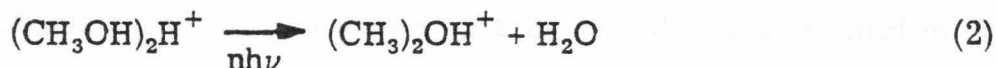
Chemists are understandably intrigued by the possibility of selective unimolecular dissociation processes using pulsed high-power infrared lasers.¹ The fervor in this field somewhat overshadows the equally interesting possibility of utilizing infrared lasers to selectively modify bimolecular reaction rates.² We wish to report the use of a relatively low power (34 W/cm²) CW infrared laser to selectively increase the rate constant of a single bimolecular reaction by three orders of magnitude in a complex system, thus achieving a situation which is distinctly nonthermal. The reacting species are gas phase ions which are generated, stored for periods up to 1 second, and detected using the techniques of ion cyclotron resonance (ICR) spectroscopy. Full details of ICR spectroscopy^{3,4} including modifications for infrared photochemistry⁵ are published elsewhere.

The equilibrium shown below, reaction 1, is characterized by



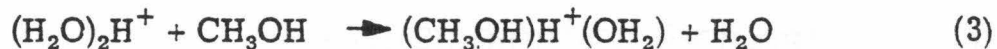
forward rate constant $k_f = 5.0 \times 10^{-10} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and reverse rate constant $k_r = 8.2 \times 10^{-15} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. k_f is measured using ICR techniques, whereas k_r is calculated from k_f and the equilibrium constant K . The value $\Delta G = -6.5 \pm 1.0 \text{ kcal/mole}$ ^{6,7} for reaction 1 gives $K = 6.1 \times 10^4$ in favor of proton-bound methanol dimer, $(\text{CH}_3\text{OH})_2\text{H}^+$, at room temperature.

During CW laser irradiation ($\bar{\nu} = 947 \text{ cm}^{-1}$) at 34 W/cm^2 , the reverse reaction rate is enhanced by more than three orders of magnitude to $k_{\text{r}}^{\text{IR}} = 2.6 \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. ICR double resonance^{3, 8} shows that the forward reaction is unaffected by laser irradiation.⁹ In addition to the infrared-driven bimolecular reaction, the proton-bound methanol dimer undergoes multiphoton excitation followed by unimolecular decomposition, reaction 2. The reaction endothermicity,

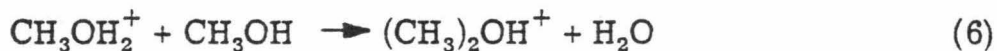
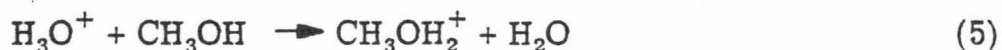


$\Delta H = 17 \text{ kcal/mole}$ ^{6, 7} (corresponding to 7 infrared photons absorbed), represents the minimum energy needed for process 2. At a total energy of $33 \pm 1 \text{ kcal/mole}$ $(\text{CH}_3\text{OH})_2\text{H}^+$ dissociates to CH_3OH_2^+ and CH_3OH .^{6, 7} Failure to observe this process indicates reaction 2 requires less than 33 kcal/mole of excitation.

At the pressures ($< 10^{-5} \text{ Torr}$) and ion trapping times (up to 1s) used in these experiments, proton bound methanol dimer is not produced in pure methanol.⁷ A recently identified sequence of bimolecular reactions in a mixture of Br_2CHCH_3 and H_2O yield the proton-bound dimer of water.¹⁰ Sequential displacement of water from $(\text{H}_2\text{O})_2\text{H}^+$ by methanol yields the proton bound dimer of methanol, reactions 3 and 4. Other reactions occur to form CH_3OH_2^+ and



$(\text{CH}_3)_2\text{OH}^+$, processes 5 and 6. Details of the ion-molecule chemistry



are given elsewhere.¹⁰

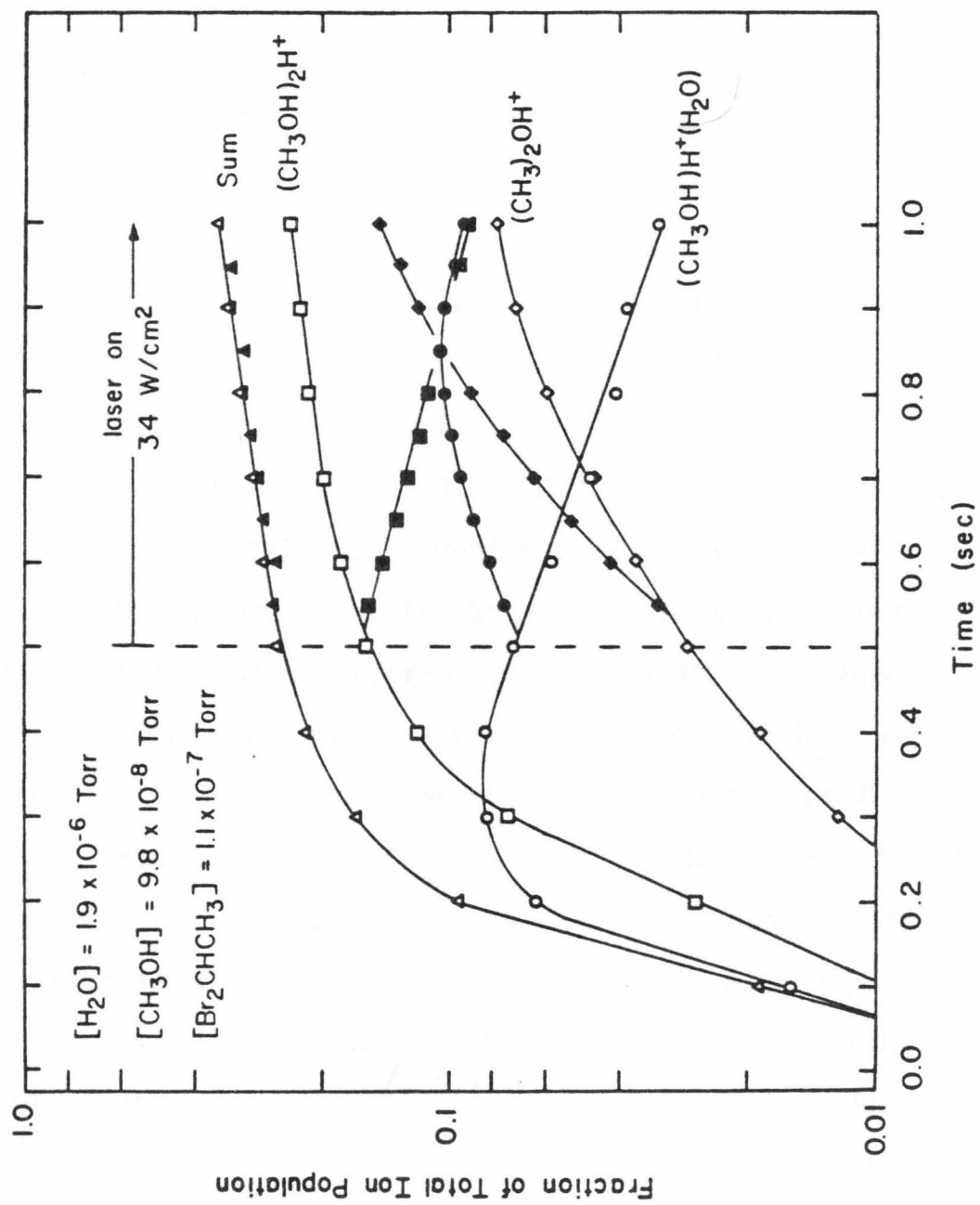
Figure 1 shows the temporal variation of ion abundance for those species involved in both the bimolecular and unimolecular infrared-driven reactions 1 and 2. The other ions in the system are omitted for clarity. Open symbols indicate normalized intensities of $(\text{CH}_3\text{OH})_2\text{H}^+$, $(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)$ and $(\text{CH}_3)_2\text{OH}^+$ in the unperturbed system. Irradiation beginning at 0.5 s of trapping time alters the intensities of the three ions as indicated by the filled symbols. All other ions present are unaffected by laser radiation. Also shown in Figure 1 are the summed intensities of $(\text{CH}_3\text{OH})_2\text{H}^+$, $(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)$ and $(\text{CH}_3)_2\text{OH}^+$ both with (filled triangles) and without (open triangles) laser irradiation. Invariance of the summed intensities to irradiation indicates these three ions are the only reactants and products of the infrared-driven reactions.

Equations 7 and 8 govern the temporal abundance of the species

$$\begin{aligned} \frac{d[(\text{CH}_3\text{OH})_2\text{H}^+]}{dt} &= -k_u[(\text{CH}_3\text{OH})_2\text{H}^+] - k_r^{\text{IR}}[(\text{CH}_3\text{OH})_2\text{H}^+][\text{H}_2\text{O}] \\ &= +k_f[(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)][\text{CH}_3\text{OH}] \end{aligned} \quad (7)$$

$$\begin{aligned} \frac{d[(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)]}{dt} &= -k_f[(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)][\text{CH}_3\text{OH}] \\ &\quad + k_r^{\text{IR}}[(\text{CH}_3\text{OH})_2\text{H}^+][\text{H}_2\text{O}] \end{aligned} \quad (8)$$

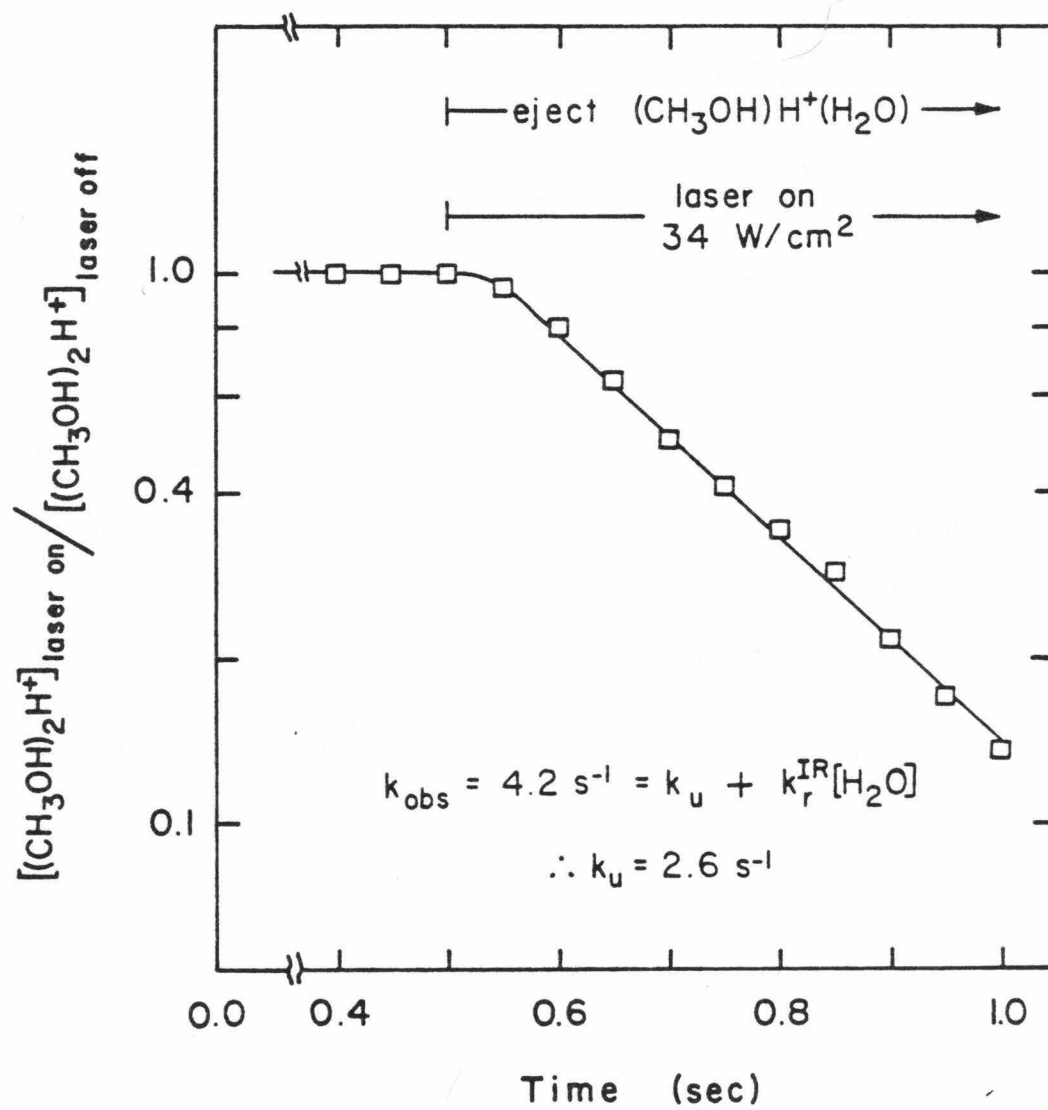
FIGURE 1. Variation of ion abundance with trapping time for the key ions derived from a mixture of 1.9×10^{-6} Torr H_2O , 9.8×10^{-8} Torr CH_3OH and 1.1×10^{-7} Torr Br_2CHCH_3 . Open symbols indicate unperturbed $(\text{CH}_3\text{OH})_2\text{H}^+$ ($\square$), $(\text{CH}_3)_2\text{OH}^+$ ($\diamond$) and $(\text{CH}_3\text{OH})\text{H}^+(\text{H}_2\text{O})$ ($\circ$), and filled symbols are ion intensities during CW laser irradiation (34 W/cm^2 at 947 cm^{-1}) beginning at 0.5 s trapping time. Triangles indicate sum of the three ion intensities with ($\blacktriangle$) and without ($\triangle$) laser irradiation. Ions are formed by a 70 eV, 10 ms electron beam pulse.



of interest in this system. At 0.5 s of trapping time, when laser irradiation starts, reaction 3 has gone to completion and so is not included in equation 8. In Figure 1, the curve drawn through (laser on) data points for $(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)$ exhibits a maximum at ~ 850 ms. At the maximum, $d[(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)]/dt = 0$ and k_r^{IR} can be evaluated using equation 8 where the ion intensities are measured at 850 ms. Substitution of the measured quantities into equation 8 gives $k_r^{\text{IR}} = 2.6 \times 10^{-11} \text{ cm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

In a second experiment ICR double resonance was used to eject $(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)$ beginning at 0.5 s of trapping time. The timescale for ejection is short compared with the time between collisions.^{4, 8} This reduces the concentration of $(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)$ to zero and prevents further formation of $(\text{CH}_3\text{OH})_2\text{H}^+$, reaction 4. Equation 7 is now modified since the third term on the right-hand side becomes zero, predicting laser-induced decomposition of $(\text{CH}_3\text{OH})_2\text{H}^+$ to be pseudo-first order (in dimer concentration) with an observed rate $k_{\text{obs}} = k_u + k_r^{\text{IR}} [\text{H}_2\text{O}]$. Figure 2 shows a semilog plot of fractional $(\text{CH}_3\text{OH})_2\text{H}^+$ abundance (defined as the ratio of ion intensity with the laser on to the signal intensity with the laser off) as a function of trapping time when both ejection of $(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)$ and laser irradiation begin at 0.5 s. Decomposition is first-order as predicted, with the negative of the slope of the straight line in Figure 2 equal to $k_{\text{obs}} = 4.2 \text{ s}^{-1}$. Thus, $k_u = 2.6 \text{ s}^{-1}$. For the laser power and neutral gas pressures used, the unimolecular decomposition is favored over the laser-driven bimolecular reaction by a factor of 1.6:1.

FIGURE 2. Semilog plot of fractional ion abundance vs. trapping time for laser induced reaction of $(\text{CH}_3\text{OH})_2\text{H}^+$. Both double resonance ejection of $(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)$ and laser irradiation begin at 0.5 s. Neutral pressures and laser parameters are the same as in Figure 1.



Both the forward and backward reactions in equilibrium 1 proceed through a common intermediate, $(\text{CH}_3\text{OH})_2\text{H}^+(\text{OH}_2)$.¹¹ The competitive dissociation of this species is evaluated using RRKM theory,¹²⁻¹⁴ where the internal energy is taken as absorbed infrared energy added to a 300° K Boltzmann distribution of vibrational energy. At an added energy of 10.5 kcal/mole the calculated ratio of H_2O to CH_3OH loss is equal to the observed value of $k_f/k_r^{\text{IR}} = 19.8$. This implies $(\text{CH}_3\text{OH})_2\text{H}^+$ absorbs an average of 3.9 infrared photons ($\bar{\nu} = 947 \text{ cm}^{-1}$) prior to bimolecular reaction with H_2O .

Selective excitation of reactants not only represents an interesting tool for experimental chemical dynamics, it offers the possibility of using measured changes in reaction rates as a spectroscopic probe. The use of infrared excitation to alter bimolecular reaction rates should provide a general technique of obtaining vibrational spectra of ions and transient molecules.

Acknowledgment. We wish to thank Professor R. Marcus for helpful discussions. This work was supported by the United States Department of Energy.

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discussed in detail elsewhere.^{15a} Since both CH_3OH ^{15b} and $(\text{CH}_3\text{OH})_2\text{H}^+$ absorb in the $10\ \mu\text{m}$ region it might be expected that $(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)$ also absorbs. However, no evidence is obtained for laser excitation enhancing the reverse of reaction 3 or for multiphoton dissociation of $(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)$ to CH_3OH_2^+ and H_2O (25 kcal/mole).⁶ Both results suggest $(\text{CH}_3\text{OH})\text{H}^+(\text{OH}_2)$, in comparison to $(\text{CH}_3\text{OH})_2\text{H}^+$, is not heated significantly by the infrared laser. Based on the proposed kinetic scheme, heating might result in a slight decrease in k_f for reaction 1, which would be difficult to detect.

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CHAPTER VII

INFRARED PHOTOCHEMISTRY OF ETHYLENE CLUSTERS.

Infrared Photochemistry of Ethylene Clusters

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Abstract

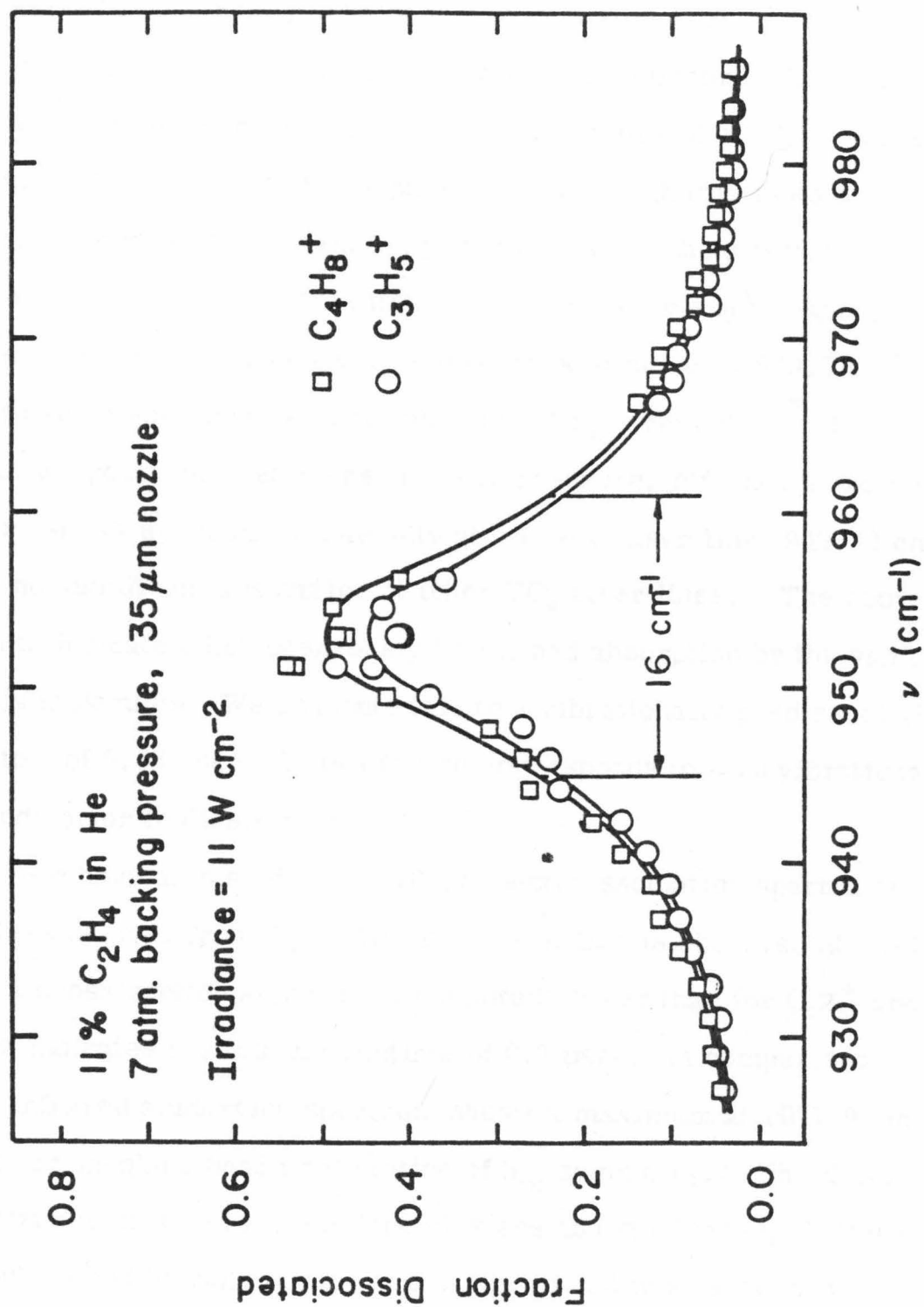
Infrared irradiation of ethylene clusters formed in supersonic molecular beams, using a low power cw CO₂ laser, results in the photodissociation of a large fraction of the van der Waals molecules. Under such conditions, infrared absorption intensity exhibits first-order power dependence and is readily detected as loss in molecular beam intensity. Intramolecular energy transfer rates, determined by measuring spectral linewidths, are shown to vary with the vibrational mode initially excited. Ethylene clusters containing one quantum of vibrational energy corresponding to the ν_7 fundamental in the monomer (949 cm⁻¹) have a vibrationally predissociative lifetime of 0.33 psec. In comparison, the relaxation rate of ethylene-d₄ clusters with one quantum of excitation corresponding to the ν_{12} (1078 cm⁻¹) mode of C₂D₄ is 0.7 psec.

Considerable experimental¹⁻⁴ and theoretical^{5,6} effort has been applied to the study of decomposition processes of electronically and vibrationally excited van der Waals molecules. These are relatively simple systems for studying dynamics of intramolecular energy transfer. When high-power pulsed CO₂ lasers are used to dissociate (C₂H₄)₂, a broad spectrum is observed in the region of the ν_7 vibrational mode of the monomer.¹ We report direct observation of efficient infrared photodissociation of ethylene clusters using low-power cw laser radiation. When low-power radiation is used, the homogeneous linewidth observed is significantly narrower than suggested by the pulsed laser experiments of Gentry.¹

Ethylene clusters are formed in a molecular beam by supersonic expansion of ethylene mixed with helium. The molecular beam composition is monitored with a quadrupole mass spectrometer positioned 65 cm from the nozzle. An unfocussed infrared CO₂ laser beam is directed coaxially to the molecular beam through the ionizer of the mass spectrometer. Photodissociation is detected as the laser-induced change in the molecular beam mass spectrum.

A typical infrared photodissociation spectrum is shown in Figure 1. In this case, the molecular beam is formed by expansion of an 11% C₂H₄-He mixture at 7 atm pressure using a 35 μ m nozzle. Data are given for fractional attenuation of C₃H₅⁺ (m/e 41) and C₄H₈⁺ (m/e 56) signal intensities as a function of laser wavelength. At the maximum laser power available at 951 cm⁻¹ (laser linewidth <10⁻² cm⁻¹) 80% of the van der Waals molecules are dissociated

FIGURE 1. Infrared photodissociation spectra of ethylene clusters.
The solid curves are Lorentzian profiles.



without saturating the transition. In both cases the spectra exhibit Lorentzian lineshapes with maxima at $\nu_0 = 953 \text{ cm}^{-1}$ and linewidths (FWHM) of $16 \pm 3 \text{ cm}^{-1}$. The observed photodissociation lineshapes are invariant to changes in laser power. Furthermore, the position and width of the bands are independent of changes of ethylene concentration (3.6% to 100%) in the expansion even though this is equivalent to altering the molecular beam temperature and the distribution of ethylene cluster sizes. Within the CO_2 laser wavelength region, monomeric ethylene has a single absorption band, $\nu_7 = 949.2 \text{ cm}^{-1}$, due to an out-of-plane bending vibration of b_{2u} symmetry.⁷ The photoacoustic spectrum of ethylene at 1 atm pressure, obtained using a CO_2 laser, shows appreciable intensity at a single laser line, 949.48 cm^{-1} , with no significant absorption at other CO_2 laser lines.⁸ The above results indicate a homogeneously broadened absorption by the van der Waals molecules. We attribute this to a vibrationally predissociative lifetime of 0.33 psec. This lifetime corresponds to ~ 10 vibrational periods prior to dissociation.

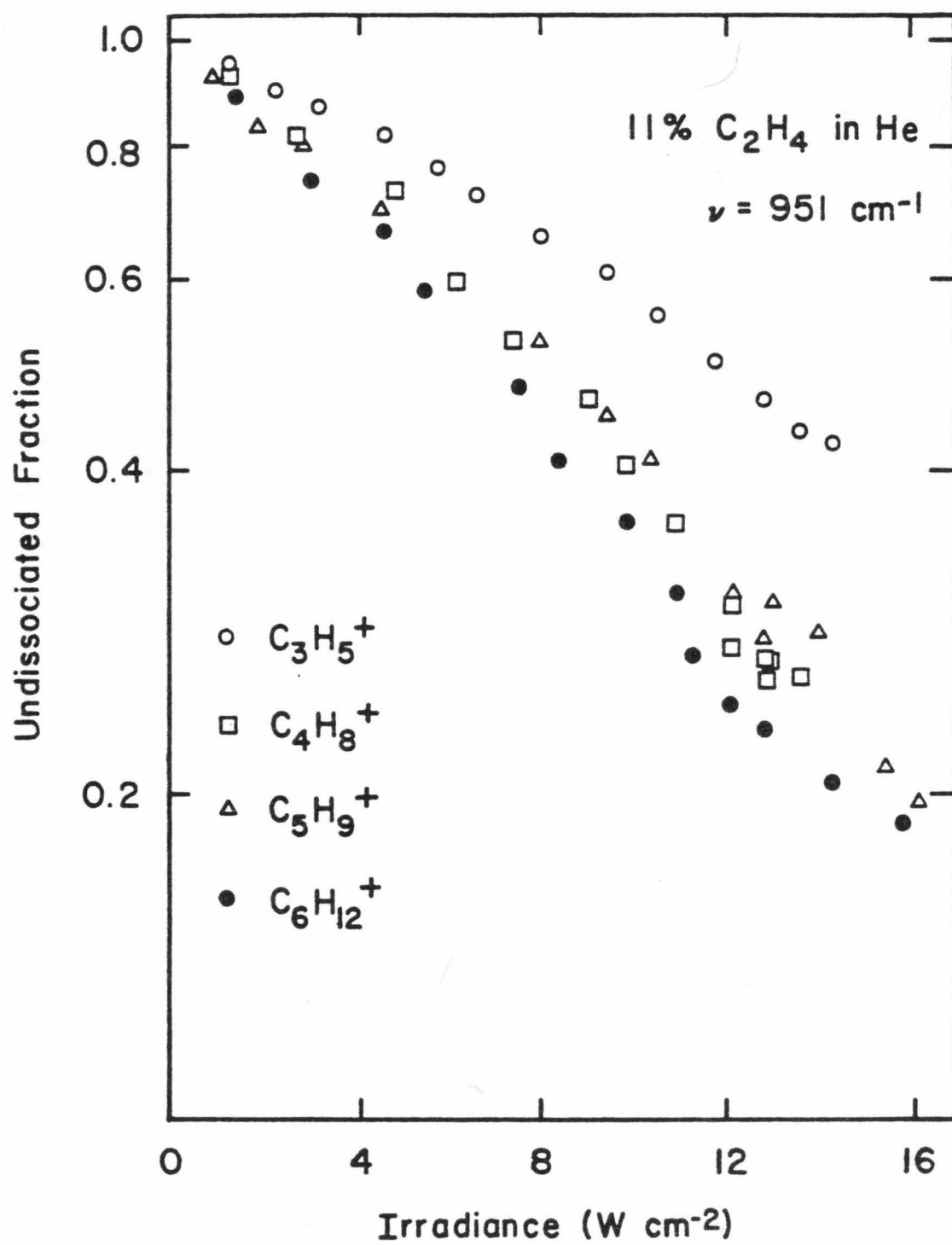
We have also studied the $10 \mu\text{m}$ photodissociation spectra of clusters derived from C_2D_4 (10% in He). A line is observed at 1074 cm^{-1} with a cross section an order of magnitude lower than for C_3H_5^+ and which indicates a minimum lifetime of 0.7 psec. In comparison, the C_2D_4 infrared absorption spectrum shows a maximum at 1077.9 cm^{-1} due to an in-plane bending vibration of b_{3u} symmetry.⁷ The difference in lifetimes obtained for ethylene clusters and ethylene- d_4 clusters can be understood by examination of the vibrational modes excited.¹ Assuming ethylene clusters form with molecular planes parallel, as

is observed in the crystal,⁹ then the out-of-plane bending mode should be more efficient than an in-plane vibration at leading to dissociation.

Figure 2 shows the variation of the logarithm of photodissociation yield, monitored at four ion masses, as a function of laser power at fixed wavelength. The ions are $C_3H_5^+$ (m/e 41), $C_4H_8^+$ (m/e 56), $C_5H_9^+$ (m/e 69), and $C_6H_{12}^+$ (m/e 84). In each case data points fall on a straight line indicating that the undissociated fraction of molecules, F , follows $F = \exp(-\Phi\sigma t)$, where Φ is the photon flux, σ is the photodissociation cross section, and t is the irradiation time. No saturation is observed at irradiances up to 17 W cm^{-2} . The four apparent cross sections are unequal and depend on the ethylene concentration in the expansion indicating that photodissociation of several cluster sizes is detected as intensity loss at a single mass peak. For example, electron impact ionization of ethylene trimers, $(C_2H_4)_3$, forms fragment ions $C_3H_5^+$, $C_4H_8^+$, and $C_5H_9^+$ as well as the parent ion $C_6H_{12}^+$. Analysis of the changes in infrared photodissociation cross section with molecular beam composition yields an upper bound value for the ethylene dimer cross section of $\sigma_2 = 9.2 \times 10^{-19} \text{ cm}^2$ and a lower bound value for the ethylene trimer cross section of $\sigma_3 = 1.7 \times 10^{-18} \text{ cm}^2$.

In the power regime of these experiments, photodissociation spectral linewidths are dominated by lifetime broadening providing valuable information on intramolecular energy transfer rates. Differences in observed lifetimes of ethylene clusters and ethylene- d_4 clusters show relaxation rates vary with the vibrational mode initially excited. Dimers and trimers of ethylene exhibit similar photodissociation maxima and lifetimes.

FIGURE 2. Power dependences of the photodissociation yield. The supersonic expansion conditions are 7 atm backing pressure and 35 μm nozzle diameter.



The narrow linewidths and efficient cross sections of low-power IR photodissociation enhance prospects of isotope selective dissociation at greatly reduced photon expense compared to standard techniques. Similarly, these results suggest that cluster intensities can be conveniently modulated for phase sensitive detection in spectroscopic or scattering experiments. There are many aspects of this process which merit further investigation.

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CHAPTER VIII

INFRARED PHOTODISSOCIATION OF VAN DER WAALS
MOLECULES CONTAINING ETHYLENE.

Infrared Photodissociation of van der Waals
Molecules Containing Ethylene

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Abstract

Infrared ($925\text{--}1080\text{ cm}^{-1}$) photodissociation of van der Waals molecules containing ethylene are described. $(\text{C}_2\text{H}_4)_2$, $(\text{C}_2\text{H}_4)_3$, $(\text{C}_2\text{H}_4)_5$, $(\text{C}_2\text{H}_4)_7$, $(\text{C}_2\text{D}_4)_2$, $\text{Ar}\cdot\text{C}_2\text{H}_4$, $\text{Kr}\cdot\text{C}_2\text{H}_4$, and $\text{C}_2\text{F}_4\cdot\text{C}_2\text{H}_4$ are formed in supersonic molecular beams and irradiated by a cw CO_2 laser (power $< 20\text{ W cm}^{-2}$). Photodissociation lineshapes and power dependences give excellent agreement with a lineshape function derived from a two-level-plus-decay model. Results are also compared with theoretical descriptions of pre-dissociation of triatomic van der Waals molecules. Absolute transition probabilities are obtained from the infrared photodissociation results. Pre-dissociative lifetimes are $0.3\text{--}0.9\text{ psec}$ for the clusters studied. Evidence for at least two distinct sites in higher clusters $[(\text{C}_2\text{H}_4)_5\text{ and }(\text{C}_2\text{H}_4)_7]$ is reported. Absorption by ethylene molecules on the periphery of the cluster leads to a very rapid dissociation as observed in $(\text{C}_2\text{H}_4)_2$ and $(\text{C}_2\text{H}_4)_3$. Following excitation of ethylene molecules located at the cluster center, many van der Waals bonds need be broken with the result that the cluster remains intact during the timescale of the experiment.

INTRODUCTION

Many current studies of intramolecular energy transfer utilize van der Waals molecules as the reacting species.¹⁻⁶ In particular, van der Waals molecules provide relatively simple systems amenable to detailed investigation by experimentalists and theoreticians. These species, formed in supersonic molecular beams, are rotationally and vibrationally cold. Excitation with a narrow band laser prepared a well-defined, well-characterized state of the van der Waals molecules. Energy transfer occurs in a collision-free environment resulting in rupture of the very weak bond.

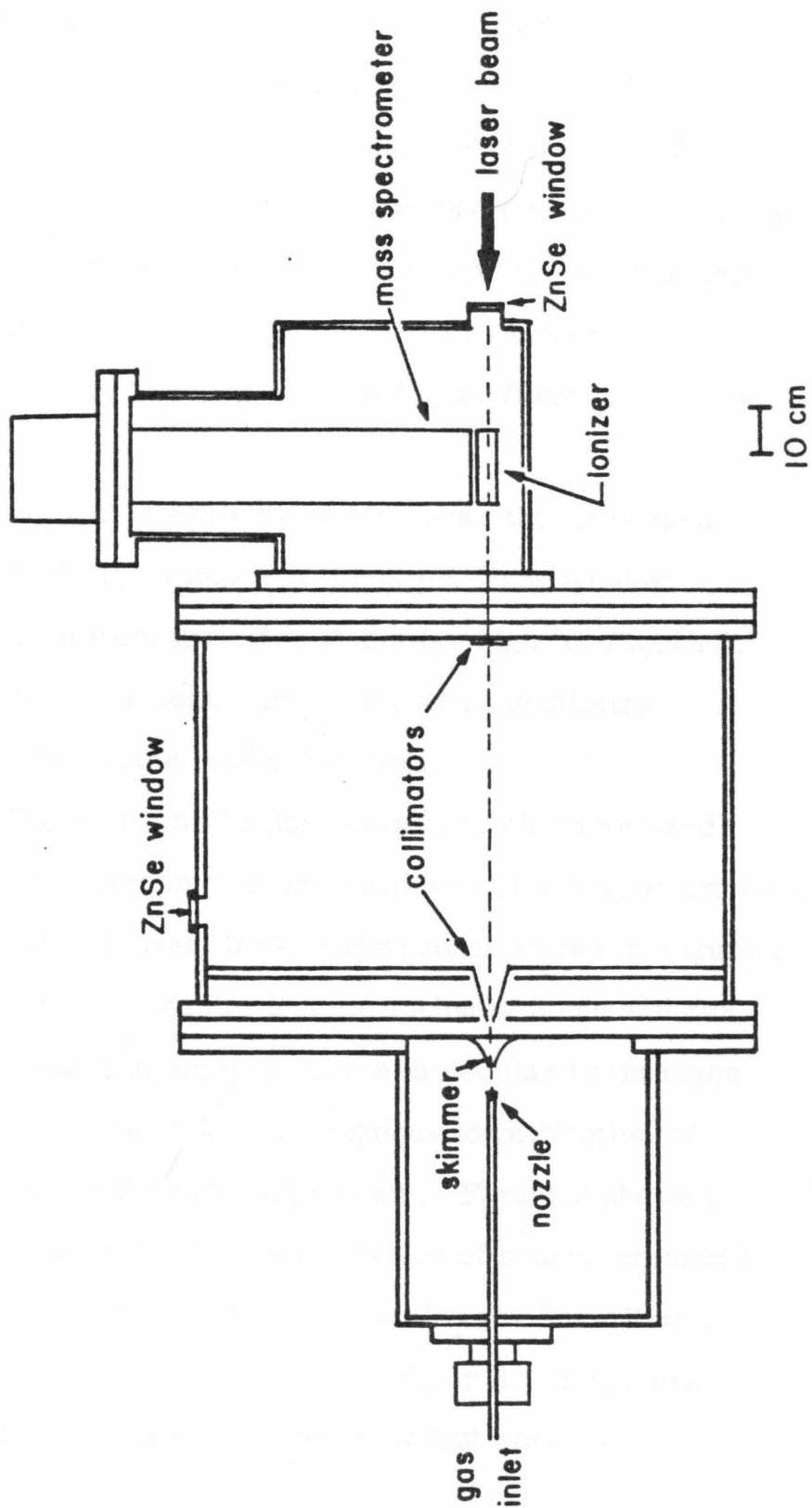
Recently, we reported observation of efficient infrared photodissociation of ethylene clusters using low-power cw laser radiation.⁷ Low-power radiation yields photodissociation spectra considerably narrower than obtained by Gentry using high-power pulsed laser radiation.³ In the present study we expand the number of ethylene-containing clusters investigated to include $(C_2H_4)_2$, $(C_2H_4)_3$, $(C_2H_4)_5$, $(C_2H_4)_7$, $(C_2D_4)_2$, $C_2H_4 \cdot Ar$, $C_2H_4 \cdot Kr$ and $C_2H_4 \cdot C_2F_4$. Photodissociation spectra ($925-1080\text{ cm}^{-1}$) and absolute absorption intensities, are reported for each van der Waals compound. Effects of varying laser power are also investigated. The experimental results are interpreted in terms of a lineshape calculated from a two-level-plus-decay model. Also, ethylene cluster pre-dissociation is analyzed using the theory of Beswick and Jortner.⁵

EXPERIMENTAL

A schematic of the molecular beam instrument is shown in Figure 1. Four levels of pumping are used so that low background pressures required for van der Waals molecule spectroscopy and mass spectrometry are maintained, despite the high throughput of the supersonic nozzle. The nozzle source is a 0.25 in. OD stainless steel pipe capped with a nickel utility pinhole (Ealing Corporation). The source chamber (at the far left in Figure 1) is pumped by an unbaffled 4 in. Pennwalt Stokes booster pump backed by a Leybold-Heraecus E150 mechanical pump. Throughput of this configuration is $2800 \text{ Torr cm}^3 \text{ sec}^{-1}$ at 10^{-2} Torr. The first aperture downstream of the nozzle is a skimmer (Beam Dynamics model 2) with a 0.1 cm entrance diameter. Optimum nozzle-skinner distance is ~ 1.0 cm. Nozzle position is completely adjustable while all downstream apertures are fixed in optical alignment. Typically gases at 5 to 10 atm and 300°K are expanded through a $35 \mu\text{m}$ pinhole and maintain a background pressure of the order of 10^{-3} Torr in the source chamber. The molecular beam emerging from the skimmer (moving left to right in Figure 1) traverses a 4.5 cm region of differential pumping before encountering a cone-shaped collimator with an entrance diameter of 0.2 cm. Differential pumping is supplied by an unbaffled 6 in Varian VHS-6 diffusion pump which maintains a pressure in this region of $\sim 10^{-5}$ Torr during operation. Passing through the first collimator the molecular beam enters the largest vacuum chamber and travels 40 cm further to a second collimator. Pressure in the main chamber is maintained at 10^{-6} Torr by an Edwards 160/700 diffusion pump having an internal

FIGURE 1. Schematic diagram of the molecular beam spectrometer.
See Experimental section for details.

MOLECULAR BEAM SPECTROMETER
(TOP VIEW)



water-cooled baffle. After the second collimator, the molecular beam enters a fourth vacuum chamber (far right in Figure 1) which houses an Extranuclear quadrupole mass spectrometer equipped with a crossed-beam electron impact ionizer and channeltron particle multiplier. The mass spectrometer chamber is pumped by an Edwards CR-760 diffusion pump equipped with internal water and nitrogen-cooled baffles which provides ambient pressures of $\sim 10^{-8}$ Torr during experiments. Total distance from the nozzle source to the ionizer of the mass spectrometer is 60 cm corresponding to a molecular flight time on the order of 0.5 msec.

For most infrared photochemistry experiments the unfocused laser beam is directed into the apparatus through a ZnSe window (supplied by II-VI incorporated) indicated at the far right in Figure 1. The laser beam and molecular beam are co-linear to maximize irradiation time of species in the molecular beam.

As indicated in Figure 1, molecular beams are characterized using a quadrupole mass spectrometer equipped with an electron impact ionizer. A typical molecular beam mass spectrum is shown in Figure 2. Ionization conditions employed lead to fragmentation of some van der Waals molecular ions. Careful analysis of the molecular beam mass spectrum is needed in order to make unambiguous identification of neutral cluster molecules in the molecular beam. Figure 3 shows a plot of mass spectrum ion intensities as a function of source pressure for an Ar:C₂H₄:He mixture. In Figure 3 both scales are logarithmic. Only those ions not produced by ionization of C₂H₄ or Ar monomers are considered. At low pressures the most abundant species is the



FIGURE 2. Molecular beam mass spectrum indicating formation of ethylene clusters. Note changes in detector sensitivity. Molecular beam formed by expanding 7 atm. of 11% C₂H₄ in He. Nozzle diameter is 35 μ m.

MOLECULAR BEAM MASS SPECTRUM

11% C₂H₄ in He

7 atm. backing pressure

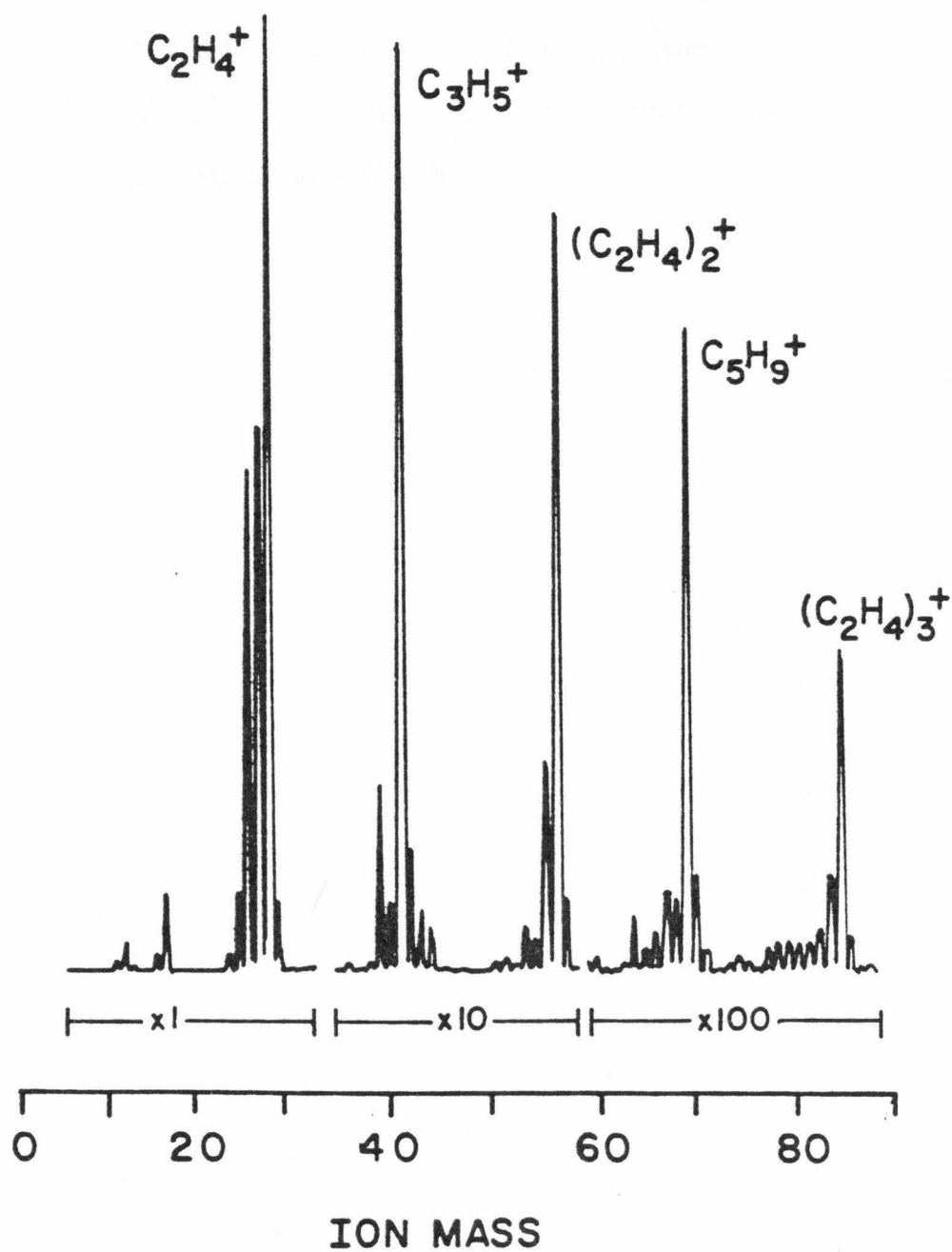
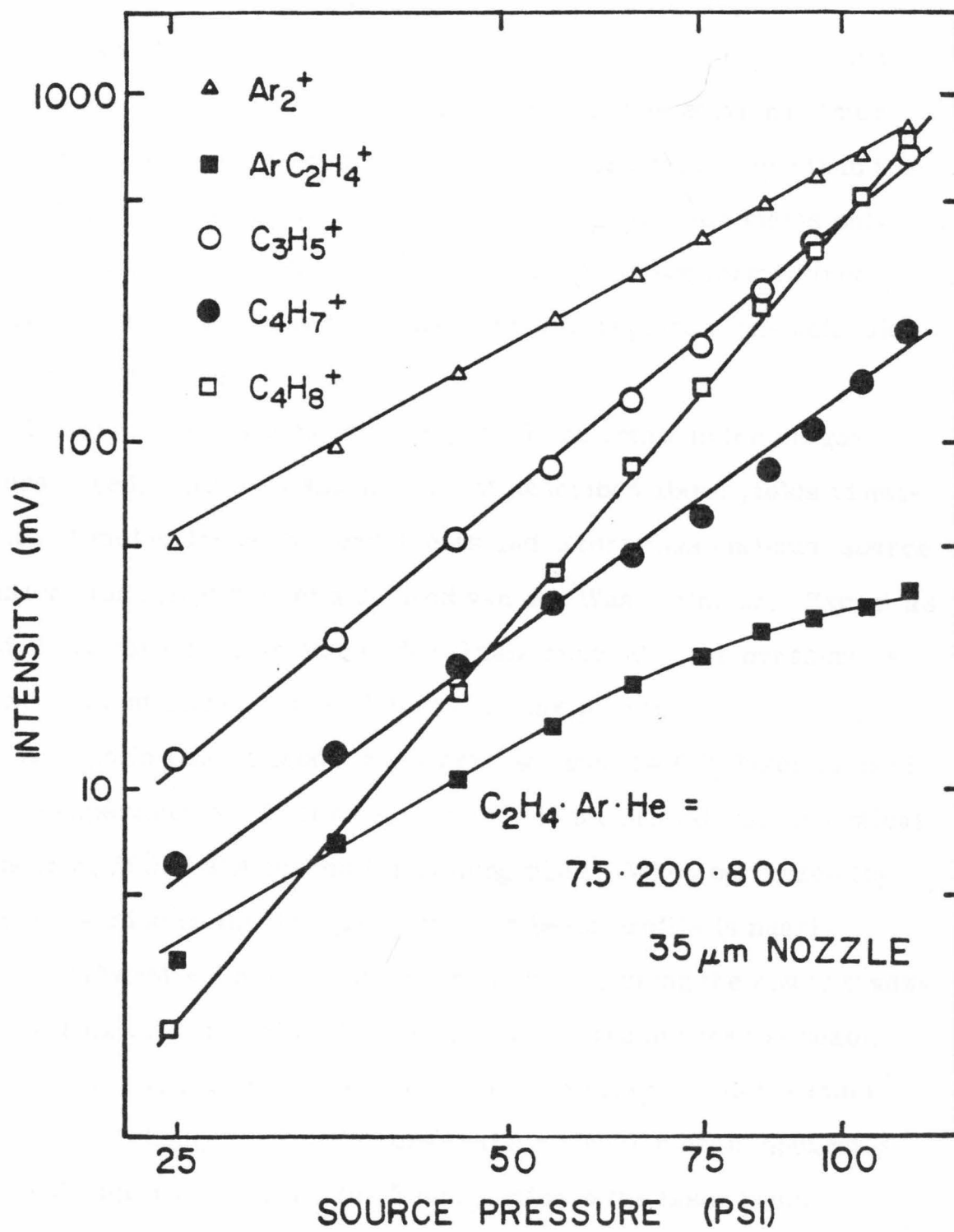
35 μ m nozzle

FIGURE 3. Variation of van der Waals molecules mass spectral intensity with source pressure. Both scales are logarithmic. Data for Ar_2^+ , $\text{Ar} \cdot \text{C}_2\text{H}_4^+$, C_3H_5^+ , C_4H_7^+ and C_4H_8^+ are included. Gas mixture is 0.75% C_2H_4 , 20% Ar and 80% He.



parent ion of argon dimer, Ar_2^+ at m/e 80. As the backing pressure is increased, $\text{C}_2\text{H}_4\text{Ar}^+$ is observed. The next group of ions detected as the pressure is increased further are the two at m/e 41 (C_3H_5^+) and m/e 55 (C_4H_7^+). Data points for these two species lie on parallel, straight lines (Figure 3) with slopes 2.6 and 2.3 for C_3H_5^+ and C_4H_7^+ , respectively. The ion nominally identified as ethylene dimer parent ion (m/e 56) shows a higher order pressure dependence than the $\text{C}_3\text{H}_5^+/\text{C}_4\text{H}_7^+$ pair. We conclude ionization of $(\text{C}_2\text{H}_4)_2$ leads yields only daughter ions, C_3H_5^+ , C_4H_7^+ , C_2H_5^+ , etc.; $(\text{C}_2\text{H}_4)_2^+$ is not formed from ethylene dimer. This result is consistent with reported ion-molecule reactions of ethylene.^{8,9}

Data such as those shown in Figure 3 are obtained for all gas mixtures used. Analysis similar to that described above yields identification of molecular beam constituents and determines optimum source conditions for production of a desired van der Waals cluster. Except as noted, in studies of selected van der Waals molecules the pressure is adjusted so that higher order clusters are not present.

An Apollo Lasers Model 550A grating tuned cw CO_2 laser is used in these experiments. Laser beam quality is monitored with an Optical Engineering Model 22A thermal imaging plate. When optimized (by visual inspection on the imaging plate) the beam profile is nearly Gaussian (FWHM = 6 mm) as determined by measuring the power transmitted through a 1 mm diameter pinhole translated across the beam. Reproducible variations in mode structure are observed as the laser wavelength is changed. Collimators in the molecular beam apparatus (Figure 1) select only the center 2 mm portion of the laser beam.

Measurement of the infrared beam intensity within the apparatus indicate 30 % of the incident power is transmitted. Irradiances are calculated using this calibration constant and assuming a laser beam area of 0.13 cm^2 . Power measurements use a Laser Precision Corp. Model RkP-345 pyroelectric radiometer. Fluctuations in laser power are less than $\pm 5\%$ during an experiment. Infrared laser wavelengths are measured with an Optical Engineering Model 16A spectrum analyzer. Band widths are estimated to be $\sim 50 \text{ MHz}$ ($\sim 0.002 \text{ cm}^{-1}$).

For most infrared photodissociation experiments the laser beam is mechanically chopped (usually 100-150 Hz). The intensity of a given peak in the molecular beam mass spectrum is measured both in the presence and absence of infrared radiation using a two-channel boxcar. Direct electronic division of the two values yields a fractional change in mass spectrometer signal intensity due to laser irradiation. Fine adjustments in laser beam position are made to maximize extent of photodissociation.

In one set of experiments the unfocused laser beam is directed into the apparatus through the auxiliary window (Figure 1, top) and intersects the molecular beam at right angles before being absorbed by a graphite beam stop. The infrared beam is chopped at 1000 Hz and resulting changes in mass spectrometer signal are measured using a lock-in amplifier.

RESULTS

Infrared photodissociation is observed for all ethylene-containing van der Waals molecules studied. Identities of the clusters along with ion fragments monitored are listed in Table 1. Also tabulated are gas mixtures and source conditions used to produce the complexes.

Photodissociation spectra of van der Waals molecules are obtained by monitoring attenuation of mass spectrometer signal intensities as the CO₂ laser wavelength is varied. In all cases except (C₂D₄)₂ no dissociation was detected at higher energies than 1000 cm⁻¹. Therefore, data for only half of the CO₂ laser wavelength range are presented. Figure 4 shows infrared photodissociation spectra of ethylene dimer and ethylene trimer. Data for this figure as well as for all spectra shown below were obtained using co-axial laser beams and molecular beams. Note that the spectra (Figure 1) are presented with logarithmic ordinates. The reason for this choice is presented in the discussion section. Both spectra shown in Figure 1 consist of a single symmetric band, centered at ~953 cm⁻¹, and both exhibit the same width. The photodissociation cross section of ethylene trimer is larger than that for (C₂H₄)₂ at all laser wavelengths shown. Relatively low laser power is used to obtain data shown in Figure 4, yet it is possible to dissociate 25% of the dimer and 50% of the trimer.

Changes in laser power in the range 1 to 10 W cm⁻² does not alter photodissociation bandwidths. Furthermore, the width and position of photodissociation profiles are independent of expansion conditions even though varying ethylene concentration and stagnation pressure alters molecular beam temperature.

Table I. Experimental Conditions for Production of Ethylene-Containing Clusters in Molecular Beams

Cluster	Gas Mixture	Nozzle Diam. (μm)	Pressure (psi)	t (ms)	Ion Detected
$(\text{C}_2\text{H}_4)_2$	0.7% C_2H_4 +20% Ar+80% He	35	51.5	0.73	C_3H_5^+
$(\text{C}_2\text{H}_4)_3$	0.7% C_2H_4 +20% Ar+80% He	35	51.5	0.73	C_4H_8^+
$(\text{C}_2\text{H}_4)_5$	11% C_2H_4 +39% Ar+50% He	25	290	0.92	$\text{C}_{10}\text{H}_{20}^+$
$(\text{C}_2\text{H}_4)_7$	11% C_2H_4 +39% Ar+50% He	25	290	0.92	$\text{C}_{14}\text{H}_{28}^+$
$\text{C}_2\text{H}_4 \cdot \text{C}_2\text{F}_4$	0.7% C_2H_4 +0.5% C_2F_4 +20% Ar+80% He	35	111	0.74	$\text{C}_3\text{H}_4\text{F}^+ \text{ a)}$
$\text{Ar} \cdot \text{C}_2\text{H}_4$	0.7% C_2H_4 +20% Ar+80% He	35	115	0.73	ArC_2H_4^+
$\text{Kr} \cdot \text{C}_2\text{H}_4$	0.7% C_2H_4 +20% Kr+80% He	35	115	0.98	$\text{KrC}_2\text{H}_4^+ \text{ b)}$

a) Identical results obtained when monitoring $\text{C}_3\text{H}_3\text{F}_2^+$.

b) Sum of all Kr isotopes.

FIGURE 4. Infrared photodissociation spectra of $(C_2H_4)_2$ and $(C_2H_4)_3$. The dimer is detected as $C_3H_5^+$ and the trimer is detected as $C_4H_8^+$. No photodissociation of either species is observed at CO_2 laser wavelengths $> 1000\text{ cm}^{-1}$. Laser power is 11 W cm^{-2} . Molecular beam conditions are listed in Table I. $|C_0|^2$ is the fraction of undissociated van der Waals molecules.

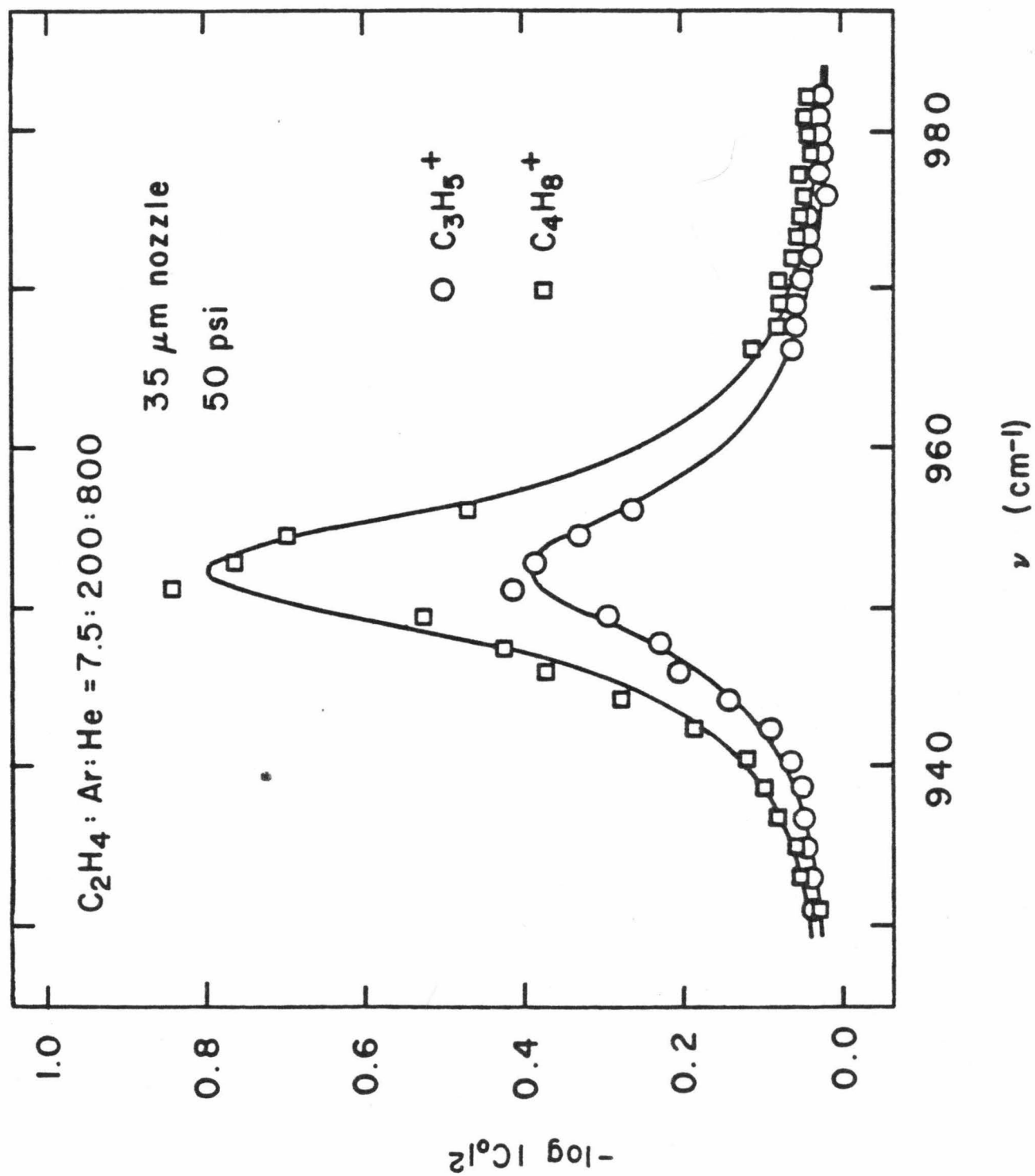


FIGURE 5. Measured power dependence of infrared photodissociation of $(\text{C}_2\text{H}_4)_2$, $(\text{C}_2\text{H}_4)_3$ and $\text{Ar} \cdot \text{C}_2\text{H}_4$. Ordinate is logarithmic. Laser wavelength is nearly identical to λ_{max} for infrared photodissociation spectra of these van der Waals molecules.

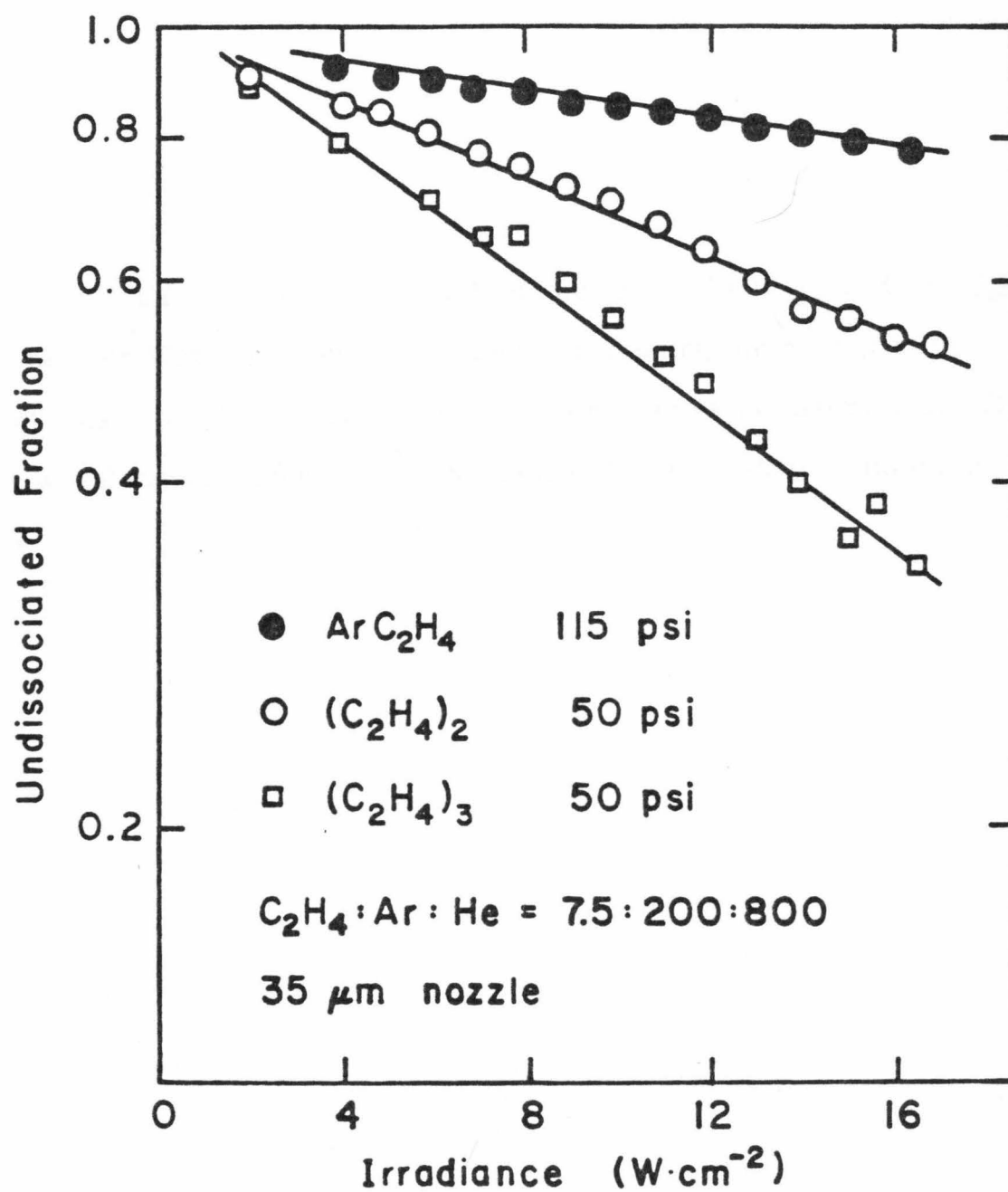


FIGURE 6. Infrared photodissociation spectra of $\text{Ar} \cdot \text{C}_2\text{H}_4$ and $\text{Kr} \cdot \text{C}_2\text{H}_4$. Both van der Waals molecules are monitored using their respective parent ions. No photodissociation of either species is observed at CO_2 laser wavelengths $> 1000 \text{ cm}^{-1}$. Molecular beam conditions listed in Table I.

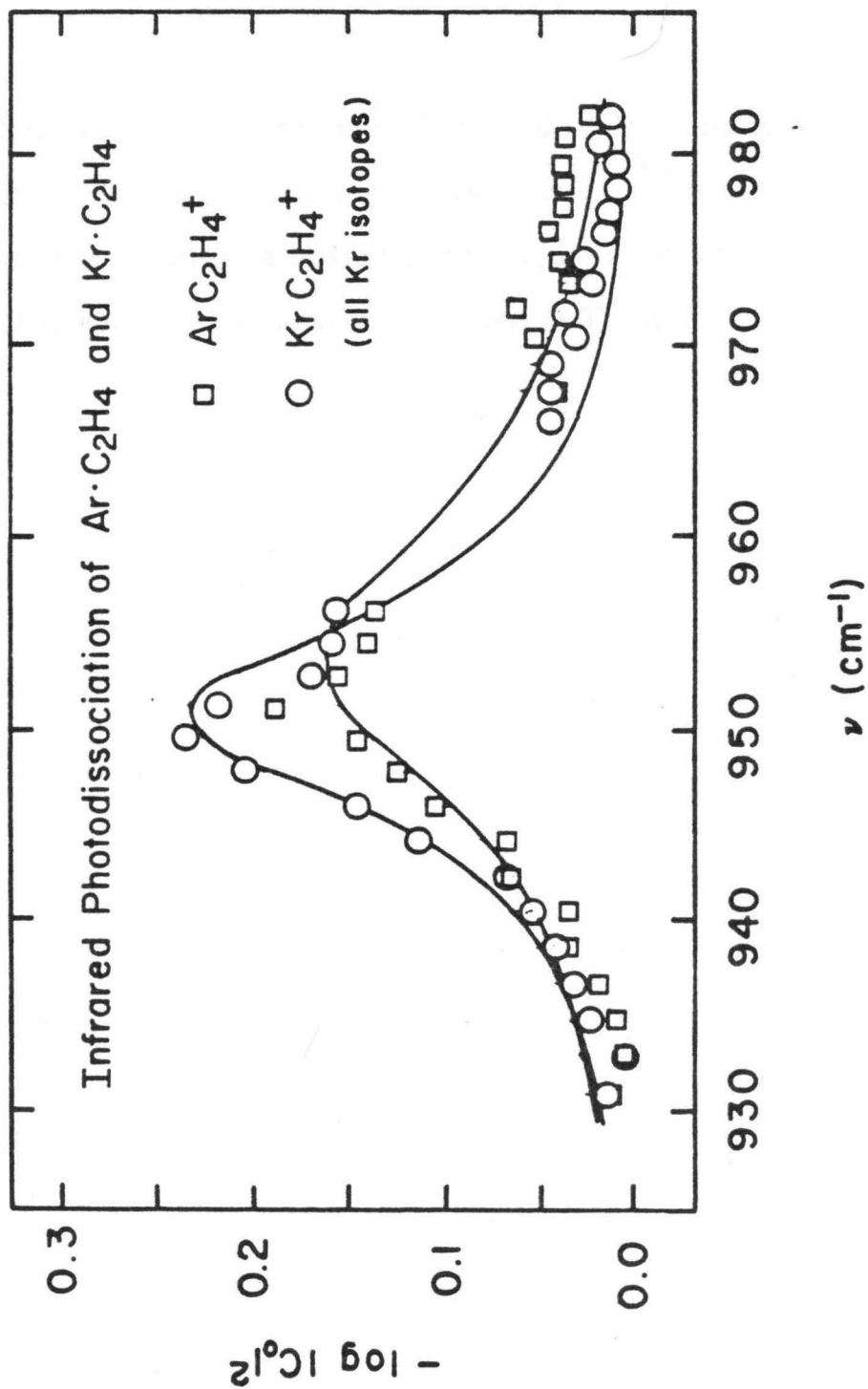


FIGURE 7. Infrared photodissociation spectra of $(\text{C}_2\text{H}_4)_5$ and $(\text{C}_2\text{H}_4)_7$. Both clusters are monitored using their parent ions. No photodissociation of either species is observed at CO_2 laser wavelengths $> 1000 \text{ cm}^{-1}$. Molecular beam conditions listed in Table I.

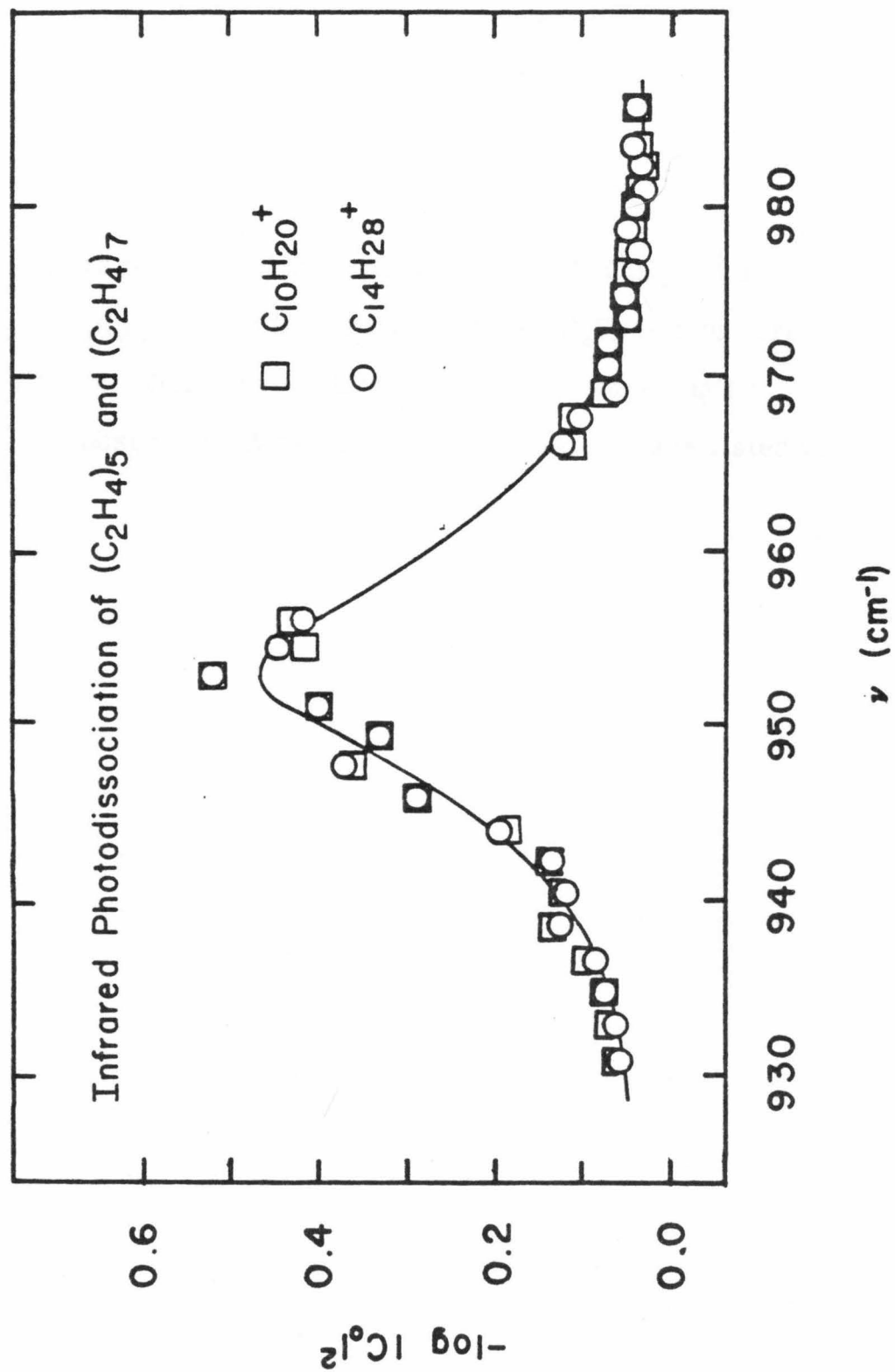
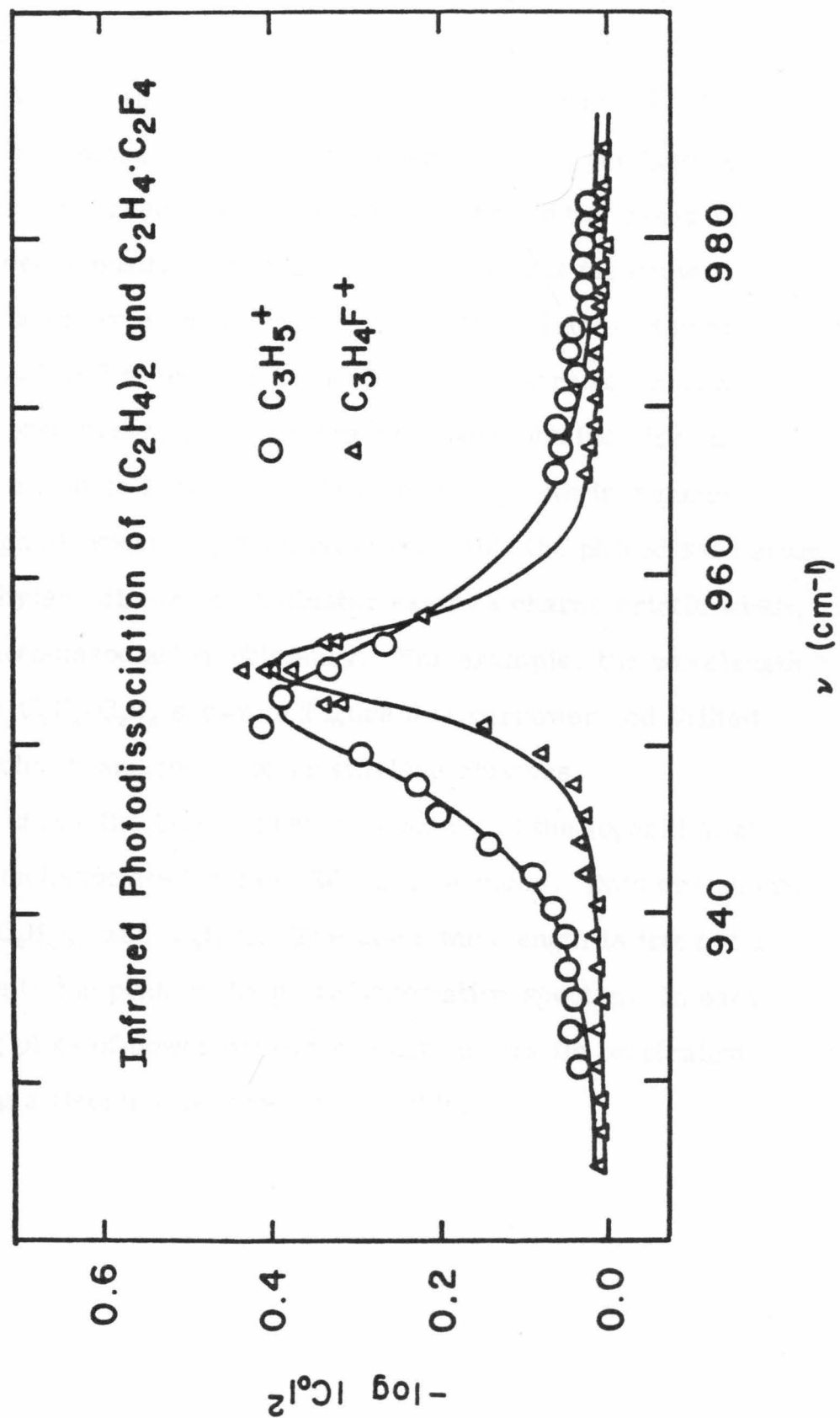


FIGURE 8. Infrared photodissociation spectra of $(\text{C}_2\text{H}_4)_2$ and $\text{C}_2\text{H}_4 \cdot \text{C}_2\text{F}_4$. $(\text{C}_2\text{H}_4)_2$ data as in Figure 1. $\text{C}_2\text{H}_4 \cdot \text{C}_2\text{F}_4$ is monitored using $\text{C}_3\text{H}_4\text{F}^+$. No photodissociation at CO_2 laser wavelengths $> 1000 \text{ cm}^{-1}$ is observed. Molecular beam conditions are listed in Table I.



Irradiation of ethylene clusters in the crossed laser beam-molecular beam configuration yields the same wavelength dependence observed in the colinear geometry experiments. Relative cross sections for dissociation of $(C_2H_4)_3$ and $(C_2H_4)_2$ are identical for both types of experiment. This indicates heating of the expansion by the laser beam does not occur. Observed infrared photochemistry is the result of excitation and decomposition of isolated van der Waals molecules. In the crossed beam experiments photodissociation yield of ethylene trimer is only ~ 0.005 at 953 cm^{-1} due to the short irradiation time.

Infrared photodissociation spectra have been obtained for each van der Waals molecule listed in Table 1 and are shown in Figures 6, 7 and 8. Though all spectra qualitatively resemble the photodissociation spectrum of ethylene dimer, each cluster exhibits characteristic width, position and photodissociation efficiency. For example, the wavelength dependence for $C_2F_4 \cdot C_2H_4$ shown in Figure 8 is narrower and shifted slightly to the blue compared to other ethylene clusters.

Figure 5 shows the laser power dependence of the logarithm of the fraction of undissociated van der Waals molecules. Data are shown for $Ar \cdot C_2H_4$, $(C_2H_4)_2$, and $(C_2H_4)_3$. The laser wavelength is fixed at a frequency close to the peak of the photodissociation spectra. In each case, semi-log plots of power dependence data points lie on straight lines suggesting a Beer's Law-type relationship.

DISCUSSION

Photodissociation spectra of van der Waals molecules containing ethylene (Figures 4-7) all show maxima between 950 and 955 cm^{-1} . Within the CO_2 laser wavelength region, monomeric ethylene has a single absorption band, $\nu_7 = 949.2 \text{ cm}^{-1}$.¹¹ Results presented are consistent with vibrational predissociation of the van der Waals molecules. Invariance of observed photodissociation lineshapes to changes in laser power and molecular beam temperature as well as the lack of saturation are all indicative of a homogeneous, lifetime broadened transition. No direct measure of cluster rotational temperature was made. However, similar experimental conditions are known to produce rotational temperatures $\sim 1.0^\circ\text{K}$. Thus, any heterogeneous broadening of photodissociation spectra due to various rotational components is $\sim 1 \text{ cm}^{-1}$ which is less than the uncertainty in measured linewidths. A model for predissociation is a two-level system in which the upper state undergoes unimolecular decay. In this case the $v = 0$ and $v = 1$ states of the ethylene ν_7 mode correspond to the states of the two-level system. Derivation of an exact lineshape equation from this model is described in the Appendix. In the present study, unimolecular dissociation rates of vibrationally excited van der Waals molecules are more than 5 orders of magnitude faster than rates of stimulated absorption and stimulated emission. Thus it is possible to make simplifying approximations to the lineshape function (see Appendix) from which we obtain equation 1. $|C_0(\omega, t)|^2$ is the fraction of undissociated van der Waals molecules.

$$|C_0(\omega, t)|^2 = \exp \left\{ -\omega_R^2 \tau t \cdot \frac{\tau^{-2}}{4(\omega - \omega_0)^2 + \tau^{-2}} \right\} \quad (1)$$

t is the irradiation time, ω the laser frequency, ω_R the Rabi Frequency

(see Appendix), τ the dissociation rate of molecules in the excited state and ω_0 is the band center. Equation 1 is the exponential of a scaled Lorentzian curve. Typically, $\omega_R^2 \tau t \sim 10^{-4}$ implying $|C_0(\omega, t)|^2$ it nearly identical to a simple Lorentzian lineshape.

Solid lines drawn in the infrared dissociation spectra (Figure 4 and 6-8) are results of a non-linear, least squares fit of the data points to equation 1. Values of ω_0 and τ^{-1} for each ethylene-containing cluster studied are listed in Table II.

At resonance, $\omega = \omega_0$, equation 1 simplifies further to equation 2. Note that ω_R^2 is proportional to the laser intensity. Equations 1 and 2

$$|C_0(\omega_0, t)|^2 = \exp \{-\omega_R^2 \tau t\} \quad (2)$$

predict the logarithm of the undissociated fraction of clusters decreases linearly with increasing laser power. This is in excellent agreement with the observed power dependence of infrared photodissociation shown in Figure 5. The Rabi Frequency, ω_R , is also a function of the transition moment $\langle \mu \rangle$ of the two-level system. Results obtained from photodissociation wavelength dependence combined with power dependence data allow determination of $\langle \mu \rangle$ for the van der Waals cluster studied. The square of the transition moment is proportional to the transition probability. Values of the $\langle \mu \rangle^2$ are listed in Table II. Also, the measured transition probability for the $v = 0 \rightarrow v = 1$ infrared absorption by the ν_7 mode in ethylene monomer is entered in Table I.¹³

Among clusters $\text{Ar} \cdot \text{C}_2\text{H}_4$, $\text{Kr} \cdot \text{C}_2\text{H}_4$, $\text{C}_2\text{F}_4 \cdot \text{C}_2\text{H}_4$, $(\text{C}_2\text{H}_4)_2$ and $(\text{C}_2\text{H}_4)_3$ transition probabilities are proportional to the number of ethylene molecules in the cluster. The average contribution per ethylene is $4.3 \times 10^{-3} \text{ D}^2$ which is comparable to the transition probability of free

Table II. Parameters Obtained from Lineshape Fit to Photodissociation Spectra and Photodissociation Power Dependence Data

Cluster	ω_0 (cm^{-1})	τ (psec)	$\langle \mu \rangle^2$ (10^{-3} D^2)
$(\text{C}_2\text{H}_4)_2$	952 ± 1	0.44 ± 0.95	9.3 ± 1.7
$(\text{C}_2\text{H}_4)_3$	952 ± 1	0.50 ± 0.07	13.6 ± 2.5
$(\text{C}_2\text{H}_4)_5$	953 ± 1	0.33 ± 0.05	10.3 ± 2.0
$(\text{C}_2\text{H}_4)_7$	953 ± 1	0.33 ± 0.05	10.5 ± 2.0
$\text{Ar} \cdot \text{C}_2\text{H}_4$	954 ± 2	0.28 ± 0.07	5.2 ± 1.6
$\text{Kr} \cdot \text{C}_2\text{H}_4$	951 ± 1	0.42 ± 0.08	2.8 ± 0.7
$\text{C}_2\text{H}_4 \cdot \text{C}_2\text{F}_4$	955 ± 0.5	0.89 ± 0.10	4.5 ± 0.6
C_2H_4	$949.1^{\text{a})}$	-	$3.1^{\text{b})}$

a) Reference 11.

b) Reference 13.

ethylene, $\langle \mu \rangle^2 = 3.1 \times 10^{-3} \text{D}^2$. Large van der Waals molecules $(\text{C}_2\text{H}_4)_5$ and $(\text{C}_2\text{H}_4)_7$ exhibit transition moments of $(10.3 \pm 2.0) \times 10^{-3} \text{D}^2$ and $(10.5 \pm 2.0) \times 10^{-3} \text{D}^2$, respectively, which are nearly identical to each other and to the transition probability for $(\text{C}_2\text{H}_4)_2$. In these higher clusters ethylene molecules at the interior are bound to several partners. Following absorption of one infrared photon, multiple bond breaking is required for dissociation. If this process is very much slower than the direct cleavage of a single van der Waals bond, photodissociation will not be observed on the timescale of the experiment. Thus, predissociation is detected only when an ethylene at the cluster "surface" is activated by infrared excitation. Photodissociation cross sections remain approximately constant despite increasing size of the van der Waals molecules.

Detailed theoretical treatments of van der Waals predissociation are limited to triatomic systems, X-BC.⁵ BC is a stable, well characterized diatomic such as I_2 and X represents a rare gas atom. The simplicity of the model system compared to van der Waals dimers containing ethylene indicates only qualitative aspects of theoretical treatments are applicable to this study. According to Beswick and Jortner⁵ the dominant factor in determining dissociation rates is the ratio of BC vibrational frequency to the van der Waals bond energy. Close matching of these two energies (small energy gap) enhances the dissociation rate. Furthermore if all other parameters remain fixed the predissociation rate increases as the mass of the rare gas atom decreases. The theoretical study also explores effects due to changes in vibrational quantum number, both in the BC vibration and the van der Waals stretch. However, in the present experiments only single quantum transitions

in ethylene are possible and there is no evidence for direct excitation of the stretching vibration in the van der Waals coordinate.

Linewidths listed in Table II vary by only a factor of three through the series of seven ethylene clusters studied. This is an extremely small range of predissociative lifetimes compared to the calculated ratio of $\sim 10^{10}$ for $\text{ArFCl}(v = 1)$ and $\text{ArHCl}(v = 1)$ dissociation rates.⁵ The latter ratio reflects differences BC vibrational frequency at fixed van der Waals bond strengths. In ethylene clusters the vibrational frequency (analogous to the BC vibrational frequency) remains fixed at $\sim 950 \text{ cm}^{-1}$. Change in the van der Waals partner results in variation of bond strength hence change in the energy gap. Beswick-Jortner theory applied to ethylene clusters predicts decreasing predissociative lifetime with increasing bond strength because the energy gap is reduced. Krypton is more polarizable than Ar, so the van der Waals bond in $\text{Kr} \cdot \text{C}_2\text{H}_4$ should be stronger than in $\text{Ar} \cdot \text{C}_2\text{H}_4$. However, results from Figure 6 and Table II indicate vibrationally excited $\text{Ar} \cdot \text{C}_2\text{H}_4$ dissociates more rapidly ($\tau = 0.28 \text{ ps}$) than does $\text{Kr} \cdot \text{C}_2\text{H}_4$ ($\tau = 0.42 \text{ ps}$) which is consistent with predicted mass effects but contrary to the energy gap law. A similar trend is observed in comparison of $\text{C}_2\text{H}_4 \cdot \text{C}_2\text{F}_4$ and $(\text{C}_2\text{H}_4)_2$. Partial charge transfer from C_2F_4 to C_2H_4 strengthens the van der Waals bond in $\text{C}_2\text{F}_4 \cdot \text{C}_2\text{H}_4$ relative to ethylene dimer, yet $\text{C}_2\text{F}_4 \cdot \text{C}_2\text{H}_4$ has a lifetime twice that of $(\text{C}_2\text{H}_4)_2$ (Table II). Again, mass effects run opposite to energy gap considerations with the mass effect dominating.

Photodissociation spectra of ethylene clusters (Figures 4 and 6-8) all show maxima blue-shifted compared to $\nu_7 = 949.2 \text{ cm}^{-1}$ in ethylene monomer (Table II). An identical trend is observed in wavelength

shifts in condensed ethylene. Liquid C_2H_4 exhibits $\nu_7 = 961 \text{ cm}^{-1}$ ¹⁴ and in the crystal $\nu_7 = 970 \text{ cm}^{-1}$.¹⁴ One expects the infrared frequency of absorption band maxima in ethylene clusters to increase with increasing cluster size until a limiting value characteristic of the liquid or solid is reached. However, in the homologous series $(\text{C}_2\text{H}_4)_2$, $(\text{C}_2\text{H}_4)_3$, $(\text{C}_2\text{H}_4)_5$ and $(\text{C}_2\text{H}_4)_7$ photodissociation bands are shifted, at most, by 5 cm^{-1} relative to the monomer fundamental. The anticipated progression towards 970 cm^{-1} is not observed. The photodissociation wavelength dependence as well as the power dependence of larger clusters, $(\text{C}_2\text{H}_4)_5$ and $(\text{C}_2\text{H}_4)_7$, are nearly identical to those of ethylene trimers. As described above, dissociation results following infrared absorption by an ethylene molecule located on the periphery of the cluster. Excitation of C_2H_4 at the cluster center does not result in photodissociation on the timescale of the molecular beam flight time.

In our previous communication⁷ we reported infrared photodissociation of $(\text{C}_2\text{D}_4)_2$. A line is observed at 1074 cm^{-1} with a cross section an order of magnitude lower than for $(\text{C}_2\text{H}_4)_2$ and linewidth characteristic of a 0.7 psec lifetime. In comparison, the C_2D_4 infrared spectrum shows a maximum at 1077.9 cm^{-1} due to an in-plane bending vibration of b_{3u} symmetry.¹¹ Differences in lifetimes for $(\text{C}_2\text{D}_4)_2$ and $(\text{C}_2\text{H}_4)_2$ are understood by examination of the molecular motion in the vibrational modes excited. Assuming ethylene dimers form with molecular planes parallel, as is observed in the crystal, the ν_7 out of plane bending of C_2H_4 should be more efficient at leading to dissociation than the in-plane motion excited in C_2D_4 .³

All ethylene clusters in this study are formed from non-polar molecules. Van der Waals bonding is due to electron correlation

effects exclusively. One exception is the $\text{C}_2\text{H}_4 \cdot \text{C}_2\text{F}_4$ cluster. In this species electron donation from fluorine atom lone pair orbitals in C_2F_4 to the unoccupied π^* orbital in C_2H_4 is expected to occur and should strengthen the van der Waals bond. A consequence of this partial charge transfer is a weakening of the C-C double bond in ethylene which, in turn, implies a diminution of the ν_7 bending force constant. However, $\text{C}_2\text{H}_4 \cdot \text{C}_2\text{F}_4$ exhibits the highest energy photodissociation band of those studied; $\omega_0 = 955 \text{ cm}^{-1}$ (Figure 7 and Table II). We infer steric repulsions between the two van der Waals partners are responsible for the increase in vibrational frequency of this out-of-plane bending mode and the steric effects dominate any frequency shift due to weakening of the C-C double bond. Similar steric interactions lead to the above mentioned increase of ν_7 in ethylene upon condensation. The difference in size of fluorine atoms compared to hydrogen atoms makes the effect more pronounced in $\text{C}_2\text{H}_4 \cdot \text{C}_2\text{F}_4$ than in $(\text{C}_2\text{H}_4)_2$.

CONCLUSIONS

Vibrational predissociation of van der Waals molecules containing ethylene has been observed. Use of relatively low power ($< 20 \text{ W cm}^{-2}$), unfocused laser radiation avoids saturation. Infrared photodissociation spectra ($925\text{--}1080 \text{ cm}^{-1}$) are characterized by lifetime broadened homogeneous lines. Observed wavelength dependences and power dependences show excellent agreement with a lineshape derived from a two-level-plus-decay model. Predissociative lifetimes lie in the range 0.3 psec (for $\text{Ar} \cdot \text{C}_2\text{H}_4$) to 0.9 psec (for $\text{C}_2\text{H}_4 \cdot \text{C}_2\text{F}_4$). This corresponds to 9–26 vibrational periods prior to dissociation.

Absolute magnitudes of infrared transition moments are obtained. For $(\text{C}_2\text{H}_4)_2$, $(\text{C}_2\text{H}_4)_3$, $\text{Ar} \cdot \text{C}_2\text{H}_4$, $\text{Kr} \cdot \text{C}_2\text{H}_4$ and $\text{C}_2\text{H}_4 \cdot \text{C}_2\text{F}_4$ the transition moment per ethylene unit is in good agreement with the reported transition moment for infrared absorption in ethylene (ν_7 vibration).¹³ The molecular beam technique used in this study appears to be an excellent general method for measuring infrared transition intensities.

Larger ethylene clusters, $(\text{C}_2\text{H}_4)_5$ and $(\text{C}_2\text{H}_4)_7$, show infrared photochemistry similar to $(\text{C}_2\text{H}_4)_3$. It is inferred that present experiments (in which total photon energy is $\sim 950 \text{ cm}^{-1}$) sample only those ethylene molecules on the surface of larger clusters. Excitation of a C_2H_4 unit which is bound to many other ethylenes may not yield cluster dissociation on the timescale of the experiment.

Qualitative aspects of Beswick-Jortner theory⁵ applied to ethylene clusters indicate mass effects are more important than van der Waals bond strengths (energy defects) in determining predissociative lifetimes. This may reflect a narrow range of bond energies among the dimeric species studied. Alternatively, theory developed for triatomic systems

may not prove applicable to the more complex polyatomic species containing ethylene.

Comparison of photodissociation lifetimes of $(C_2H_4)_2$ and $(C_2D_4)_2$ indicate dissociation rates vary with vibrational mode excited. A more complete mapping of intramolecular energy transfer dynamics can be obtained by extending the wavelength region studied. Ethylene has four C-H stretching vibrations (two are infrared active) between 2990 cm^{-1} and 3272 cm^{-1} .¹¹ Vibrational predissociation utilizing these higher energy excitations should provide interesting comparison with the present study. In particular, greater variation in lifetimes and transition probabilities among large clusters might be observed.

APPENDIX (Photodissociation Lineshapes)

The large fractions of van der Waals molecules photodissociated indicate that populations of initial states are changed drastically by infrared laser irradiation. Therefore, the conventional perturbation theory for absorption lineshapes requiring that initial state populations be only slightly altered does not apply. An applicable approach following Sargent, *et al*¹⁵ and Hemminger, *et al*¹⁶ is offered here.

The simplest picture of vibrational predissociation induced by light absorption involves two vibrational states separated by frequency ω_0 . Populations of the lower and upper states are given by $|C_0|^2$ and $|C_1|^2$, respectively. Molecules are initially found in the lowest level but can be excited into the upper level by laser irradiation at frequency ω . Molecules in the excited state can either return to the ground state with stimulated emission or decay into a dissociative continuum at a rate given by γ . The differential equations describing the time evolu-

tion of C_1 and C_2 are where $\Delta\omega = \omega_0 - \omega$ and ω_R in the Rabi frequency.

$$\dot{C}_0 = \frac{i\omega_R}{2} \exp[-i\Delta\omega t] C_1 \quad (3)$$

$$\dot{C}_1 = \frac{i\omega_R}{2} \exp(i\Delta\omega t) C_0 - \frac{\gamma}{2} C_1 \quad (4)$$

The Rabi frequency is related to the electric field amplitude E_0 , and the transition moment μ :

$$\omega_R = \frac{\mu E_0}{\hbar} \quad (5)$$

The right-hand side of equation 4 includes $\gamma/2$ so that $|C_1|^2$ will evolve at the rate given by γ in the absence of the field.

The van der Waals molecules are formed in their lowest vibrational levels so that at the nozzle $|C_0(t=0)|^2 = 1$ and $|C_1(t=0)|^2 = 0$. Molecules are then exposed to infrared irradiation until their arrival at the ionizer of the mass spectrometer defining irradiation time, t . The fraction of molecules that has survived is measured as a function of laser wavelength. In our experiments the predissociation rate is large compared to the Rabi frequency (~ 10 MHz) and quantity measured is $|C_0(\omega, t)|^2$. Using the boundary conditions given above, the solution of equations 3 and 4 for $C_0(\omega, t)$ is

$$C_0(\omega, t) = \left[\frac{\frac{\gamma}{2} + i\Delta\omega}{2} \sin \frac{zt}{2} + \cos \frac{zt}{2} \right] \exp \left[-\left(\frac{\gamma}{2} + i\Delta\omega\right) t/2 \right] \quad (6)$$

where

$$z = [(\Delta\omega^2 - \frac{\gamma^2}{4} + \omega_R^2) - i\gamma\Delta\omega]^{1/2} \quad (7)$$

Defining z as a complex number in the usual way, $z = x + iy$, we have

for the undissociated fraction of molecules:

$$\begin{aligned}
 |C_o(\omega, t)|^2 = & \left[\frac{\Delta\omega^2 + (\gamma/2)^2}{|z|^2} \left[\cosh^2 \frac{yt}{2} - \cos^2 \frac{xt}{2} \right] \right. \\
 & + \frac{2}{|z|^2} \left[\frac{\gamma}{2} x + \Delta\omega y \right] \sin \frac{xt}{2} \cos \frac{xt}{2} \\
 & + \left(\frac{\gamma}{2} y - \Delta\omega x \right) \sinh \frac{yt}{2} \cosh \frac{yt}{2} \left. \right] \\
 & + \left[\cosh^2 \frac{yt}{2} - \sin^2 \frac{xt}{2} \right] \exp(-\gamma t/2)
 \end{aligned} \quad (8)$$

Expressions for x and y can be obtained by evaluating the real and imaginary parts of z^2 :

$$\begin{aligned}
 z^2 &= (x^2 - y^2) + i(2xy) \\
 &= [\Delta\omega^2 - (\gamma/2)^2 + \omega_R^2] + i(-\gamma\Delta\omega)
 \end{aligned} \quad (9)$$

Equating real and imaginary parts in equation (7) yields

$$x^2 = \frac{1}{2} \left[[\Delta\omega^2 - (\gamma/2)^2 + \omega_R^2] + [(\Delta\omega^2 - (\gamma/2)^2 + \omega_R^2)^2 + \gamma^2 \Delta\omega^2]^{1/2} \right] \quad (10a)$$

$$y^2 = \frac{1}{2} \left[-[\Delta\omega^2 - (\gamma/2)^2 + \omega_R^2] + [(\Delta\omega^2 - (\gamma/2)^2 + \omega_R^2)^2 + \gamma^2 \Delta\omega^2]^{1/2} \right] \quad (10b)$$

The signs of x and y are determined by considering the relative size of the physical quantities $\Delta\omega$, γ and ω_R involved in equation (7).

Interpretation of our experimental results using equation (6) as written proves intractable because the arguments of the hyperbolic functions are of the order 10^9 . Simplification of factors multiplying the hyperbolic function in equation (6) arise in the case of our experiment where $\omega_R \ll \gamma$:

$$\begin{aligned}
 |z|^2 &\simeq \Delta\omega^2 + (\gamma/2)^2 \\
 x &\simeq -\Delta\omega \\
 y &\simeq \gamma/2
 \end{aligned} \quad (11)$$

These simplifications cannot be applied to the arguments of the trigonometric functions, to which $[C_0(\omega, t)]^2$ is extremely sensitive. Using equation 9, the photodissociation profile, (6), reduces to

$$|C_0(\omega, t)|^2 = \exp[(y - \gamma/2)t] \quad (12)$$

Considerable algebraic manipulation of equation (8b) and application of a power series expansion valid for $\omega_R \ll \gamma$ yields, to second order,

$$\frac{2y}{\gamma} = 1 - \frac{\omega_R^2/2}{\Delta\omega^2 + (\gamma/2)^2} \quad (13)$$

Substitution of equation (11) into equation (10) yields the lineshape expression (1) with the vibrationally predissociative lifetime $\tau = \gamma^{-1}$.

$$|C_0(\omega, t)|^2 = \exp \left[-\omega_R^2 \tau t \cdot \frac{\tau^{-2}}{4(\omega - \omega_0)^2 + \tau^{-2}} \right] \quad (1)$$

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