$$g_1 = I[B^{300} - B^{030} - B^{210} + B^{120}]/2 \qquad (18)$$

where $B^{ijk}$ is a constant characteristic of the ion multiplet that contains $i$ cations of the first salt, $j$ cations of the second salt, and $k$ anions. (For our purposes $i$ is the number of $Bu_4N^+$ or $Pr_4N^+$ ions, $j$ is the number of $Na^+$ ions, and $k$ is the number of $Cl^-$ ions.) Thus, the negative values of $g_1$ and the increase in their absolute values with an increase in total concentration suggest an increase in the total number of triplets containing three ions with the same charge. Padova's suggestion that the triplet, $Pr_4N^+$–$Cl^-$–$Na^+$, may be the major contributor to $g_1$ seems unreasonable as such 111 type triplets do not even enter into eq 18.

It is probably reasonable to assume that the pairwise interactions are the major contributors to the interaction parameter $g_0$ and that the triplet interactions are negligible. Therefore, the positive values of $g_0$ suggest that like ions pairs such as $Na^+$–$Na^+$ and $Bu_4N^+$–$Bu_4N^+$ are preferred over mixed ion pairs such as $Bu_4N^+$–$Na^+$. Further, when one considers charge densities and the hydrophobic nature of clathrate-forming ions, such as $Bu_4N^+$ and $Pr_4N^+$, it becomes clear that $Bu_4N^+$–$Bu_4N^+$ and $Pr_4N^+$–$Pr_4N^+$ interactions are more likely to occur than $Na^+$–$Na^+$ interactions.

The concentration dependence of $g_0$ suggests that below a total molality of 2.25 *m*, like ion pairing, such as $Pr_4N^+$–$Pr_4N^+$, is more enhanced in the TPAC–NaCl–$H_2O$ system than is the like ion pairing, such as $Bu_4N^+$–$Bu_4N^+$ in the TBAC–NaCl–$H_2O$ system. However, this situation is reversed at higher concentrations. We believe that this behavior supports the fact that $Bu_4N^+$ has stronger hydrophobic characteristics than does $Pr_4N^+$. This is further supported by the fact that the decrease in $g_0$ with increase in concentration is greater for the TPAC–NaCl–$H_2O$ system than for the TBAC–NaCl–$H_2O$ system. This suggests that while the number of like ion pairs is decreasing with increasing total concentration for both systems, the $Pr_4N^+$–$Pr_4N^+$ ion pair is not as stable as the $Bu_4N^+$–$Bu_4N^+$ ion pair. Further, comparison of the slopes of the concentration dependence of $g_0$ and $g_1$ for both the TBAC–NaCl–$H_2O$ system and the TPAC–NaCl–$H_2O$ system seems to indicate that the magnitude of the decrease in the number of like ion pairs with increase in total concentration does not correspond to the magnitude of the increase in the number of triplets formed in the TPAC–NaCl–$H_2O$ system. This suggests that like ion pairs in the TPAC–NaCl–$H_2O$ system are breaking apart, possibly forming $Pr_4N^+$–$Na^+$ ion pairs, with increasing total concentration rather than forming triplets. However, the like ion pairs of the TBAC–NaCl–$H_2O$ system are more likely to form triplets rather than the mixed ion pairs with increasing total concentration. This behavior also indicates that $Bu_4NCl$ has stronger hydrophobic characteristics than does $Pr_4NCl$.

## Conclusion

Osmotic coefficients, activity coefficients, and free energies of mixing for the system TBAC–NaCl–$H_2O$ were determined over a wide range of total ionic strengths and ionic strength fractions. From these results we find that Harned's rule is not obeyed above total ionic strength of approximately 1 *m* for either TBAC or NaCl. Free energies of mixing curves are skewed toward higher $Y_{NaCl}$ values, indicating nonzero values of the Friedman interaction parameter $g_1$. These nonzero values of $g_1$ are in direct conflict with the results of the assumption made by Reilly and Wood for mixtures of 1–1 electrolytes. From our results and those reported by Padova et al. we conclude that in the calculation of $g_0$ and $g_1$ the formation of triplets among ions of like charge must be taken into account in a 1–1 system containing clathrate-forming salts.

Further, our results indicate that like ion pairs are preferred to mixed pairs of the same charge type and $R_4N^+$–$R_4N^+$ pairs are preferred to $Na^+$–$Na^+$ pairs. Padova's suggestion of ion triplets of the form $R_4N^+$–$Cl^-$–$Na^+$ is not likely to be correct due to the absence of a $B^{111}$ term in eq 18.

Studies of the thermodynamics of mixtures of clathrate-forming salts are currently under way in our laboratory. $g_0$ and $g_1$ values will be of interest in these systems.

**Registry No.** NaCl, 7647-14-5; TBAC, 1112-67-0.

---

# Infrared Laser Photodetachment of Electrons from Vibrationally Excited Allyl Anions

**Charles A. Wight***[†] **and J. L. Beauchamp**

*Arthur Amos Noyes Laboratory of Chemical Physics,*[‡] *California Institute of Technology,*
*Pasadena, California 91125* *(Received: November 4, 1983; In Final Form: March 13, 1984)*

Infrared laser photodetachment of allyl anions has been investigated using the techniques of ion cyclotron resonance (ICR) spectroscopy. Facile detachment of vibrationally excited anions occurs with a phenomenologically defined cross section, $\sigma^* = (6.5 \pm 2) \times 10^{-20}$ cm$^2$ at 945 cm$^{-1}$, using a low-power CW $CO_2$ laser. The detachment yield decreases with increasing photon energy in the range 900–1100 cm$^{-1}$. Photodetachment from vibrationally relaxed anions also occurs but with a much lower cross section, $\sigma = (6.3 \pm 3) \times 10^{-23}$ cm$^2$. When fluoride ion reacts with allyltrimethylsilane, about 30% of the nascent allyl anions are vibrationally excited. The predominant relaxation mechanism below $10^{-6}$ torr is radiative emission with a measured rate constant of $53 \pm 10$ s$^{-1}$.

## Introduction

It has been known for some years that vibrational excitation can influence ion–molecule reaction rates.[1] Knowledge of vibrational relaxation rates is thus crucial for assessing the role of these excited species in the chemistry of planetary atmospheres or laboratory plasmas. State-specific collisional relaxation rate coefficients have only recently been measured for $N_2^+$, $O_2^+$, and $NO^+$ by using selected ion-flow drift tube techniques.[2–6] Quenching efficiencies for various neutral collision partners vary

---

[†] Present address: Joint Institute for Laboratory Astrophysics, University of Colorado and National Bureau of Standards, Boulder, CO 80309.

[‡] Contribution No. 6554.

(1) See, for example: Lindinger, W.; McFarland, M.; Fehsenfeld, F. C.; Albritton, D. L.; Schmeltekopf, A. L.; Ferguson, E. E. *J. Chem. Phys.* **1975**, *63*, 2175.

(2) Dobler, W.; Howorka, F.; Lindinger, W. *Plasma Chem. Plasma Process.* **1982**, *2*, 353.

(3) Dobler, W.; Ramler, H.; Villinger, H.; Howorka, F.; Lindinger, W. *Chem. Phys. Lett.* **1983**, *97*, 553.

(4) Böhringer, H.; Durup-Ferguson, M.; Ferguson, E. E.; Fahey, D. W. *Planet. Space Sci.* **1983**, *31*, 483.

from $10^{-3}$ to nearly unity, depending on whether near-resonant V–V energy-transfer or symmetric charge-transfer channels are accessible. For triatomic and polyatomic ions, relaxation of vibrationally excited populations has been monitored by using photodissociation[7-10] or photodetachment[11] techniques. These methods use visible and/or infrared lasers to interrogate excited ions which have enhanced photoexcitation cross sections relative to ground-state ions. Again, quenching efficiencies are found to vary over a wide range, depending on the neutral collision partner.

In ICR trapping experiments where ions are spatially confined for long periods, radiative relaxation rates may be obtained by extrapolating relaxation rates to their zero pressure values. This method has been used to determine radiative relaxation rates for $CF_3O^-$ (21 $s^{-1}$)[12] and $CF_3I^+$ (11.3 $s^{-1}$),[13] the latter corresponding to electronic spin–orbit relaxation. Much of the current interest in radiative relaxation of polyatomic ions stems from efforts to calculate rate coefficients for radiative association reactions.[14,15] This process, in which the collision complex of an ion and neutral molecule is stabilized by photon emission, is believed to play a key role in the chemical evolution of interstellar clouds.[16-18]

In this paper we report a study of infrared laser photodetachment from vibrationally excited allyl anions, $C_3H_5^-$. Relaxation of the anions results in a large decrease in the photodetachment cross section. This is in contrast to multiphoton detachment studies of several larger organic anions in which no distinction between excited and relaxed anions is observed.[19-23] The allyl anion photodetachment probability is only weakly dependent on the pressure of added neutral gases, indicating that, below $10^{-6}$ torr, the principal vibrational relaxation mechanism is radiative. The unimolecular rate constant, 53 ± 10 $s^{-1}$, is more than 1 order of magnitude larger than the calculated radiative rate constant for propene, demonstrating that large errors may be encountered by using spectroscopic constants of neutral molecules to estimate radiative rates for analogous polyatomic ions.

## Experimental Section

The theory, techniques, and instrumentation of trapped-ion ICR spectroscopy have been described in detail elsewhere.[24,25] The ICR cell has been modified for photochemical studies by replacing one of the source drift plates with a 92% transmittance wire mesh. The unfocused laser beam enters the vacuum enclosure through a polished NaCl window, passes through the mesh and the ion-trapping region, and is reflected off the rear drift plate back out the window after a second pass through the ion trap. Power from the line-tunable CW $CO_2$ laser (Apollo Model 550A) is measured with a Laser Precision Corp. pyroelectric radiometer (Model RkP-345), and the beam shape is monitored with an Optical Engineering Model 22A thermal imaging plate. Wavelength calibration is performed using an Optical Engineering Model 16A spectrum analyzer. An electronically controlled mechanical shutter (Uniblitz Model 225L0A14X5) is used to irradiate the ions only during alternate trapping cycles. The corresponding ion intensities (laser on and laser off) are monitored and averaged by a two-channel boxcar integrator. These signals are then processed in a straightforward fashion to yield photodetachment yields even in the presence of ion loss due to diffusion and reaction. Additional details are presented elsewhere.[26]

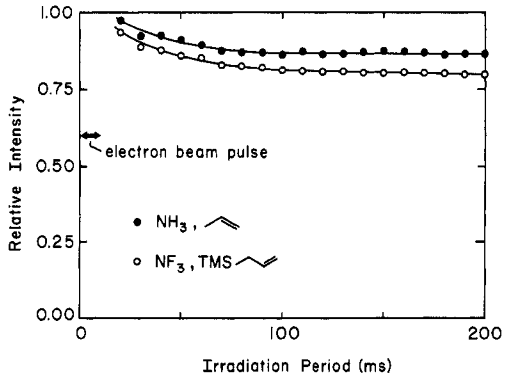


**Figure 1.** Decay of allyl anion signal intensity as a function of laser irradiation period. Laser intensity is 40 $W/cm^2$ at 942.4 $cm^{-1}$. Open circles indicate allyl anion produced by reaction 1 with $P(NF_3) = 5.1 \times 10^{-7}$ torr and $P$(allyltrimethylsilane) = $1.4 \times 10^{-6}$ torr. Solid points indicate allyl anion produced by reaction 2 with $P(NH_3) = 3 \times 10^{-6}$ torr and $P(C_3H_6) = 1.5 \times 10^{-6}$ torr. Ion formation is initiated by a 10-ms electron beam pulse, and production of allyl anion is >95% complete by 100 ms in each case.

Nitrogen trifluoride, ammonia, propene, allyltrimethylsilane, and nitrogen were obtained from commercial sources and were used without further purification except for degassing at liquid nitrogen temperature. Pressures of neutral gases were measured with a Schulz-Phelps type ionization gauge which was calibrated for each gas at higher pressures with an MKS Instruments Baratron Model 90H1-E capacitance manometer. It is estimated that absolute pressure determinations are within ±20% using this method.

The infrared spectrum of propene at 50 torr was obtained by using a 10-cm gas cell with NaCl windows in a Beckman Model 4240 infrared spectrophotometer.

## Results

*Ion Formation.* Allyl anions are conveniently generated by two different methods in the ICR spectrometer. Reaction of fluoride ion with allyltrimethylsilane is estimated to be exothermic by 14 kcal/mol:[27]

$$F^- + (CH_3)_3Si(C_3H_5) \rightarrow C_3H_5^- + (CH_3)_3SiF \qquad (1)$$

The measured rate constant for reaction 1 is $9 \times 10^{-10}$ $cm^3/$(molecule s). Fluoride ion is formed by low-energy dissociative electron attachment of $NF_3$ within the ion trap. A second method for forming allyl anion is by proton abstraction from propene with a strong anionic base:

$$B^- + CH_3CHCH_2 \rightarrow C_3H_5^- + BH \qquad (2)$$

Dissociative electron attachment of 5-eV electrons to ammonia forms $NH_2^-$ and $H^-$, both of which react with propene. Reaction 2 is exothermic by 8.8 and 9.6 kcal/mol for these bases, respectively.[28]

---

[5] Böhringer, H.; Durup-Ferguson, M.; Fahey, D. W.; Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* **1983**, *79*, 4201.

[6] Dobler, W.; Federer, W.; Howorka, F.; Lindinger, W.; Durup-Ferguson, M.; Ferguson, E. *J. Chem. Phys.* **1983**, *79*, 1543.

[7] Kim, M. S.; Dunbar, R. C. *Chem. Phys. Lett.* **1979**, *60*, 247.

[8] Lev, N. B.; Dunbar, R. C. *J. Phys. Chem.* **1983**, *87*, 1924.

[9] Orlowski, T. E.; Freiser, B. S.; Beauchamp, J. L. *Chem. Phys.* **1976**, *16*, 439.

[10] Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1979**, *101*, 3999.

[11] Huber, B. A.; Cosby, P. C.; Peterson, J. R.; Moseley, J. T. *J. Chem. Phys.* **1977**, *66*, 4520.

[12] Jasinski, J. M.; Brauman, J. I. *J. Chem. Phys.* **1980**, *73*, 6191.

[13] Thorne, L. R.; Beauchamp, J. L. *J. Chem. Phys.* **1981**, *74*, 5100.

[14] Herbst, E. *Chem. Phys.* **1982**, *65*, 185.

[15] Woodin, R. L. Ph.D. Thesis, California Institute of Technology, 1979.

[16] Watson, W. D. *Rev. Mod. Phys.* **1976**, *48*, 513.

[17] Huntress, W. T.; Mitchell, G. F. *Astrophys. J.* **1979**, *231*, 456.

[18] Smith, D.; Adams, N. G. *Astrophys. J.* **1978**, *220*, L87.

[19] Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *J. Chem. Phys.* **1979**, *71*, 1030.

[20] Meyer, F. K.; Jasinski, J. M.; Rosenfeld, R. N.; Brauman, J. I. *J. Am. Chem. Soc.* **1982**, *104*, 663.

[21] Wight, C. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 6499.

[22] Wight, C. A.; Beauchamp, J. L. *Chem. Phys.*, in press.

[23] Wight, C. A.; Beauchamp, J. L. *J. Am. Chem. Soc.*, in press.

[24] Lehman, T. A.; Bursey, M. M. "Ion Cyclotron Resonance Spectrometry"; Wiley-Interscience: New York, 1976.

[25] (a) McMahon, T. B.; Beauchamp, J. L. *Rev. Sci. Instrum.* **1972**, *43*, 509. (b) Beauchamp, J. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 527.

[26] Bomse, D. S.; Woodin, R. L.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5503.

[27] DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J.; Sullivan, S. A. *J. Am. Chem. Soc.* **1980**, *102*, 5012.

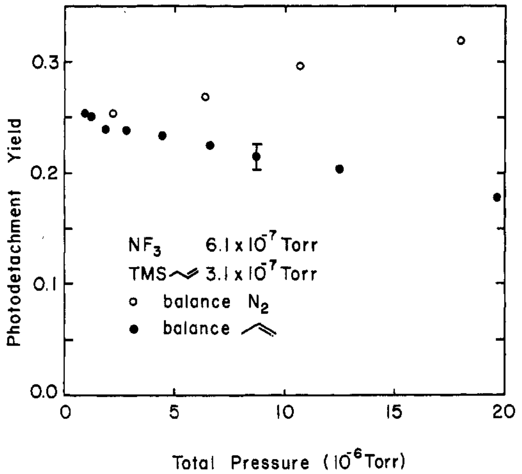


**Figure 2.** Photodetachment yield of allyl anion vs. neutral gas pressure. Irradiation is for 200 ms beginning at the start of the 10-ms electron beam pulse. Laser intensity is 90 W/cm$^2$ at 942.4 cm$^{-1}$. Use of $N_2$ as the buffer gas results in an increase in photodetachment yield (open circles) whereas a decrease is observed with propene (solid points). The error bars indicate the estimated uncertainty for each point.

*Infrared Laser Photodetachment.* When allyl anions are irradiated with the continuous output of a $CO_2$ laser in the region 900–1100 cm$^{-1}$, a photodetachment signal is observed. Figure 1 illustrates that photodetachment occurs mainly in the first 100 ms, during formation of allyl anion by reaction 1 or 2. At longer times, photodetachment is quite slow, even at laser intensities in excess of 100 W/cm$^2$. If the laser irradiation period is delayed until after allyl ion formation is complete, only the slow photodetachment signal is observed. This behavior strongly suggests that reactions 1 and 2 produce internally excited anions which undergo rapid photodetachment. Relaxation reduces the internal energy of the anions to states which undergo only slow photodetachment. Since no excited electronic states of allyl anions are known, the nature of the internal excitation is presumed to be vibrational.

To test whether the vibrational relaxation is collisional or radiative, the photodetachment yield is observed as a function of added neutral gas pressure. Addition of propene up to $2 \times 10^{-5}$ torr results in a modest decrease in the photodetachment yield while addition of $N_2$ actually increases the yield, as shown in Figure 2. The collision rates in this experiment vary from 30 to approximately 600 s$^{-1}$. The weak dependence of the photodetachment yield on the pressure of added buffer gas indicates clearly that, below $10^{-6}$ torr, the principal relaxation mechanism is radiative.

In order to estimate the radiative relaxation rate, the time delay between allyl ion formation and laser irradiation is systematically increased. Reaction 1 is terminated 50 ms after the electron beam pulse by double-resonance ejection of the reactant ion, F$^-$. Laser irradiation is limited to 50 ms duration following ejection of F$^-$. The results are shown in Figure 3. If the start of the irradiation period is successively delayed with respect to ejection of F$^-$, the photodetachment yield decreases exponentially to a constant value of 1%. This residual signal is present even at very long delay times and is attributed to photodetachment of the relaxed anions. Alternatively, a small fraction of the ion population may remain in a long-lived excited vibrational state which is not relaxed by radiation or by collisions on the time scale of this experiment. The radiative relaxation rate obtained from the exponential decay is 53 ± 10 s$^{-1}$. The photodetachment cross section of the relaxed anions is phenomenologically defined as the detachment rate constant divided by the laser photon flux and has the value $\sigma = (6.3 \pm 3) \times 10^{-23}$ cm$^2$.

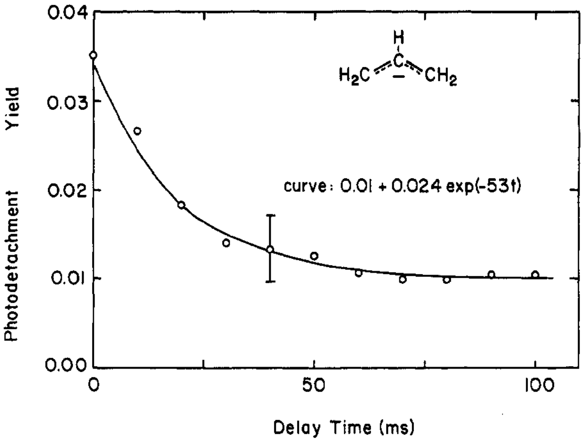
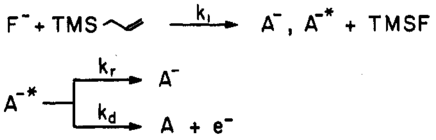


**Figure 3.** Photodetachment yield as a function of relaxation time for allyl anions. A 10-ms electron beam pulse is followed by a 40-ms ion formation period after which fluoride ion is ejected from the ion trap, halting the production of $C_3H_5^-$. The start of a 50-ms irradiation period is delayed with respect to the start of F$^-$ ejection. Detection of $C_3H_5^-$ immediately follows the irradiation period in all cases. Laser intensity is 60 W/cm$^2$ at 948 cm$^{-1}$. Neutral pressures of $NF_3$ and allyltrimethylsilane are $5.1 \times 10^{-7}$ and $1.5 \times 10^{-6}$ torr, respectively. The estimated uncertainty is indicated by the bars at 40-ms delay.

Scheme I



A determination of the photodetachment cross section for vibrationally excited ions requires a closer examination of the overall kinetics of the detachment process. In the simplest treatment (Scheme I), ion formation is assumed to result in two populations of allyl anions corresponding to relaxed (A$^-$) and vibrationally excited (A$^{-*}$) ions. Vibrationally excited ions may either relax to A$^-$ or, in the presence of laser irradiation, undergo electron detachment to form allyl radical (A). The population of A$^{-*}$ as a function of time is given by

$$[A^{-*}](t) = \frac{f k_1 F_0}{k_r + k_d - k_1}\{\exp[-k_1 t] - \exp[-(k_r + k_d)t]\} \tag{3}$$

where $k_1$ is the first-order rate constant for reaction 1 (including the concentration of allyltrimethylsilane), $F_0$ is the number of fluoride ions originally produced by the electron beam, and $f$ is the fraction of those ions which react to form vibrationally excited allyl anions. The number of allyl radicals produced is then given by

$$[A](t) = \frac{k_d k_1 f F_0}{(k_r + k_d - k_1)k_1(k_r + k_d)}\{k_r + k_d - k_1 + k_1 \exp[-(k_r + k_d)t] - [k_r + k_d] \exp[-k_1 t]\} \tag{4}$$

which simplifies at long times ($t >> k_1^{-1}, k_r^{-1}$) to

$$[A](t \rightarrow \infty) = k_d F_0 f/(k_r + k_d) \tag{5}$$

Substituting $\Phi\sigma^*$ for $k_d$, where $\Phi$ is the photon flux and $\sigma^*$ is the cross section for photodetachment of vibrationally excited anions, and putting eq 5 in terms of experimental observables, we obtain

$$\frac{A_0^-}{A_0^- - A^-} = \frac{k_r}{f\sigma^*\Phi} + \frac{1}{f} \tag{6}$$

where $A^-$ and $A_0^-$ are the allyl anion intensities at long times in the presence and absence of laser radiation, respectively. A plot of the left-hand side of eq 6 vs. $\Phi^{-1}$ is given in Figure 4. The $y$ intercept yields $f = 0.29 \pm 0.04$, and the slope gives $k_r(\sigma^*)^{-1} = 8.21 \times 10^{20}$ cm$^{-2}$ s$^{-1}$. Using $k_r = 53$ s$^{-1}$ from Figure 3, we obtain $\sigma^* = (6.5 \pm 2) \times 10^{-20}$ cm$^2$. In the analysis we have ignored the fact that some ion loss is due to slow photodetachment of relaxed

---

(28) Bartmess, J. E.; McIver, R. T. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2.

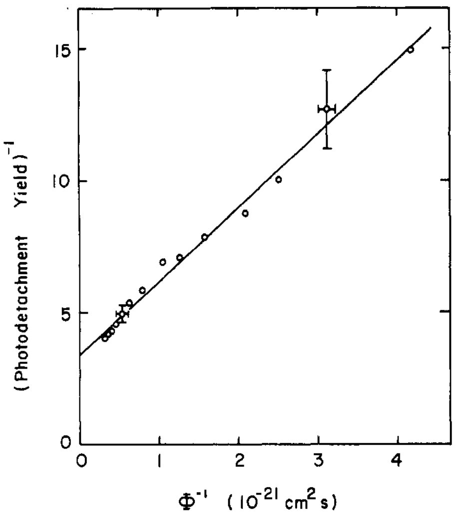


**Figure 4.** The reciprocal of the photodetachment yield (lhs of eq 6) plotted vs. the reciprocal of laser photon flux yields the least-squares fit shown. The slope is 2.79 × $10^{21}$ cm$^{-2}$ s$^{-1}$, and the $y$ intercept is 3.4. The 200-ms irradiation period begins at the initiation of ion formation. Laser intensity is varied from 60 to 4.5 W/cm$^2$ at 948 cm$^{-1}$. Neutral pressures of $NF_3$ and allyltrimethylsilane are 5.1 × $10^{-7}$ and 6.9 × $10^{-7}$ torr, respectively.

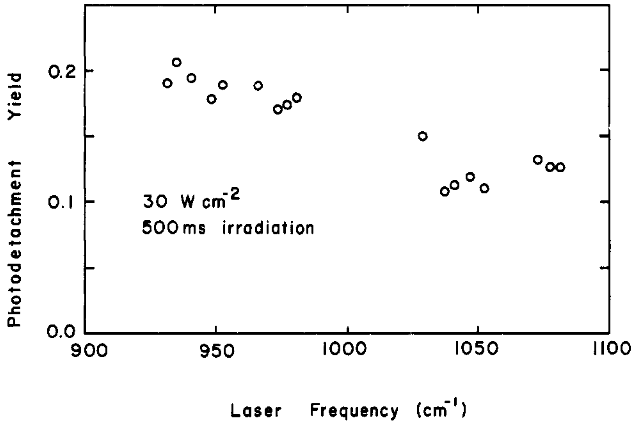


**Figure 5.** Infrared photodetachment spectrum of vibrationally excited allyl anions obtained by monitoring the detachment yield as a function of $CO_2$ laser frequency. The 500-ms irradiation period begins at the initiation of ion formation. Laser intensity at each point is 30 W/cm$^2$. Neutral pressures of $NF_3$ and allyltrimethylsilane are 5.1 × $10^{-7}$ and 1.7 × $10^{-7}$ torr, respectively.

anions. This is not expected to introduce a significant error since $\sigma^*/\sigma = 10^3$.

The infrared photodetachment yield exhibits only a modest dependence on the laser photon energy in the 900–1100-cm$^{-1}$ region (Figure 5), with a general decrease toward higher energy. This behavior is opposite to the usual case for direct photodetachment, in which the cross section increases with photon energy near threshold. It is therefore likely that photoexcitation occurs in a vibrational mode (or combination of modes) of allyl anion, followed by vibrational autodetachment of an electron. Since photodetachment occurs mainly from vibrationally excited allyl anions, the spectrum is actually that of the excited anions and could be significantly different from the infrared spectrum of ground-state allyl anions. Photodetachment with a pulsed $CO_2$ laser has also been reported to have only a modest wavelength dependence.[19,20]

## Discussion

A key observation in this study is that $C_3H_5^-$ ions may exist as at least two different populations with greatly differing cross sections for photodetachment by the infrared laser. This inhomogeneity could be caused by the presence of more than one stable isomer[29] or by differences in either vibrational[12] or electronic[13] energy within the ion population. In the absence of any known or postulated excited electronic states or isomers of $C_3H_5^-$, it is quite likely that the observed difference in photodetachment cross sections results from different degrees of vibrational excitation. Of course, reactions 1 or 2 form allyl anions with a range of internal energies. However, the observations are consistent with the simplest kinetic treatment, that ions with one range of internal energies interact strongly with the laser field while the remainder interact only weakly.

The adiabatic electron affinity represents a practical upper limit to the internal energy of the excited anions since those molecules with higher energies are unstable with respect to autodetachment. Autodetachment lifetimes are difficult to calculate for polyatomic anions[30] but are expected to lie in the range $10^{-6}$–$10^{-10}$ s for most diatomic negative ions.[31] Typical lifetimes of temporary negative ion states formed in low-energy electron-scattering experiments range from $10^{-10}$ to $10^{-15}$ s.[32] The electron affinity of $C_3H_5$, 0.360 ± 0.035 eV (or 8.3 ± 0.8 kcal/mol), has recently been obtained from the photoelectron spectrum of allyl anion[33] and is in excellent agreement with the value 0.36 ± 0.09 eV calculated from related thermodynamic data.[34-36] It is unlikely that allyl anions with more than 9 kcal/mol vibrational energy will be stable with respect to autodetachment on the millisecond time scale of this study.

To estimate a lower limit to the internal energy of the excited allyl anions, it is necessary to postulate a mechanism for the photodetachment. The large decrease in apparent cross section of relaxed anions compared with that of excited ones could be due to an energetic requirement that relaxed anions must absorb more than one infrared photon to reach the detachment threshold. There is no direct evidence to support this hypothesis, but if it is true, the lower limit would be 5.6 kcal/mol. This is simply the difference between the adiabatic electron affinity and the laser photon energy at 945 cm$^{-1}$.

Other possible mechanisms could be responsible for the observed multicomponent population behavior.[37-40] For instance, the presence of a dynamic bottleneck in the multiphoton absorption mechanism could cause the lower limit of energy in the excited anions to be as low as 3 kcal/mol; this is the upper end of the thermally populated ion population at room temperature for which the average energy is about 0.5 kcal/mol. Alternatively, it is possible that the multicomponent populations result from resonant absorption character in the quasi-continuum of states at energies between 6 and 9 kcal/mol. Such a mechanism has been postulated[40] to explain saturation effects in the pulsed laser dissociation of chemically activated $CH_3OHF^-$. Thus, while it seems reasonable that the internal energy of the excited anions lies between 6 and 9 kcal/mol, the evidence supporting the lower limit of this range is weak. As we shall see, it is the upper limit of 9 kcal/mol which is most important for comparing observed and calculated rates of radiative relaxation for allyl anions.

Having established approximate limits to the internal energy of vibrationally excited allyl anions, it is worthwhile to comment on the reaction energy disposal in reactions 1 and 2. In the case

---

(29) (a) Herbst, E.; Patterson, T. A.; Lineberger, W. C. *J. Chem. Phys.* **1974**, *61*, 1300. (b) Richardson, J. H.; Stephenson, L. M.; Brauman, J. I. *Chem. Phys. Lett.* **1974**, *25*, 318.

(30) Simons, J. *J. Am. Chem. Soc.* **1981**, *103*, 3971.

(31) Acharya, P.; Kendall, R.; Simons, J. *J. Am. Chem. Soc.* **1984**, *106*, 3402.

(32) Compton, R. N. In "Electronic and Atomic Collisions"; Oda, N., Takayanagi, K., Eds.; North-Holland Publishing Co.: Amsterdam, 1980; p 251.

(33) Oakes, J. M.; Ellison, G. B., unpublished results.

(34) Buttrill, S. E.; Williamson, A. D.; LeBreton, P. *J. Chem. Phys.* **1975**, *62*, 1586.

(35) Houle, F. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 3290.

(36) Mackay, G. I.; Lien, M. H.; Hopkinson, A. C.; Bohme, D. K. *Can. J. Chem.* **1978**, *56*, 131.

(37) Quack, M.; Humbert, P.; van den Bergh, H. *J. Chem. Phys.* **1980**, *73*, 247.

(38) Golden, D. M.; Rossi, M. J.; Baldwin, A. C.; Barker, J. R. *Acc. Chem. Res.* **1981**, *14*, 56.

(39) Baldwin, A. C.; Barker, J. R. *J. Chem. Phys.* **1981**, *74*, 3823.

(40) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *Chem. Phys. Lett.* **1980**, *71*, 400.

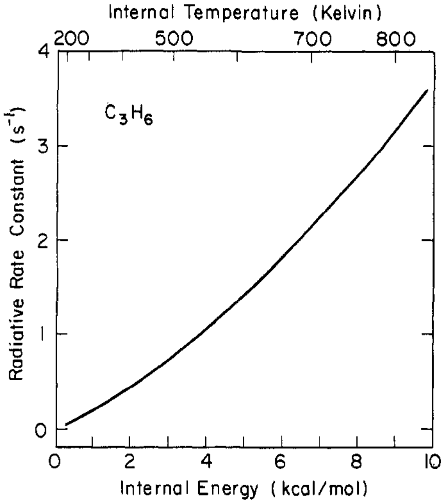


**Figure 6.** Calculated radiative emission rate for propene as a function of internal energy.

of proton abstraction from propene by $NH_2^-$ and $H^-$, it is not surprising that a significant fraction of the reaction exothermicity is found in the allyl anion product. Statistical theories[41-43] of reaction energy disposal predict that the product having the highest density of states will also receive the greater share of internal energy. In the case of reaction 1, nearly all of the excess energy would be expected to remain in the trimethylfluorosilane product. It appears, however, that in at least 30% of the reactive collisions, a substantial fraction of the excess energy is partitioned into allyl anion vibration. A nonstatistical partitioning of the energy in reaction 1 can be rationalized by considering the electronic structure of the reaction complex. After breaking the carbon–silicon bond, the allyl anion can delocalize the charge of its extra electron by forming a four-electron, three-center bond across the carbon skeleton. The accompanying decrease in electronic energy is released as vibrational energy. The separation to products may be so great by this time that the excess energy cannot be distributed statistically throughout the entire complex but instead remains as vibrational excitation of the allyl anion product. Farneth and Brauman have suggested that this type of charge localization in the transition state may be responsible for unusually slow rates of proton-transfer reactions observed for many delocalized anions.[44]

It is instructive to compare the observed radiative relaxation rate with the calculated radiative emission rate for allyl anions. The radiative emission rate will in general be an upper limit to the overall radiative relaxation rate, and the two will be the same if each photon carries away enough energy to convert an "excited" anion to a "relaxed" one. Following the quasi-thermodynamic treatment due to Dunbar,[45] the data needed to calculate the radiative emission rate are the vibrational frequencies and integrated absorption band intensities for the anion. Unfortunately, none of these quantities are known. This is the case for all but a very few positive or negative ions and represents a major obstacle to the comparison of calculated and experimental radiative rate constants. One approach to this problem is to calculate the radiative emission rate for an analogous neutral compound for which the necessary data are available. The calculated emission rate for propene is shown as a function of internal energy in Figure 6. Frequencies were obtained from spectroscopic studies,[46] and the absorption band intensities were estimated from an infrared spectrum of propene. It is immediately evident that the calculated emission rate for propene underestimates the experimental radiative relaxation rate for allyl anion by more than 1 order of magnitude at energies below 9 kcal/mol.

In considering possible sources of error in the calculation, it is unlikely that the assumption of electrical and mechanical harmonicity leads to such a large discrepancy. An analysis by Herbst[14] indicates that the model works best for polyatomic molecules at modest internal energies, which are exactly the conditions of the present experiments. The fact that propene has three extra vibrational modes does not introduce a large error; using the vibrational frequencies of the allyl radical[47] gives nearly identical results. Rather, it is the larger vibrational transition moments of allyl anion compared with those of propene which most likely account for the large difference in experimental vs. calculated rates. The spontaneous emission rates for ions are expected to be larger than for analogous neutral molecules for two main reasons. First, the dipole moment of an ion becomes infinite at large internuclear separations; for neutrals it approaches zero. Since the vibrational transition probability depends on the change in dipole moment with internuclear distance, it is natural that such transitions should be stronger in ions. Rosmus and co-workers have calculated radiative emission rates for several diatomic neutrals and ions. They find that $OH^+$ and $OH^-$ emission rates are about 10 times that of OH.[48] Similarly, the radiative emission rate for $ArH^+$ is more than 10 times faster than for the isoelectronic neutral HCl.[49] A second factor contributing to the differences between propene and allyl anion is that certain vibrations of the anion, especially $CH_2$ twisting motion, can force the negative charge to become more localized on one of the carbon atoms. Such motions are expected to be associated with large changes in dipole moment and therefore have large infrared transition probabilities. While recognizing the dangers of drawing parallels between diatomic and polyatomic ions, we are nevertheless forced to conclude that using the vibrational transition moments of neutral molecules to estimate radiative emission rates of analogous ions may lead to very large errors indeed. Valid comparisons between calculated and experimental radiative relaxation rates for most polyatomic ions will probably require accurate spectroscopic constants derived from experimental data or quantum calculations.

*Acknowledgment.* We thank the reviewer for helpful comments and Dr. B. S. Ault for providing the sample of $NF_3$. This work is supported in part by the President's Fund of the California Institute of Technology and by the U.S. Department of Energy.

**Registry No.** $C_3H_5^-$, 1724-46-5; $F^-$, 16984-48-8; $(CH_3)_3Si(C_3H_5)$, 762-72-1; $CH_3CHCH_2$, 115-07-1.

---

(41) Levine, R. D.; Bernstein, R. B. In "Dynamics of Molecular Collisions"; Miller, W. H., Ed.; Plenum Press: New York, 1976; Part B.

(42) Rabinovitch, B. S.; Lin, Y. N. *J. Phys. Chem.* **1970**, *74*, 1769.

(43) Lau, K. H.; Lin, S. H. *J. Phys. Chem.* **1971**, *75*, 2458.

(44) Farneth, W. E.; Brauman, J. I. *J. Am. Chem. Soc.* **1976**, *98*, 7891.

(45) Dunbar, R. C. *Spectrochim. Acta, Part A* **1975**, *31A*, 797.

(46) Silui, B.; Labarbe, P.; Perchard, J. P. *Spectrochim. Acta, Part A* **1973**, *29A*, 263.

(47) Takada, T.; Dupuis, M. *J. Am. Chem. Soc.* **1983**, *105*, 1713.

(48) Werner, H.-J.; Rosmus, P.; Reinsch, E.-A. *J. Chem. Phys.* **1983**, *79*, 905.

(49) Rosmus, P. *Theor. Chim. Acta* **1979**, *51*, 359.