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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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Abstract: 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 925–1080 cm^{-1} wavelength range. Ions are formed, stored, and detected with the use of techniques of ion cyclotron resonance spectroscopy. Infrared multiphoton excitation is effected by using low-power, continuous-wave laser radiation. The "fingerprint" spectrum of the molecular ion of perfluorocyclopropane is identical with 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 system. Photoionization mass spectroscopy results yield $\Delta H_f(\text{c-}C_3F_6) = -233.8$ kcal/mol.

Mass spectrometric 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 by 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 reduce 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 and 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 by 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 W cm^{-2}), continuous-wave, CO_2 laser irradiation induces multiphoton infrared excitation and dissociation of gas-phase ions.[14-17] Low laser power avoids line broadening and sharply peaked infrared photodissociation spectra can be obtained which appear to mimic absorption spectra over the same wavelength region.[16] 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 with the use of the techniques of ion cyclotron resonance (ICR) spectroscopy.

Experimental Section

Ion cyclotron resonance techniques have been described in detail in the literature.[18,19] Ions formed by electron-impact ionization are stored

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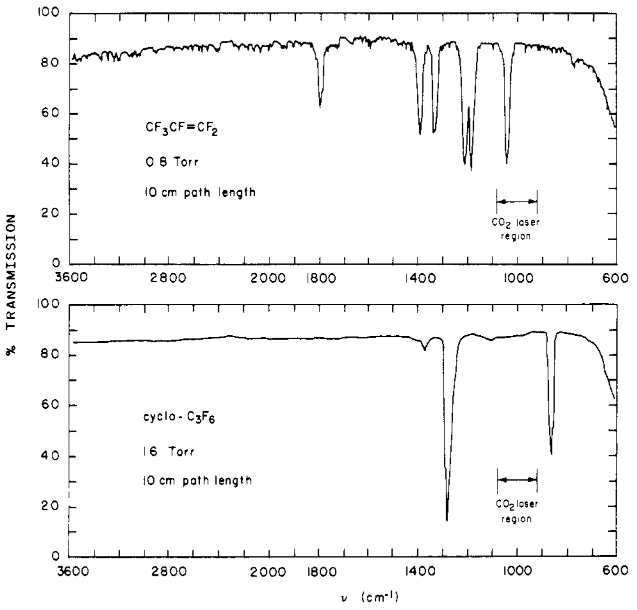

Figure 1. Gas-phase infrared absorption spectra of perfluoropropylene (top) and perfluorocyclopropane (bottom). See Experimental Section for details.

Table I. Heats of Formation of Neutral Molecules and Ions Pertinent to This Study

M	ΔH_f(M), kcal/mol	IP(M), eV	ΔH_f(M^+), kcal/mol
$CF_3CF{=}CF_2$	−268.9[a]	10.60[b] (10.62[c])	−24.5[b]
c-C_3F_6	−233.8[b]	11.18[b] (11.20[c])	(24)[b]
C_2F_4	−157.4[d]	10.12[e]	76.0
CF_2	−43.8[b]	11.42[f]	219.6

[a] Bryant, W. M. D. *J. Polym. Sci.* 1962, *56*, 277. [b] Thermochemical results presented are from a study of the isomers of C_3F_6 employing photoionization mass spectrometry. Details are reported in ref 27. [c] Adiabatic IP from photoelectron spectrum. [d] Locker, J. R.; Skinner, H. A. *J. Chem. Soc. A* 1968, 1034. [e] Reference 26. [f] J. M. Dyke, L. Golub, N. Jonathan, A. Morris, and M. Okuda, *J. Chem. Soc., Faraday Trans. 2* 1978, *70*, 1828.

in crossed electric and magnetic fields for times up to 2 s 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 with the use of 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 ±20%.

ICR modifications for infrared photochemistry are described elsewhere.[15] Briefly, unfocused output from a grating tuned Apollo 550A, continuous-wave, CO_2 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.

Gas-phase infrared absorption spectra of neutrals were recorded with a Beckman IR-12 spectrometer, using 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 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 ~10 μs.

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 noncondensible 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 ~2 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 suggests 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 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 c-C_3F_6. Table I lists thermochemical data obtained for perfluorocyclopropane by photoionization mass spectrometry. Also included is the c-C_3F_6 adiabatic ionization potential measured by photoelectron spectroscopy. By analogy to the Walsh molecular orbital analysis of cyclopropane[23] the highest occupied molecular orbital (HOMO) in c-C_3F_6 is an in-plane, ring-bonding orbital of e' symmetry. Energies of fluorine nonbonding orbitals[24,25] (typically <-15 eV) are considerably below the HOMO energy (−11.18 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.

The energetics of C_3F_6 and $C_3F_6^+$ ions along with their decomposition products are illustrated in Figure 2.[26,27] Also shown are the corresponding diagrams depicting energetics of the $C_3H_6/C_3H_6^+$ system.[26] It should be particularly noted that thermolysis of neutral c-C_3F_6 does not result in isomerization to perfluoropropylene.[28] Instead the observed pyrolysis reaction is

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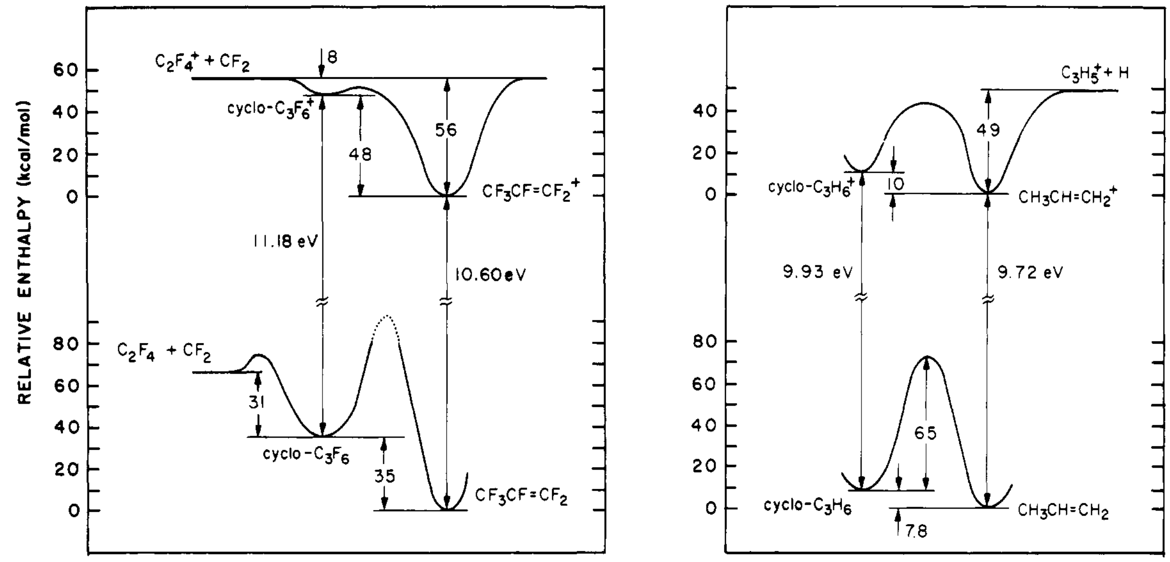

Figure 2. Energetics of C_3F_6 and $C_3F_6^+$ ions along with their decomposition products (at left) and energetics of the $C_3H_6/C_3H_6^+$ system (at right). Data compiled from Table I and ref 26.

CF_2 elimination. The barrier to unimolecular isomerization must exceed the measured 38 kcal/mol 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 reports[29] 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. A reported comparison of $C_3H_6^+$ metastable ion decompositions indicates detectable differences between ions obtained from cyclic and acyclic precursors. However, the authors are careful to point out that the results may be due to internal energy differences rather than the presence of structural isomers.[30] 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/mol below the energy required for production of $C_2F_4^+ + CF_2$. thus the base peak in the electron-impact ionization mass spectrum of c-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 1 s.

The abundance of $C_2F_4^+$ at the optimum electron energy (20 eV) for production and detection of c-C_3F_6 parent cation causes space charge problems which result in a loss of ICR trapping efficiency. To offset this problem during trapped ion studies of $C_3F_6^+$, ICR double resonance[31] 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 $C_3F_6^+$ obtained by ionization of c-C_3F_6 (bottom). In the upper spectrum there are two sets of photodissociation data points corresponding to electron impact ionization energies of 20 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_3CFCF_2 absorption band at 1037 cm^{-1} also seen in Figure 1 is the only discernable 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 (1047 cm^{-1}) coincides exactly with the maximum in the photodissociation spectrum of the 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 2 s of continuous laser irradiation at 34 W cm^{-2}. In the results shown for the c-C_3F_6 cation P_D corresponds to photodissociation yield following 0.45 s of 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 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 CF_3CFCF_2, compensates for the shorter irradiation time yet limits the number of useable CO_2 laser lines. Thus it is not possible to obtain as many data points near 1000 cm^{-1} for the perfluorocyclopropane system as for perfluoropropylene. Any small feature in the lower spectrum in Figure 3 comparable to the shoulder at ~1000 cm^{-1} in the upper spectrum is close to the limit of detectability due to the poorer signal-to-noise ratio for all data points in the lower spectrum as well as the more limited laser tuning range. It is possible that the maximum at ~1000 cm^{-1} in the upper spectrum in Figure 3 results from a vibrational hot band in the perfluoropropylene cation which may not be present in the infrared dissociation spectrum of the perfluorocyclopropane cation (see below).

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

$$C_3F_6^+ + nh\nu \rightarrow C_2F_4^+ + CF_2 \qquad (1)$$

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/mol (19 photons at 1047 cm^{-1}) endothermic for the perfluoropropylene ion and 8 kcal/mol (3 photons) endothermic

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[30] Gross, M. L.; Lin, P.-H. *Org. Mass Spectrom.* **1973**, *7*, 795.

[31] ICR double resonance is a technique which allows selective ejection from the ICR cell of ions with a given mass while detecting ions of another mass.[18]

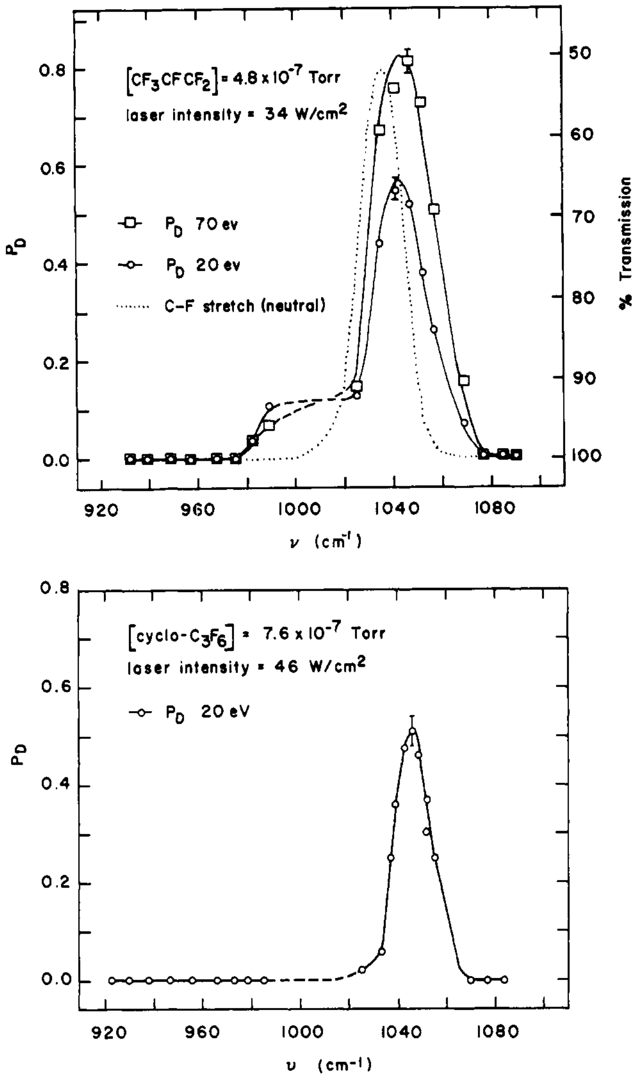

Figure 3. Photodissociation spectra of $C_3F_6^+$ isomers over the CO_2 laser spectral range. Upper spectrum is for the perfluoropropylene parent ion. Left ordinate is the fraction of $C_3F_6^+$ dissociated after 2 s of irradiation at 34 W cm^{-2}. The two solid curves are for ionization energies of 70 eV (□) and 20 eV (○). 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 the fraction of $C_3F_6^+$ dissociated following 450 ms of irradiation at 46 W cm^{-2}. Perfluorocyclopropane pressure is 7.6 × 10^{-7} torr.

for the 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 with 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 0.5 s trapping time there is an induction period of ~180 ms followed by an exponential decay of the $C_3F_6^+$ population. Induction periods are a characteristic of the multistep excitation process and have been discussed in detail elsewhere.[15] The entire $C_3F_6^+$ population appears to be characterized by a single photodissociation rate constant. If a second population is present, the abundance is below 10%. Unlike reported results for cyclopropane,[29] electron-impact ionization of c-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 I and Figure 2 indicate the ring-opening reaction, process 2, imparts 48 kcal/mol internal energy to the

$$c\text{-}C_3F_6^+ \rightarrow CF_3CFCF_2^+ \qquad (2)$$

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. Available evidence suggests that nonresonant collisional energy transfer is an inefficient process.[32,33] The recently reported[33] 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. Note that continuous laser irradiation is used to dissociate $C_3F_6^+$ derived from perfluoropropylene. In this case vibrationally excited ions do not have the opportunity to relax radiatively prior to the onset of multiphoton excitation. As a result, effects attributed to vibrationally hot perfluoropropylene cations are observed as discussed above.

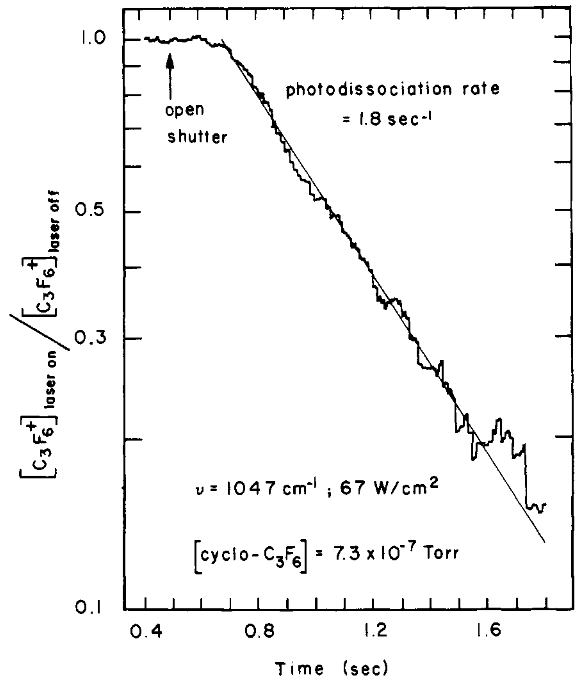

Figure 4. Temporal dependence of perfluorocyclopropane cation photodissociation. Ordinate is normalized ("laser on" divided by "laser off") ion signal intensity plotted on a logarithmic scale. Irradiation (67 W cm^{-2} at 1047 cm^{-1}) begins at 500 ms trapping time. Perfluoropropylene pressure is 7.3 × 10^{-7} torr.

Conclusions

Infrared photodissociation spectroscopy is an effective method for obtaining structural information on 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 with the perfluoropropylene parent cation.

Other commercially available infrared lasers can be used to extend the available wavelength range. Multiphoton dissociation

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using high power pulsed lasers[33,34] is suitable for more conventional mass spectrometers in which ion-residence times are $\sim 10^{-6}$ 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 the structure of the precursor ion.[2,35]

Acknowledgment. This work was supported by the United States Department of Energy and the President's Fund of the California Institute of Technology. We are grateful to Ms. Jocelyn Schultz for providing the photoelectron spectrum of c-C_3F_6.

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Propensity Rules for Vibration-Induced Electron Detachment of Anions

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Abstract: Vibration-induced detachment of electrons from molecular anions has recently been experimentally observed. In this paper, the coupling of the anion's vibration–rotation motion to its electronic degrees of freedom is analyzed in an attempt to predict under what circumstances efficient detachment would be expected. A set of propensity rules based upon the shapes of the anion and neutral potential-energy surfaces is put forth and applied to several prototypical situations. The development is not aimed at permitting ab initio calculations of electron detachment rates. Rather, it is designed to provide a useful tool both for interpreting experimental data and for designing especially interesting experiments to carry out.

Recently it has been obsd.[1] that electrons can be detached from molecular anions by using infrared (IR) laser light to vibrationally excite the parent ions. The nature of the coupling between the nuclear motions, as excited by the IR light, and the electronic degrees of freedom has not been thoroughly analyzed. Analogous couplings which give rise to vibration-induced ionization of molecular Rydberg states have been analyzed by Berry and others.[2] Clearly what characterizes both anions and Rydberg states in this perspective is that the amount of energy required to cause ionization is often substantially less than the dissociation energies of bonds in the parent species. Such vibration-induced ionization would not be expected to occur for the ground states of most neutral molecules (e.g., for ethylene the lowest ionization potential is 10.5 eV, whereas the C–H bond energy is only 4.2 eV).

The primary purposes of the present manuscript are to (1) describe a physical mechanism which gives rise to the conversion of intramolecular vibrational (and/or rotational) energy into electronic energy, (2) give an expression for the electron-detachment rate which permits one to predict the propensity rules which govern these ionization events, and (3) make qualitative predictions concerning those anions which would or would not be expected to efficiently undergo vibration-induced electron detachment. The mathematical machinery used to express the rate of electron loss is not new to this development. It is the commonly employed non-Born Oppenheimer coupling picture[3] which Berry used[2] in an elegant fashion to provide insight into the autoionization lifetimes to Rydberg states. This manuscript is intended to analyze in chemical terms those factors which affect the rate of electron detachment so as to give a wide range of chemists an understanding of those circumstances under which molecular anions would be expected to autodetach upon excitation of their vibrational/rotational motion (either by heating or laser IR radiation or formation via exothermic chemical reaction).

Before beginning the quantum mechanical treatment of the coupling between the nuclear and electronic motions as it pertains to this autodetachment problem, it is useful to distinguish among several types of anion/neutral potential-energy surface juxtapositions which might arise. In Figures 1–5 we represent a few of the more likely arrangements of anion (A^-) and neutral (N) potential-energy surfaces as functions of some (unspecified at this time) geometrical coordinate Q. The features which distinguish among these surfaces are (1) whether or not the surfaces intersect at some value(s) of Q, (2) how rapidly the anion–neutral electronic energy difference varies with Q, and (3) whether the intersections of the two surfaces occur at the limits of Q (e.g., $R = 0$ or $R \to \infty$) or for some intermediate value of Q. The situation depicted in Figure 1 is likely to arise when the neutral's molecular orbital (ϕ) to which the "extra" electron is added is not bound for Q near the equilibrium geometry for the neutral but becomes bound as Q increases. Figures 2 and 3 might pertain to molecules whose lowest unoccupied molecular orbital (LUMO) is bound for all values of Q except perhaps (Figure 2) for Q at its extreme value. Figure 4 describes situations in which the binding energy of the neutral's LUMO varies strongly with Q, whereas in Figure 5 the electron affinity (EA) is weakly dependent upon Q, in which case the LUMO could be a nonbonding "passive" orbital.

For systems in which the anion and neutral potential surfaces actually intersect, there exists the possibility that when E^- lies *above* E^0 the anion's electronic state could undergo detachment by way of purely *electronic* shape or Feshbach mechanism[4] at a rate which is competitive with that of the mechanism discussed below. In this case, the anion state would have a nonzero width $\Gamma(Q)$ due to the electronic decay mechanism. The *total* rate of

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