

not apply to the entire ensemble of molecules. Subsequent to the preliminary publication of our observations,⁴ considerable speculation concerning such behavior within the context of the master equation approach has appeared in the literature and several experimental examples have been suggested.^{34,42,43} The case reported here for CH_3OH^- is particularly interesting because the saturation behavior in the fluence plots is quite dramatic and because the ions already contain excess vibrational energy prior to irradiation. Although the discussion presented above is given in terms of two population components for the chemically activated CH_3OH^- , the conclusions remain valid if more than two components are present. It is possible that chemically activated CH_3OH^- dissociates via three or more mechanisms but that the corresponding changes in slope in the plots in Figure 8 cannot be resolved. It is probably necessary, however, that there not be too wide a dispersion of subpopulations and rates or the sharp curvature would not be seen.³⁴

The energetics of reaction 2, combined with an estimate of the density of internal states of CH_3OH^- as a function of energy, suggests that chemically activated CH_3OH^- is in the vibrational quasi-continuum.^{14a} Two frequency experiments on neutrals have been interpreted as indicating that molecules in the quasi-continuum have relatively unstructured absorption spectra.^{14,44} The results described above indicate that CH_3OH^- in the quasi-continuum can be characterized in terms of a resonant population component. This component varies in size and exhibits a different cross section for multiphoton dissociation depending on the irradiation wavelength. This result suggests that at least in this case some form of structure persists in the quasi-continuum, and it raises the interesting possibility of spectroscopically, and hence structurally, characterizing species near their dissociation thresholds via absorption or photodissociation spectroscopy.

Figure 7 shows that collisionally relaxed CH_3OH^- exhibits a linear plot of $-\ln(1 - F_D)$ vs. fluence. However, we find that even this data cannot be fit quantitatively by using a simple master equation^{45a} primarily because the experimental data remain linear

to such small fractional decomposition rather than showing an induction period. Such data can be fit if one invokes bottlenecks in the absorption mechanism;^{45b} however, the physical interpretation of such an assumption is not clear at present.

Conclusion

We have shown that IR photodissociation spectroscopy provides a useful technique for probing the collisional relaxation of internal energy in gas-phase ions. In the case of chemically activated CH_3OH^- , we find that 40–80 collisions are required for collisional relaxation. The photodissociation spectra of activated and relaxed CH_3OH^- indicate that the chromophoric character of conventional IR absorption spectra can be preserved, to some extent, in IR multiphoton dissociation spectra. The fluence dependence of the CH_3OH^- photodissociation yield was examined. In the case of activated CH_3OH^- , saturation of the photodissociation yield with increasing fluence was observed. This result indicates that the IR photodissociation of this ion occurs via at least two distinct mechanisms, identified with resonant and continuum absorption. These mechanisms apply to ion population components that cannot differ simply in internal energy content or structure. A master equation model for IR multiphoton dissociation which assumes that all molecules in the sample respond similarly to the laser field is not consistent with these results. However, the deviation of these results from the predictions of such a model provides useful information on the mechanism of IR laser photoactivation. The observation that the fraction of ions which undergoes efficient photodissociation depends on the irradiation wavelength indicates that a species in the quasi-continuum can show structured IR absorption behavior.

Acknowledgment. We are grateful to the National Science Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We thank the National Science Foundation for fellowship support to J.M.J.

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(45) (a) The basic model is summarized in ref 1 and discussed in detail in ref 35–39. Calculations were performed by assuming single-photon absorption cross sections which monotonically increased or decreased or remained constant with increasing internal energy. (b) Dr. A. C. Baldwin, SRI International, personal communication.

Infrared Multiphoton Photodetachment of Negative Ions in the Gas Phase

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Abstract: Electron photodetachment induced by infrared multiphoton absorption under collisionless conditions has been observed for benzyl, allyl, 2,4-hexadienyl, cycloheptadienyl, and anilide anions in the gas phase. The variety of ions which exhibit this behavior suggests that vibrational photodetachment is a fairly general process for anions with low electron detachment thresholds and that, as in the case of vibrational autoionization of neutrals, a potential energy surface crossing is not required for autodetachment to occur.

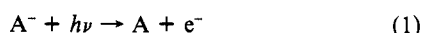
This paper describes our work on electron photodetachment from negative ions induced by infrared multiphoton absorption. Infrared photoactivation typically results in adiabatic fragmentations,¹ i.e., dissociation processes occurring on the ground electronic state potential surface. The present work was motivated

by the hypothesis that, if the barrier to adiabatic bond cleavage was significantly larger than the thermodynamic electron detachment threshold, electron detachment might compete favorably with dissociation following multiphoton absorption. This situation is quite common, since electron affinities are often² less than 3 eV whereas bond energies³ are of the order of 3–5 eV.

(1) See, for example: (a) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *J. Am. Chem. Soc.* 1979, 101, 3999. (b) Rosenfeld, R. N.; Jasinski, J. M.; Brauman, J. I. *Chem. Phys. Lett.* 1980, 71, 400.

(2) Janousek, B. K.; Brauman, J. I. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. 2, pp 53–85.

Electron detachment (eq 1) is the most commonly observed



photoprocess following the UV-visible excitation of negative ions in the gas phase.² Photodetachment is an example of a bound-free, rather than bound-bound, electronic transition. It thus resembles photoionization in neutrals. The electronic spectroscopy of a variety of organic anions in the gas phase has been studied either by measuring the depletion of $[A^-]$ as a function of photon energy (photodetachment spectroscopy²) or by measuring the photoelectron kinetic energy spectrum using a fixed frequency photon source (photoelectron spectroscopy^{2,4}). Both methods have yielded important results that allow the photophysics of processes such as (1) to be characterized. Generally, photodetachment (using UV-visible sources) can be understood within the framework of the Born-Oppenheimer approximation.⁵ The process is sufficiently fast that the Franck-Condon principle holds. Additionally, the relative transition probability has been found to follow dipole selection rules so the likelihood of a given transition is determined by the symmetries of the initial and final state electronic wave functions.⁵ Infrared multiphoton absorption, however, leads to the excitation of nuclear degrees of freedom (vibration and rotation) so, if electron detachment occurs under these conditions, a different theoretical explanation is required for the process. The infrared photodetachment studies described are prototypical examples of electronic processes induced by vibrational excitation and represent a class of chemical and physical problems not previously accessible to experimental study in this way. We describe below work on the IR-driven photodetachment of benzyl, allyl, 2,4-hexadienyl, cycloheptadienyl, and anilide anions in the gas phase. A preliminary report of the results on the benzyl anion has appeared elsewhere.⁶

Experimental Section

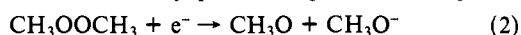
Ions were generated, trapped, and detected by using a pulsed ion cyclotron resonance spectrometer (ICR) as described previously.⁷ Experiments were performed at a total pressure of $\sim 10^{-6}$ torr. The laser was typically fired 500 ms after the electron-beam pulse which initiates the primary ion formation and the detection pulse was set 100 ms after the laser pulse. Infrared-induced electron detachment was followed by measuring the concentration, i.e., the intensity of the signal of a given anion with and without laser irradiation. Thermal electrons were continuously ejected at the trapping plates of the ICR cell in all experiments except those explicitly noted below.

The light source used was a grating tuned Lumonics TEA-103-2 CO₂ laser which was operated multimode. Laser pulse energies were measured with a calibrated Scientech 360-001 power meter; the laser fluence inside the ICR cell was typically ~ 6 J/cm². The optical train employed has been described elsewhere.^{7a} The laser pulse consisted of 150-ns spike followed by a 3- μ s tail, each containing $\sim 50\%$ of the total pulse energy.

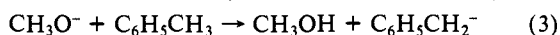
The following reagents were used without further purification: toluene (MCB), allyltrimethylsilane (Aldrich), 2,4-hexadiene (cis-trans) (Columbia Organic Chemicals), 1,3-cycloheptadiene (Aldrich), aniline (Baker), and *tert*-butyl peroxide (MCB). Dimethyl peroxide was prepared according to the method of Hanst and Calvert.⁸

Results

A. Benzyl Anion. The methoxide anion, formed by dissociative electron attachment to dimethyl peroxide (eq 2) abstracts a proton



from toluene,⁹ forming the benzyl anion (eq 3). The latter process



(3) Kerr, A. "Bond Strengths in Polyatomic Molecules" in "Handbook of Chemistry and Physics"; CRC Press: Cleveland, OH, 1979-1980.

(4) Lineberger, W. C. "Chemical and Biochemical Applications of Lasers"; Academic Press: New York, 1974; Vol. 1, p 71.

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(8) Hanst, P. L.; Calvert, J. G. *J. Phys. Chem.* **1959**, *63*, 105.

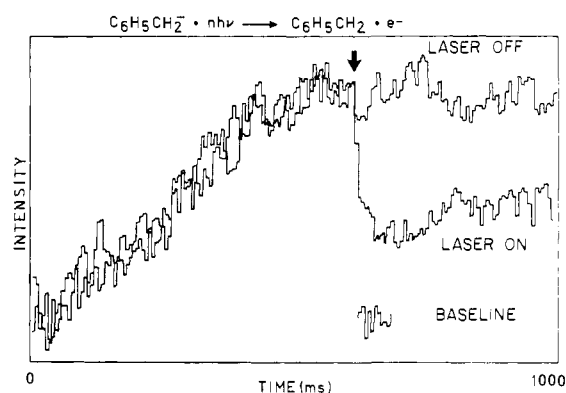


Figure 1. Time dependence of the benzyl anion signal intensity with the laser beam entering the ICR cell (laser on) and with the laser beam blocked from entering the ICR cell (laser off). The arrow indicates the time in the duty cycle at which the laser is triggered. Irradiation wavelength is 948 cm⁻¹ and the laser fluence is ~ 2.0 J cm⁻².

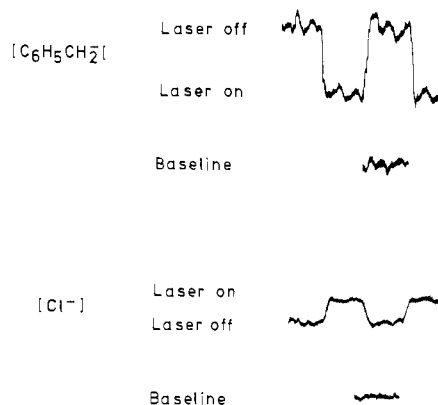
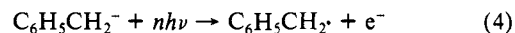
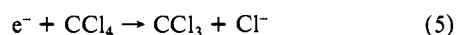


Figure 2. Signal intensities due to benzyl anion and chloride ion in the presence and absence of laser irradiation. All ICR pulses are fixed in time. Note that decreases in the benzyl anion signal correspond to increases in the chloride signal. Absolute signal intensities are not the same for both ions.

is approximately thermoneutral.¹⁰ The electron affinity of the benzyl radical has been determined¹¹ to be 0.88 eV, so the ground-state anion must absorb at least seven CO₂ laser photons to achieve the thermodynamic electron detachment threshold. Irradiation of the benzyl anion with the output of the CO₂ TEA laser results in photodetachment (eq 4). The signal decrease



shown in Figure 1 is due solely to photodetachment. This was determined by observing the negative ion mass spectrum following the laser pulse (no signals were observed aside from that due to the benzyl anion) and by chemically trapping the photoelectrons with carbon tetrachloride (eq 5). In the trapping experiments,



the electron ejector normally used in negative ion experiments is turned off, a small amount of CCl₄ (less than 1×10^{-7} torr) is added to the ICR cell, and the increase in Cl⁻ signal due to photoelectron capture after the laser pulse is followed (see Figure 2). No increase in Cl⁻ signal was observed in the absence of the benzyl anion. These results indicate, within the limits of our detection sensitivity, that electron detachment is the only IR-induced photoprocess in the benzyl anion.

(9) Brauman, J. I.; Lieder, C. A.; White, M. J. *J. Am. Chem. Soc.* **1973**, *95*, 927.

(10) Bartmess, J. E.; McIver, R. T., Jr. In "Gas Phase Ion Chemistry"; Bowers, M. T., Ed.; Academic Press: New York, 1979; Vol. II, pp 88-121.

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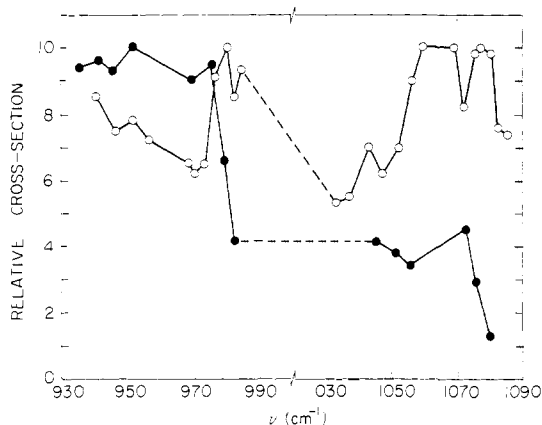
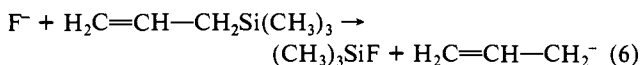


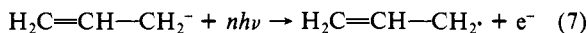
Figure 3. Infrared photodetachment spectrum of the benzyl (●) and the allyl (○) anions.

The photodetachment yield was found to be independent of pressure between 5×10^{-7} and 5×10^{-6} torr and was independent of the delay between the laser and grid pulses (from 400 to 900 ms). This suggests that, in these experiments, the benzyl anion is thermalized (at ca. 300 K) prior to irradiation.^{1a,7b,c} The IR photodetachment spectrum of the benzyl anion at constant fluence is shown in Figure 3; the relative photodetachment cross section is largest near 950 cm^{-1} . The infrared absorption spectra of gaseous toluene and aniline were examined for comparative purposes. Aniline, which is isoelectronic with the benzyl anion, shows no absorption features between 900 and 1100 cm^{-1} . Toluene shows absorption maxima near 1030 and 1080 cm^{-1} . Thus, the IR photodetachment spectrum of $\text{C}_6\text{H}_5\text{CH}_2^-$ cannot easily be interpreted in terms of vibrational chromophores (e.g., C—C stretch, C—H bend, etc.) of closely related neutral compounds. In Figure 3 and in all other photodetachment spectra presented here the error bars are estimated to be $\pm 10\%$. Lines have been drawn simply by connecting the points and are not intended to imply sharp spectral features.

B. Allyl Anion. The allyl anion can be conveniently prepared by the reaction of F^- (from NF_3) with allyltrimethylsilane¹² (eq 6). The electron affinity of the allyl radical has been determined¹³



to be 0.55 eV. Thus, a vibrationally cold anion must absorb at least five CO_2 laser photons to achieve the electron detachment threshold. When the allyl anion is irradiated with the pulsed CO_2 laser, electron detachment (eq 7) is observed. The relative cross



section for photodetachment shows modest wavelength dependence (Figure 3). No photofragments could be observed, suggesting that photodetachment was the only process occurring. However, attempts to trap photoelectrons with CCl_4 (vide supra) were unsuccessful owing to the small fraction of ions which actually photodetached.

C. 2,4-Hexadienyl and 1,3-Cycloheptadienyl Anions. The *tert*-butoxide anion can be conveniently used to generate both hexadienyl and cycloheptadienyl anions from 2,4-hexadiene and 1,3-cycloheptadiene, respectively, via proton abstraction.

The electron affinities of the corresponding radicals are not known but can be estimated to be around 0.9 ± 0.1 eV, similar to that of the pentadienyl radical¹⁴ (0.91 eV), assuming that additional carbons in the chain and the constrained *cis* geometry

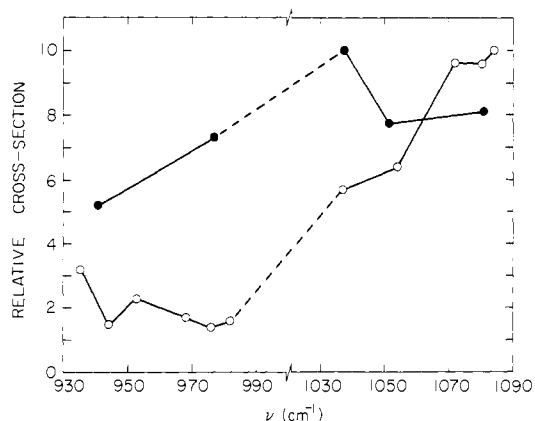


Figure 4. Infrared photodetachment spectrum of the 2,4-hexadienyl (●) and 1,3-cycloheptadienyl (○) anions.

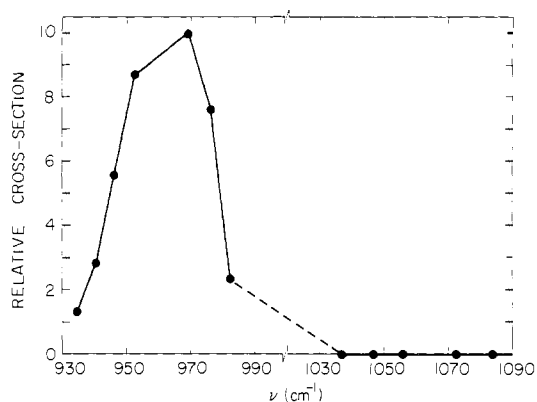
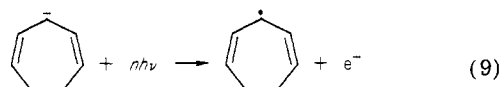
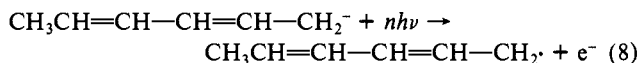


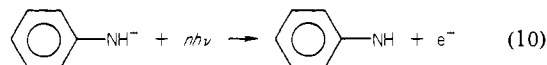
Figure 5. Infrared photodetachment spectrum of anilide anion.

have no significant effect. When these anions are irradiated with the pulsed CO_2 laser, electron detachment (eq 8 and 9) is observed.



No ions other than hexadienyl and cycloheptadienyl could be observed following the laser pulse, and the Cl^- experiment (see above) was also positive in both cases, thus suggesting that electron detachment is the only process occurring. The relative cross sections for IR photodetachment as a function of laser frequency are shown in Figure 4 for both ions. For the cycloheptadienyl anion, there is a slight increase in cross section with increasing frequency.

D. Anilide Anion. The anilide anion was prepared from aniline by proton abstraction by *tert*-butoxide. When the anilide anion is irradiated with the pulsed CO_2 laser, electron detachment (eq 10) is observed. No ions other than anilide could be observed



following the laser pulse. The electron affinity of the radical has been calculated by Kerr¹⁵ from bond energy and the gas-phase acidity data. He obtains a value of 1.15 ± 0.3 eV. Photodetachment of the vibrationally cold anion therefore requires more than 10 CO_2 laser photons.

The relative cross sections for IR photodetachment as a function of laser frequency are shown in Figure 5. The spectrum, as for benzyl, has its maximum around 970 cm^{-1} .

(12) DePuy, C. H.; Bierbaum, V. M.; Flippin, L. A.; Grabowski, J. J.; King, G. K.; Schmitt, R. J. *J. Am. Chem. Soc.* **1979**, *101*, 6443.

(13) Zimmerman, A. H.; Brauman, J. I. *J. Am. Chem. Soc.* **1977**, *99*, 3565.

(14) Zimmerman, A. H.; Gygas, R.; Brauman, J. I. *J. Am. Chem. Soc.* **1978**, *100*, 5595.

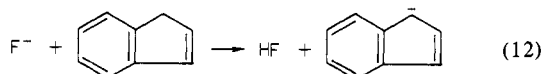
(15) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

Table I. Photodetachment Data

anion	cross section, ^{a,b} cm ²	electron affinity, ^h eV
benzyl	3.7×10^{-21} (935 cm ⁻¹)	0.88 ^c
allyl	0.7×10^{-21} (1052 cm ⁻¹)	0.55 ^d
2,4-hexadienyl	9.1×10^{-21} (1050 cm ⁻¹)	~0.9 ^e
1,3-cycloheptadienyl	2.7×10^{-21} (1047 cm ⁻¹)	~0.9 ^e
anilide	1.5×10^{-21} (969 cm ⁻¹)	1.15 ^f
indenyl	no photodetachment	1.8 ^g

^a See text for definition of cross section. ^b Wavelength of laser irradiation given in parentheses. ^c Reference 11. ^d Reference 13. ^e Estimated. ^f Reference 15. ^g Reference 16. ^h Electron affinity of the corresponding radical.

E. Indenyl Anion. The indenyl anion was prepared from the reaction of F⁻ with indene according to eq 11 and 12. The electron



affinity of the indenyl radical has been determined¹⁶ to be 1.87 ± 0.03 eV. The indenyl anion does not exhibit observable (<5%) photodetachment or photodissociation upon irradiation with our CO₂ laser at any of the following frequencies: 944, 976, and 1047 cm⁻¹ with up to 6 J/pulse.

Discussion

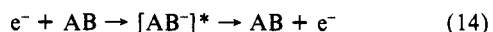
A summary of the relevant data available for the five anions for which photodetachment has been observed upon IR irradiation is given in Table I. The phenomenological cross sections given were calculated by assuming $\ln(I/I_0) = -\sigma F$, where I/I_0 is the ratio of signal intensities with and without irradiation, respectively, and F is the number of photons per cm². This definition of the cross section, computed at extensive fractional decomposition, is an approximation to the behavior expected at steady state¹⁷ and provides a useful method for characterizing the wavelength dependence of the photodetachment yield.

These results unambiguously demonstrate that electron detachment, a bound-free electronic transition, can be induced in some gas-phase anions by intense IR irradiation under collisionless conditions.⁷ Since such irradiation excites only nuclear degrees of freedom (vibration, rotation) in these anions, the photodetachment process is an important new example of intramolecular vibrational to electronic (V-E) energy transfer.

Some phenomena which may be related to vibrational photodetachment include the nuclear excited Feshbach resonances observed in electron scattering experiments on neutrals,¹⁸ associative detachment,¹⁹ and inverse electronic relaxation (IER). IER is a bound-bound nonradiative transition which has been claimed recently²⁰ in conjunction with the observation of luminescence following IR multiphoton excitation of some neutral molecules. A closer analogy can be drawn between IR photodetachment and processes such as associative detachment (eq 13) or electron



scattering via a nuclear excited Feshbach resonance (eq 14). In



the former case the ion-molecule collision between A⁻ and B produces a vibrationally excited ion [AB⁻]^{*} which relaxes via electron autodetachment.¹⁹ In the latter case the collision of an electron with a molecule AB results in the formation of a transient anion [AB⁻]^{*} in which the electron is temporarily bound owing to energy being trapped in nuclear degrees of freedom of AB⁻.

(16) Rynard, C., personal communication.

(17) (a) Quack, M. *J. Chem. Phys.* **1978**, *69*, 1282. (b) Troe, J. *Ibid.* **1980**, *73*, 3205.

(18) Christophorou, L. G. *Adv. Electron. Electron Phys.* **1978**, *46*, 55.

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The resonance observed in electron scattering cross sections owing to the transient formation of [AB⁻]^{*} followed by its autodetachment is thus referred to as a nuclear excited Feshbach resonance.¹⁸ In both the associative detachment process and the nuclear excited Feshbach resonance, autodetachment of the electron occurs from a vibrationally excited anion via a bound-free transition following V-E energy exchange. This is precisely the type of process we believe occurs in IR-induced photodetachment. Thus, a thorough understanding of Feshbach resonances and associative detachment should provide useful information on the mechanism of IR photodetachment and conversely. Data from all three types of experiments should be important in addressing the nature of V-E coupling in electron autodetachment from vibrationally excited anions.

Christophorou¹⁸ has discussed the lifetimes of autodetaching states encountered in electron-scattering experiments. He employs a simple statistical model first proposed by Compton et al.²¹ which gives the rate constant for autodetachment, k_a , for a negative ion supported by vibrational excitation as

$$k_a = v\sigma_a(\rho^0/\rho^-) \quad (15)$$

In eq 15 σ_a is the electron attachment cross section (experimentally determined in the scattering experiment), v is the relative electron velocity, and ρ^0/ρ^- is the ratio of the density of states for the neutral molecule plus free electron to that for the negative ion. This model predicts that the V-E energy transfer required for autodetachment occurs at a rate determined solely by statistical factors, i.e., the relevant densities of states.

This statistical approach, as it is usually employed, assumes that all of the internal degrees of freedom participate fully and thus provides a lower limit to the autodetachment rate. Typical autodetachment rates are found experimentally to be 10^4 – 10^6 s⁻¹ for moderate size molecules near threshold (i.e., using low energy electrons in the scattering experiment). In the case of IR-driven photodetachment, proceeding via sequential one-photon absorption, one expects that absorption will continue until the rate of autodetachment is equal to the rate of further photon absorption.^{7a} Under typical conditions we estimate the rate of single photon absorption to be 10^6 – 10^9 s⁻¹ in our experiment. Furthermore, because of the low pressures employed, following the end of the laser pulse the ions have times on the order of tens of milliseconds before they are collisionally relaxed and times of at least 1 ms before they begin to relax radiatively. Thus, even though vibrationally induced autodetachment may be inefficient at threshold it is still readily observable under our experimental conditions.

The statistical approach does not require and Christophorou¹⁸ does not suggest a physical mechanism for V-E coupling. In our preliminary report,⁶ we proposed a simple mechanism that might account for the ready observation of IR-induced photodetachment of the benzyl anion without requiring significant breakdown of the Born-Oppenheimer approximation, i.e., without requiring excessive V-E coupling. The most stable conformation of the benzyl anion is planar, with the methylene group in the plane of the benzene ring. This planar species has an adiabatic electron detachment threshold of¹¹ 0.88 eV. Vibrational excitation of the benzyl anion, followed by randomization of this internal energy, can lead to excitation of the methylene torsion. This, in turn, can lead to the transient formation of the perpendicular conformer of the benzyl anion, i.e., that conformation where the methylene group is orthogonal to the plane of the benzene ring. In this perpendicular conformation, the most weakly bound electron is localized on the methylene group and is not stabilized by any π -type interaction with the benzene ring. Thus, the electron detachment threshold for the perpendicular conformer of the benzyl anion should be reduced relative to that for the planar conformer. In fact, the only stabilization effect due to the perpendicular benzene ring will be that resulting from the inductive effect of the sp²-hybridized carbon adjacent to the methylene center. As an approximation then, we expect the electron de-

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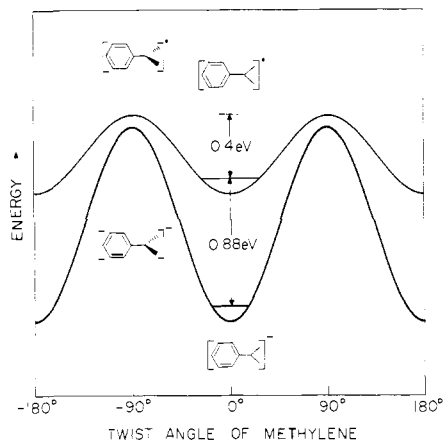


Figure 6. Schematic potential surface for the vibrationally driven photodetachment of the benzyl anion.

tachment threshold of the perpendicular benzyl anion to be comparable to that for an unstabilized carbanion such as the methyl anion. Lineberger and co-workers²² have determined the electron affinity of the methyl radical to be 0.08 eV. Thus, when the methylene group of the benzyl anion undergoes a 90° rotation, the electron detachment threshold decreases by about one order of magnitude. Electron detachment may then occur from the perpendicular conformation of the anion by electron tunneling or by weak V-E coupling. The radical thus formed will be perpendicular. It can relax to a more stable, planar conformation by undergoing a 90° methylene rotation. The barrier to rotation for the benzyl radical is estimated to be about 10 kcal/mol (0.4 eV), based on its resonance energy.²³ This indicates that the threshold for IR-driven electron detachment via this mechanism could be as large as 1.3 eV, 0.4 eV in excess of the adiabatic electron affinity of the benzyl radical. Figure 6 illustrates the proposed model. The most important feature of this model is that it provides a simple means by which vibrational excitation of the anion results in a very close approach between the anion and neutral potential energy surfaces, presumably facilitating a transition from the former to the latter. Analogous considerations apply to vibrationally driven photodetachment of the allyl and 2,4-hexadienyl anions. The picture described here is an oversimplification of the photophysics of the electron detachment process. For example other promoting modes such as an out of plane bend of the methylene group in the benzyl anion may serve the same purpose as the torsional motion in facilitating close approach of the two electronic potential surfaces and promoting transitions between them.

In order to test the importance of this hypothesis, we investigated possible IR-driven photodetachment on "rigid" structures, i.e., ions which cannot change conformation to allow an easy path for photodetachment. Indanyl anion ought to have an electron

affinity and absorption behavior similar to that of benzyl anion and therefore was a straightforward choice. Unfortunately we find that attempted proton abstraction from indane yields only the aromatic indenyl anion, presumably via spontaneous loss of H₂ from the transient indane anions. The absence of photodetachment upon IR irradiation, as for indenyl anion, cannot be considered a convincing proof since poor IR absorption and/or too high an electron detachment energy may be responsible for our failure to observe photodetachment. The 1,3-cycloheptadienyl anion photodetaches to nearly the same extent as the open chain 2,4-hexadienyl anion under similar experimental conditions. Their radicals probably have similar electron affinities, but a more precise comparison of relative IR photodetachment efficiencies is not possible since we know nothing about the IR absorption spectrum of either anion and cannot determine quantum yields for detachment. According to the model proposed above, the cycloheptadienyl anion should not undergo photodetachment, or do so only poorly compared to hexadienyl. Distortion of the carbon skeleton should not be sufficient to lower the electron affinity as much as for benzyl, allyl, and hexadienyl anions. Nevertheless, substantial detachment is observed in the cycloheptadienyl anion, suggesting that while the mechanism proposed above may still be important for benzyl, allyl, and hexadienyl, it is surely not necessary. This conclusion is further supported by the experiments with the anilide anion. Since the electron affinity of NH₂ is²⁴ 0.7 eV, even if all resonance stabilization due to conjugation with the phenyl ring is lost in anilide owing to a skeletal deformation, the anion and neutral potential surfaces remain far apart in energy. This suggests that a more general mechanism for rather efficient V-E coupling, which does not require either close approach or actual crossing of the anion and neutral surfaces, must be operative. This conclusion is reminiscent of results on the vibrational autoionization of small neutral molecules which is known to occur in the absence of curve crossing.²⁵

Conclusion

We have been able to induce electron photodetachment from several negative ions by multiphoton infrared absorption. The process of electron loss is analogous to the decay of a nuclear excited Feshbach resonance. The variety of ions which exhibit this behavior indicates that curve crossing is not required for autodetachment to occur.

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Registry No. Benzyl anion, 18860-15-6; allyl anion, 1724-46-5; 2,4-hexadienyl anion, 79952-97-9; 1,3-cycloheptadienyl anion, 79952-98-0; anilide anion, 27547-14-4; indenyl anion, 12128-54-0.

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