

Conf-820853--3

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CONF-820853--3

DE82 020832

NEGATIVE-ION STATES

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To Be Presented at NATO Conference on Photophysics and
Photochemistry in Vacuum Ultraviolet,
Lake Geneva, Wisconsin, August 15-29, 1982

MASTER

Research Sponsored by the Office of Health and Environmental Research,
U.S. Department of Energy Under Contract W-7405-eng-26
With the Union Carbide Corporation

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NEGATIVE ION STATES

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ABSTRACT

In this brief review, we discuss some of the properties of atomic and molecular negative ions and their excited states. Experiments involving photon reactions with negative ions and polar dissociation are summarized.

INTRODUCTION

Negative ions play important roles in many areas of photophysics and photochemistry. Negative ions can be produced directly by photodissociation of molecules through ion-pair production or indirectly via charge-exchange between photo-excited species and electronegative atoms or molecules. The most vivid illustration of the importance of negative ions in photophysics is to be found in the radiation emitted by the sun. The solar spectrum exhibits an intense self-absorption for wavelengths longer than 5000 Å. In 1939, Wildt¹ showed that H^- might exist in the solar atmosphere in sufficient concentrations to be the main source of opacity in the infrared region of the solar spectrum. In order to explain the absorption over the entire infrared region, it is necessary to take into account both photodetachment of H^- and the so-called free-free absorption in which an electron makes a transition between two continuum states in the field of an H atom.

In this review, we will discuss only negative ion properties and photo-reactions in the gas phase. Negative ions in the condensed phase have been extensively studied by spectroscopic, electron spin resonance, and other techniques. Sanche² has recently suggested that shape resonances³ which are formed by the capture of an incident electron by its centrifugal angular momentum barrier could form tight-binding π bands in organic insulators. Electronic motion within these bands could account for electrical conductivity in organic solids. Many organic dyes which are used in dye lasers probably fluoresce and lase between negative ion transitions. Although there have been no reports of a negative ion gas phase laser, there seems to be no reason why such a device would not be possible. Since most small (3 or 4 atom) negative ions do not possess bound excited states, such a laser would probably involve large organic anions and therefore might afford some moderate tuning capabilities.

We will also omit in this discussion studies of negative ions on surfaces, although this is an interesting area of research. It has recently been shown⁴ that compound³ states of O_2^- and N_2^- can play significant roles in the scattering of electrons from surfaces covered with O_2 and N_2 .

NEGATIVE ION PROPERTIES

The potential energy surface essentially defines the physical properties of a negative ion. Obtaining experimental and theoretical information on these surfaces remains an arduous task. There is accurate information on electron affinities, vibrational frequencies, and geometries only for a number of small negative ions. In a few cases reasonably precise potential energy surfaces can be constructed.

The adiabatic electron affinity (EA) of a molecule is defined as the difference in energy between the neutral molecule in its electronic and vibrational ground state, E^0 , and the ion in its ground state E^- (i.e., $EA = E^0 - E^-$). Studies of electron photodetachment or radiative attachment have provided values for atomic EAs with accuracies often better than 0.01 eV. The first accurate measurements of halogen EAs are credited to Berry and Reimann.⁵ On the other hand, very few accurate determinations of molecular EAs have been made because of the complexity of molecular negative ions. In a few cases (notably NO and O₂) where photodetachment and photoelectron spectroscopy⁶ have been applied, EAs are known with accuracies better than 0.01 eV. In cases where the EA is negative and a well-defined vibrational progression is observed, the resonance scattering technique⁷ has provided adiabatic EAs with accuracies of ± 0.05 eV. In some cases, notably the studies of Richardson and co-workers⁸ and Herbst et al.,⁹ accurate lower limits to EAs for complex molecules have been determined from photodetachment thresholds.

The determination of energy thresholds for the transfer of an electron between heavy particles and target molecules is often used to infer molecular EAs. For example, studies of reactions of the type $X^- + M \rightarrow X + M^-$ have provided accurate EAs (± 0.2 eV) for many molecules.¹⁰⁻¹⁵

Helbing and Rothe¹⁶ first employed the alkali collisional ionization technique to determine molecular EAs. This method involves the measurement of the energy threshold for the charge exchanging reaction between an alkali atom and a molecule, i.e., $A + M \rightarrow A^+ + M^-$. In one instance, the energy of the alkali ion was measured to infer the EA of

CO_2 .¹⁷ A number of groups are actively employing the threshold collisional ionization technique for the purpose of determining molecular EAs (see the review by Baede).¹⁸ This technique has proven especially useful for polyatomic molecules where other methods are not presently applicable. However, the method suffers from three major uncertainties: (1) strictly speaking, only lower limits to EAs are deduced, (2) the thresholds are sensitive to the target gas temperature, and (3) in some cases the actual threshold is difficult to determine because of weak signal or because of the nature of the cross section (or both). In cases where the target molecules are a gas at room temperature, the Doppler motion can have serious effects on the observed threshold.

The flowing afterglow technique has provided a wealth of information on negative ion molecule reaction rates. The EAs of some molecules have also been bracketed by observing whether charge transfer does or does not proceed with the negative ions of known EA (see e.g., Refs. 19 and 20).

Electron affinity values which have been reported for atoms and small molecules (fewer than five atoms) range from ~ -2 to $+4$ eV. Figure 1 illustrates this with a plot of measured EAs for molecules made from the atoms of the first (H) and second rows of the periodic table. The EA is plotted versus the number of valence electrons (total number of electrons minus the 2K shell electrons). Note that ions with 16 and 24 valence electrons are quite stable, reflecting the fact that greatest stability exists for "closed shells."

The EAs for the molecules shown in Fig. 1 range from ~ -2 to $+4$ eV. There is evidence that most of the heavier hexafluoride molecules possess

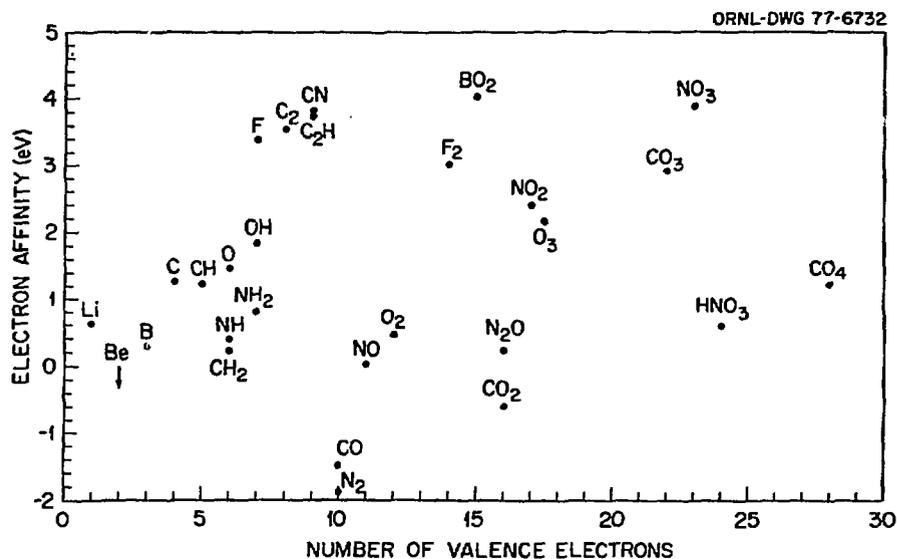


Fig. 1. Experimentally measured electron affinities for atoms and molecules made from atoms of the first (H) and second row of the periodic table versus the number of valence electrons for the neutral. Notice that the values range from ~ -2 to $+4$ eV and abrupt changes occur at a completed shell.

EAs of up to 10 eV! The first evidence of these surprising molecular negative ion properties came from thermochemistry considerations.

Bartlett²¹ analyzed the oxidizing properties of the hexafluorides of the third transition metal series and found that the EAs increase in the order $WF_6 < ReF_6 < OsF_6 < IrF_6 < PtF_6$ and $EA(ReF_6) > 3.9$ eV, $EA(IrF_6) > 5.45$ eV, and $Ea(PtF_6) > 6.75$ eV.

The EAs increase (~ 0.85 eV with unit increase in atomic number of the transition metal). More recent data of Barberi and Bartlett²² give $EA(PtF_6) = 9.3$ eV. Bartlett's recent estimate of the $EA(AuF_6)$ is 10 ± 0.5 eV (private communication)! Compton and Reinhardt²³ have studied the reaction $Cs + (AuF_5)_2 \rightarrow AuF_6^- + AuF_4$ and also find evidence for an $EA > 9$ eV for AuF_6 .

Jensen and Miller have studied electron attachment and compound formation in flames and were able to deduce the following rather large molecular EAs: BO_2 (4.07),²⁴ WO_3 (3.64),²⁴ HWO_4 (4.35),²⁵ CrO_3 (4.04),²⁶ ReO_4 (4.45),²⁷ and $HMoO_4$ (4.25).²⁸ Although these EAs are not as large as those reported for some hexafluorides, they serve to illustrate that the EAs of many molecules can be larger than the accepted values for the halogen atoms.

Burgess et al.²⁹ have studied the thermochemistry of alkali metal hexafluoromolybdates and hexafluorotungstates to derive the standard enthalpies of formation of KWF_6 , $RbWF_6$, $CsWF_6$, $KMoF_6$, $RbMoF_6$, and $CsMoF_6$. From these measurements, they estimate the gas phase EAs of WF_6 and MoF_6 to be 5.09 ± 0.05 and 5.36 ± 0.05 eV, respectively.

Charge-exchange reactions involving negative ions and hexafluorides and alkali atoms and hexafluorides have provided further evidence for very large EAs of many hexafluorides (see Ref. 30 and others cited therein). The large EAs and the complex electronic structure of these hexafluorides gives rise to low-lying bound excited states. The extra electron in UF_6^- , for example, exhibits two excited states ($^2T_{2u}$ and $^2T_{1u}$) in the region of 1-4 eV.³¹ Experimental studies of these excited states in the gas phase would be interesting.

UNIMOLECULAR ELECTRON ATTACHMENT

The attachment of a free electron to a molecule can be studied under single collision conditions in the gas phase. The electron is said to be attached if it is "temporarily" held up for at least a time greater than its normal "transit time" across the molecule. In this case, one describes the electron-molecule system as a "resonance." Bardsley and Mandl³² classified such resonances as (1) shape resonances, (2) nuclear excited Feshbach resonances, or (3) electronically excited Feshbach resonances. In the case of a shape resonance, the electron-molecule potential of interaction has a barrier, most commonly a centrifugal barrier built in by the orbital angular momentum of the colliding particles. The electron is then temporarily held up at the electron-molecule separation distance where the "potential well" exists due to the barrier. Electrons can be temporarily bound through Feshbach resonances if electronic or nuclear motion of the target molecule is excited. Thus, an electron of energy E_e is attached to a molecule to form a molecular ion with total energy E^* , i.e.



The width of the attachment resonance, Γ (i.e., the range of energies, E_e , over which attachment can occur), is related to the lifetime $\tau(E^*)$ through the uncertainty principle $\tau(E^*)\Gamma \sim h$. In many instances the width of a resonance is broader than the spacings between vibrational (and rotational) levels of the ion, and a broad resonance is observed whose width is determined by the Franck-Condon factors of the neutral and the ion. The lifetime of a resonance can be inferred from the measured width or in some cases directly measured.

The cross section is related to the lifetime through the principle of detailed balance, i.e.,

$$\sigma_a(E_e)\tau(E^*) = \frac{\rho^-(E^*)}{v\rho^o(E)} \quad (2)$$

where v is the velocity of the electron and ρ designates the density of states of the ion (-) or neutral (o). The lifetime, τ , of the ion against autodetachment is a function of the total internal energy E^* . The total internal energy is the sum of the incident electron energy and the electron affinity E_a of the molecule (i.e., $E^* = E_e + E_a$). The lifetimes of these resonances can vary from $\sim 10^{-15}$ s (e.g., H_2^-), where it becomes difficult to speak of a resonance, to $> 10^{-3}$ s (e.g., $TCNQ^-$),² where one is dealing with almost stationary states of the electron-molecule system.

When a complex molecule attaches a slow electron the total energy E^* is shared among the various degrees of freedom of the ion. Inspection of Eq. (2) shows that if $\rho^-(E^*)$ is large, the lifetime *and* cross section can be large. For negative ions with lifetimes greater than 10^{-6} s, it is possible to study these resonances directly and even to measure their lifetimes as a function of their total energy E^* . Over the past ten years we have determined the lifetimes of a large number of complex anions in a time-of-flight mass spectrometer. We measure the ratio of neutral molecules arriving at a detector at a distance from the ion source to the negative ions arriving at the same detector. The neutrals result from autodetachment of the metastable anions. The time during which autodetachment can occur is varied by changing the ion velocity or the distance of travel. As an example, Fig. 2 shows the data for electron attachment to a conjugated organic molecule, parabenzoquinone.³³ The PBQ^- ion has three excited states ${}^2\text{B}_{1u}$, ${}^2\text{A}_u$, and ${}^2\text{B}_{1u}$ which lie 3 to 4 eV above the ${}^2\text{B}_{3g}$ ground state. The second state leads to long-lived PBQ^- ions whose lifetime varies with electron energy (see Fig. 3).

Electron attachment into π -orbitals (shape resonances) of organic molecules has been extensively studied by the technique of electron transmission spectroscopy and negative ion mass spectrometry. The first study that showed vibrational structure in such resonances was due to Hasted and his colleagues.³⁴ Jordan and Burrow (see Ref. 35 for a review) have made significant recent progress in describing and categorizing shape resonances for organic molecules. They have shown that it is possible, by using electron transmission spectroscopy, to map out the spectrum of unoccupied molecular orbitals in much the same manner that

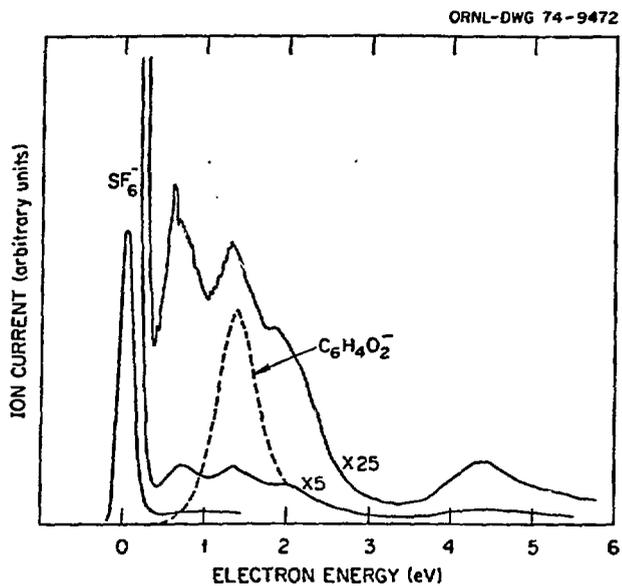


Fig. 2. Solid lines are the SF₆ scavenger spectra showing low-lying compound negative ion states in p-benzoquinone (PBQ). The PBQ⁻ negative ion signal is also shown as a dashed curve. The energy dependence of the PBQ⁻ ion lifetime is shown in Fig. 3 (Ref. 33).

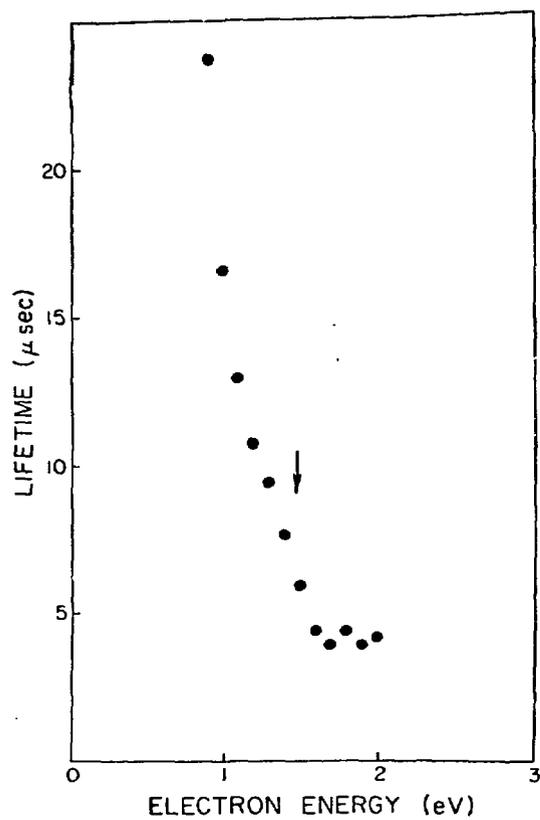


Fig. 3. The dependence of autodetachment lifetimes of PBQ^- on the bombarding electron energy. The energy dependence of the cross section for the reaction $e + \text{PBQ} \rightarrow \text{PBQ}^-$ is shown in Fig. 2 (Ref. 33).

photoelectron spectroscopy maps out the occupied orbitals. Already some remarkably simple, but useful, conclusions have been reached. For example, Younkin et al.³⁶ have used the Koopman theorem to relate the calculated energy of the lowest vacant molecular orbital to the adiabatic EA of a conjugated molecule. An excellent one-to-one correlation was found. Furthermore, the calculations and experiment provide evidence for the so-called "pairing theorem" (see Ref. 36) which states that the sum of the EA and the ionization potential is a constant for alternate hydrocarbons. (This constant is 8.18 eV in the case of Younkin et al.³⁶) This relationship is true for excited states as well as the ground states of the ion. Jordan (private communication) has suggested this could be used as a method of identifying " π " ionization potentials from photoelectron spectra. Experimentalists in this area of collision physics are making significant new contributions in organic chemistry.

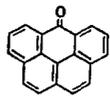
MULTIPLY CHARGED NEGATIVE IONS

Doubly charged negative ions were first reported in 1960 by Stuckey and Kiser.³⁷ Since that time there have been many claims of multiply charged negative ions. Table I summarizes these data. Note that even triply charged negative ions are reported in one field desorption mass spectrometer experiment. Recently, a lengthy review article on double charged negative ions by Kiser³⁸ concluded by asserting - "Several conclusions may be drawn from the investigations described above. Foremost among these is that doubly-charged negative ions exist." This conclusion is not unambiguously adhered to by all researchers in the field, at least as the statement applies to doubly charged atomic ions.

TABLE I. SUMMARY OF EXPERIMENTAL EVIDENCE FOR MULTIPLY
CHARGED NEGATIVE IONS

Ion Observed	Mass Spectrometer	Refs.	Comments
Cs^{\equiv}	Quadrupole	a	Cs^{\equiv} was only suggested later (private communication, L. M. Chanin) believed to be artifact.
F^{\equiv}	Quadrupole	b	Later attempts to reproduce F^{\equiv} were unsuccessful (W. S. Koski, private communication).
NO_2^{\equiv} $\text{C}_6\text{H}_4-(\text{CH}_2)_n^{\equiv}$ CO_2R (R=H or CH_3)	Magnetic	c	Lifetime must be greater than 10^{-5} s. Three distinct types of doubly charged negative ions are described.
SO_4^{\equiv} , FeF_6^{\equiv} HFeF_5^{\equiv} , RbBr_2^{\equiv}	45° Sector Magnetic	d	Ions were produced by field desorption
Cl^{\equiv} , I^{\equiv} , Br^{\equiv} , SF_6^{\equiv} , SF_5^{\equiv}	Ion Cyclotron Resonance	e	Cl^{\equiv} is suggested but <i>harmonics</i> could not be ruled out. Mechanism believed to be $\text{X}^- + \text{E} \rightarrow \text{X}^{\equiv}$.
O^{\equiv} , Te^{\equiv} , Bi^{\equiv} , F^{\equiv} , Cl^{\equiv} , Br^{\equiv} , and I	Penning Source, 60° Sector Magnetic	f	Electric and magnetic deflection was employed. I^{\equiv} observation is placed in some doubt by L. Frees, E. Heinicke, and W. S. Koski, Nucl. Instrum. Meth. <u>159</u> , 105 (1979).

Table I. (Continued)

Ion Observed	Mass Spectrometer	Refs.	Comments
$H^{\bar{}}$	Tandem mass	g	See also: M. L. Vestal, J. Chem. Phys.
$D^{\bar{}}$	(1) 30-cm Wien filter (2) 90° sector magnetic		<u>65</u> , 4331 (1976) and J. Durup, J. Chem. Phys. <u>65</u> , 4331 (1976).
$O^{\bar{}}$, $F^{\bar{}}$, $Cl^{\bar{}}$, $Br^{\bar{}}$, $CN^{\bar{}}$	0 megatron	h	See alternate interpretation (harmonics) by J. H. Fremlin, Nature <u>211</u> , 1453 (1960).
	Magnetic	i	

^aD. G. Kuehn, D. E. Sutliff, and L. M. Chanin, Appl. Phys. Lett. 33, 906 (1978).

^bJ. E. Ahnell and W. S. Koski, Nature 245, 30 (1973).

^cJ. H. Bowie and B. Jane Stapleton, J. Am. Chem. Soc. 98, 6480 (1976).

^dM. Anbar and G. A. St. John, J. Am. Chem. Soc. 97, 7195 (1975).

^eB. Jane Stapleton and J. H. Bowie, Aust. J. Chem. 30, 417 (1977).

^fH. Bauman, E. Heinicke, H. J. Kaiser, and K. Bethge, Nucl. Inst. Meth. 95, 389 (1971).

^gR. Schnitzer and M. Anbar, J. Chem. Phys. 64, 2466 (1976); see also J. Chem. Phys. 65, 4332 (1976).

^hW. K. Stuckey and R. W. Kiser, Nature 211, 963 (1966).

ⁱR. C. Dougherty, J. Chem. Phys. 50 1896 (1969).

Spence, Chupka, and Stevens³⁹ have very recently reexamined the possible existence of such species under experimental conditions as close as possible to those experiments which have reported positive identification of doubly charged $I^{\bar{\bar{}}}$, $F^{\bar{\bar{}}}$, $Cl^{\bar{\bar{}}}$, and $O^{\bar{\bar{}}}$. These authors allowed for an absolute identification of any ions which may result in false signals caused by impurities, and in which artifact peaks do not occur. They set upper limits on the ratio of $X^{\bar{\bar{}}}$ to X^- of the order 10^{-7} , whereas earlier experiments claim values of 10^{-1} - 10^{-2} . In contrast to previous experiments, they find no evidence for doubly charged atomic negative ions.

Baumann et al.⁴⁰ have reported the most detailed experiments on doubly charged ions. They reported $O^{\bar{\bar{}}}$, $Te^{\bar{\bar{}}}$, $Bi^{\bar{\bar{}}}$, $F^{\bar{\bar{}}}$, $Cl^{\bar{\bar{}}}$, $Br^{\bar{\bar{}}}$, and $I^{\bar{\bar{}}}$. Ratios of $X^{\bar{\bar{}}}$ to X^- of 10^{-3} to 10^{-4} were found. Frees et al.⁴¹ have attempted to reproduce these results for the case of $I^{\bar{\bar{}}}$ using radioactive ^{131}I sources and they conclude: "The presence of such a peak has been previously attributed to $I^{\bar{\bar{}}}$, however, application of radioactive tracer techniques shows that this peak in our apparatus was not due to iodine, but to some impurity."

Hird and Ali⁴² have searched for $O^{\bar{\bar{}}}$ from an *rf* discharge and set an upper limit of $(0.07 \pm 1.6) \times 10^{-12}$ for the ratio $O^{\bar{\bar{}}}/O^-$.

This author has searched for doubly charged negative ions during the past 20 years using electron bombardment, surface ionization, ion molecule reactions, Rydberg reactions, and cesium charge-exchange reactions and has found no evidence for doubly charged negative ions. Mass analysis of the negative ions were also performed with a time-of-flight mass spectrometer which should be free of many of the potential artifacts which are known to plague other mass spectrometers.

In the following paragraph we shall report an experimental observation which may bear on the subject of multiply charged negative ions.

P. W. Reinhard and R. N. Compton (unpublished) have recorded for the past few years a negative ion of mass 103 ± 1 amu under conditions in which gold and fluorine are present. In one experiment, a gold wire is heated in the presence of fluorine gas and an intense ion at mass 103 ± 1 amu was present. This ion was also recorded when $(\text{AuF}_5)_n$ was exposed to a hot wire (tungsten). Although impurity ions have not been ruled out, it is interesting to speculate that the ion is AuF_6^{\equiv} . The EA of AuF_6 is believed to be 10 ± 0.5 eV (N. Bartlett). An interesting, but unproven, possibility for metastability of AuF_6^{\equiv} is that the additional electrons are temporarily bound into a giant shape resonance. The potential shape is a combination of the long-range repulsive Coulomb potential and the short-range attraction due to the electron binding to the molecule (i.e., polarizability). Provided that the well is deep enough and the width of the well is wide enough, a long-lived (microseconds) metastable, multiply charged negative ion could exist. AuF_6 does, in fact, require three additional electrons to complete a "shell." In addition, the large EA and symmetry of AuF_6 makes this system a good candidate for a multiply charged long-lived shape resonance. The fact that the ion is only observed from a surface means that all of the molecular anion constituents, 3e's, 6F's, and Au, come together "at once" to yield AuF_6^{\equiv} and thereby overcoming the difficulty of adding the extra electrons, one at a time. All of these statements make for interesting speculation but much new experimental data is required. The

possibility of a molecular resonance analogous to the nucleus which is metastable toward alpha decay would be exciting.

PHOTOABSORPTION BY NEGATIVE IONS

The interaction of electromagnetic radiation with negative ions is a large field of physics and chemistry. Recent review articles summarize most of the data⁴³⁻⁴⁵ for the gas phase negative ions. There is an even larger set of data for negative ions in the condensed phase.

The cross section for photodetachment from an atomic negative ion is given by

$$\sigma_d = \frac{g_0 32\pi^4 m^2 e^2 \nu \nu}{g_i 3hc^3} |\langle \chi_j | \vec{r} | \chi_f \rangle|^2 \quad (3)$$

where ν is the light frequency, $\langle \chi_j | \vec{r} | \chi_f \rangle$ is the dipole matrix element, and g_i and g_0 are the statistical weights of the ionic and neutral states. Photodetachment cross sections have been calculated from Eq. (3) for many atomic negative ions. The accuracy of the calculated cross section is tested by applying known oscillator sum rules. The sum rule takes the form of an integral over the frequency and in the case where there are no bound excited states takes the form

$$\frac{e^2}{ha_0} \frac{mc}{\pi e} \int_{\nu_0}^{\infty} \frac{\sigma_d(\nu)}{\nu^5} d\nu = A_s \quad (4)$$

where A_s is a constant depending upon the wavefunction of the negative ion.

There are few known examples of bound excited states of negative ions. Herzberg and Lagerquist⁴⁶ observed a well-developed band system in the range from 4800-6000 Å emitted from a high intensity flash discharge in methane which was not attributable to C_2 or C_2^+ . Lineberger and Patterson⁴⁷ studied two-photon detachment of C_2^- and showed that the Herzberg-Lagerquist bands were due to $^2\Sigma_u^+ \rightarrow ^2\Sigma_g^+$ transitions in C_2^- . This study of Lineberger and Patterson was a monumental contribution to negative ion physics and to nonlinear laser spectroscopy as well.

Autodetaching states of negative ions can have a large influence on photodetachment cross sections. The somewhat analogous autoionizing states of neutral atoms have been extensively studied in optical absorption spectra. The famous Beutler lines in the rare gases (except He) are classic examples. Similarly, autodetaching states can affect the continuum photodetachment cross sections. Many "window" type resonances are observed in the alkali negative ions both experimentally and theoretically.⁴⁸ One of the most interesting recent studies of the effects of shape resonances on photodetachment is the photodetachment of $He^-(1s2s2p)^4P^o$ via the $He^-(1s2p^2)^4P^e$ shape resonance.⁴⁹ The $1s2p^2\ 4P^e$ state of He^- gives rise to a very large ($\sim 24 \text{ \AA}^2$) and narrow peak 10 meV above the 2^3P^o threshold. The transition $1s2s2p\ 4P^o \rightarrow 1s2p^2\ 4P^e$ is dipole allowed and since the state lies in the continuum of $1s2p\ 3P^o$ the resonance contributes to the photodetachment cross section. Figure 4 gives the theoretical calculation⁴⁹ along with the recent experimental cross sections.^{50,51} Note that the peak in the theoretical cross section is ~ 16 times the values shown in Fig. 4.

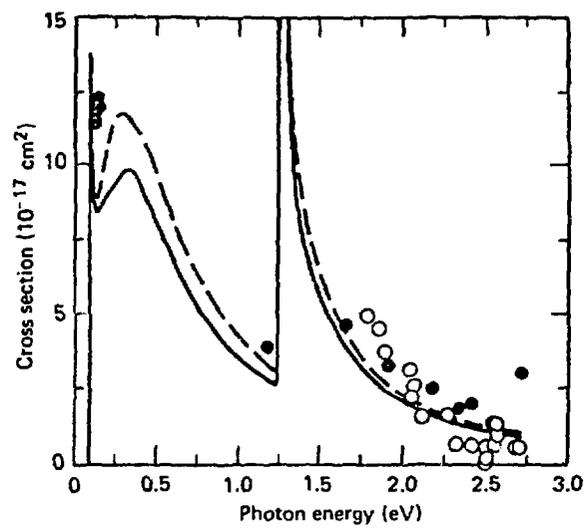


Fig. 4. Total absolute photodetachment cross section for He⁻ (4p^o); theory⁴⁹ and experiment.⁴⁰⁻⁴¹

Perhaps one of the most exciting new discoveries in negative ion physics involves studies of Li^- . There are two known excited states of Li^- which are bound relative to its parent excited neutral; $\text{Li}^- 1s2p^3 5S^\circ$ and $\text{Li}^- 1s2s2p^2 5P$.⁵² The $\text{Li}^- 5S^\circ$ state radiates to $\text{Li}^- 5P$ with a lifetime of 2.9 ns. Radiation at 3490 Å due to this transition has recently been identified in beam foil spectroscopy.⁵³

Recent studies of high-resolution photodetachment of polar anions⁵⁴ have revealed a series of very narrow, well-resolved resonances which are found just above the photodetachment thresholds for several negative ion species. The authors suggested the possibility that the resonant structures might be associated with bound excited dipole states of the molecular anions. These excited states although bound relative to the ground state neutral are so weakly bound that internal nuclear energy (rotation-vibration) allows for autodetachment. Garrett⁵⁵ found that the dipole field of the species studied in Ref. 54 were exactly in the correct range (3 to 3.5 D) to yield one or two excited dipole states with binding energies so small that the bound excited states with some finite ro-vibrational energy would overlap with the continuum of one or more lower lying ro-vibrational levels.

RECENT STUDIES OF LONG-LIVED He^- NEGATIVE IONS

Long-lived negative ions of helium have been of great theoretical curiosity and practical importance. He^- ions are routinely used as injection ions in a tandem accelerator.

Negative helium ions were first detected in a mass spectrometer in 1939 by Hiby.⁵⁶ This surprising observation required the He^- ions to be extremely long-lived ($\geq 1 \mu\text{s}$). In 1955 Holþien and Middtal⁵⁷ argued that the $^4\text{P}_{5/2}^o$ state of $(1s2s2p)^4\text{P}^o \text{He}^-$ is stable against autodetachment and might explain Hiby's observation of long-lived He^- ions. They further calculated that $^4\text{P}^o \text{He}^-$ is bound relative to $(1s2s)^3\text{S}$ by 0.075 eV. Table II provides a summary of more recent calculations and one experimental measurement of the energy level of $^4\text{P}^o \text{He}^-$.

Riviere and Sweetman⁶² in 1960 were the first to show that the He^- had a finite lifetime. The $^4\text{P}_{3/2,1/2}$ level can decay through spin-orbit and spin-spin interaction via coupling with the doublet P states while $^4\text{P}_{5/2} \text{He}^-$ can decay only through the considerably weaker spin-spin interaction. Blau, Novick, and Weinflash⁶³ established that the $J=5/2$ lifetime is $345 \pm 90 \mu\text{s}$ and that a weighted average of the $J=3/2$ and $1/2$ lifetime is $11 \mu\text{s}$. Table III presents a summary of measured lifetimes for He^- ions produced in a variety of collisions.

The theoretical values for the lifetime of the $^4\text{P}_{5/2}$ state of He^- are 303 ,⁶⁸ 505 ,⁶⁸ 505 ,⁶⁸ 266 ,⁶⁹ and 455 ⁷⁰ μs with the latter values of Estberg and LaBahn⁷⁰ expected to be the most accurate. This value is in good agreement with the experimental values shown in Table III. Manson,⁷¹ using wave functions which are less accurate than Estberg and LaBahn, obtained 10^{-3} s for the $^4\text{P}_{3/2}$ state but was unable to estimate the lifetime of $^4\text{P}_{1/2} \text{He}^-$. Manson further predicted that the energy for the fine structure levels would increase with J and that the energy excess Δ_{53} and Δ_{51} of the $5/2$ level above the $3/2$ and $1/2$ levels would be 8.43×10^{-6} eV and 3.89×10^{-5} eV. Mader and Novick⁷² used magnetic

TABLE II. ENERGY LEVELS FOR $4p^{\circ} \text{He}^{-}$

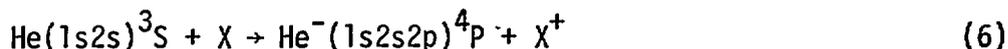
$E(1s2s)^3S - E(1s2s2p)^4P$ (eV)	$E(1s2s2p)^4P$ (eV)	Reference
≥ 0.075	19.744	57 (Theo.)
≥ 0.033	19.786	58 (Theo.)
0.067	19.752	59 (Theo.)
0.080 ± 0.02	19.739	60 (Exp.)
0.0774 ± 0.0003	19.7417	61 (Theo.)

TABLE III. MEASURED LIFETIMES OF He⁻

Source of He ⁻	Lifetime (μ s)	Reference
He ⁺ + He	18.2	64
He ⁺ + N ₂	9^{+5}_{-3}	65
He ⁺ + K	11.5 \pm 5, 345 \pm 90	63
He ⁺ + K	10 \pm 2, 16 \pm 4, 500 \pm 200	66
He ⁺ + Ca	10.5 \pm 2	67

resonance techniques to determine Δ_{53} to be 3.41×10^{-6} eV and Δ_{51} to be 3.58×10^{-5} eV.

Donnelly and Thoeming⁷³ were the first to demonstrate that He^- could be produced in a two step process, i.e.,



where X is a target atom. The alkali atoms are the most efficient electron donors. Very large beam currents can be generated in this manner. Hooper et al.,⁷⁴ for example, have been able to produce 70 mA pulses (10 ms pulse length) by charge exchange in sodium at 10.5 kV. Most tandem accelerator charge exchange sources can inject microampere beams of He^- .

Until about 1975, it was generally assumed that long-lived He^- ($\tau > 10^{-6}$ s) ions exist only in the $(1s2s2p)^4P^o$ state. Three groups⁷⁵⁻⁷⁸ have recently raised the question of whether He^- may also exist in a long-lived doublet state. This conjecture was based on the fact that He^+ can pick up two electrons from an atom or molecule with closed s shells (i.e., $\text{He}^+ + \text{Ca} \rightarrow \text{He}^- + \text{Ca}^{++}$). More recent calculations⁶¹ dispute these conjectures since no long-lived 2P states of He^- were obtained.

Previously, Compton et al.⁶⁷ measured the lifetime of He^- formed through collisions of He^+ and Ca vapor and found it to agree with earlier reported values for $\text{He}^-(1s2s2p)^4P_{3/2,1/2}^o$. This was taken as partial evidence that the He^- is formed in a quartet state. Also, the photodetachment cross sections shown in Fig. 4 are in agreement with theoretical and other experimental photodetachment data for $\text{He}^-(^4P^o)$.

The energy level of He^- formed through collisions of He^+ and Ca were also determined by directly measuring the energy of the autodetached electron. Figure 5 shows a sketch of the experimental geometry. Electrons are analyzed in the direction of the ion beam.

Figure 6 shows a typical electron energy spectrum. Two peaks are observed, one at low energy, which is due to collisionally detached or "cusp" electrons produced by background gas or from gas introduced into a scattering cell in order to enhance the "cusp" electron signal. Helium gas was introduced into the collision chamber in the particular experiment shown in Fig. 5. The autodetached energy, E_a , is related to the He^- ion kinetic energy E_i through the expression

$$E = E_c + 2 \sqrt{M_e/M_{\text{He}}} \sqrt{E_i E_a} + E_a \quad (7)$$

where $E_c = (M_e/M_i)E_i$ = energy of the "cusp." E is the electron energy in the laboratory system. Using autodetachment data over the range of incident energies from 10 to 120 keV we obtain an autodetachment energy and thereby energy level for He^- of 19.7 ± 0.1 eV which agrees very well with the values shown in Table II for $\text{He}^-(^4\text{P}^o)$. Again, we find only evidence for long-lived quartet states of He^- .

The method of autodetachment spectroscopy described above would be applicable to any metastable negative ion, e.g., Be^- , Ca^- , N^- , etc. We see considerable potential for this technique in studying metastable states of negative ions.

Finally, we mention that at low background pressures, a residual "cusp" electron peak is observed which is pressure independent for pressures below $\sim 10^{-6}$ torr. The peak is somewhat more narrow in energy

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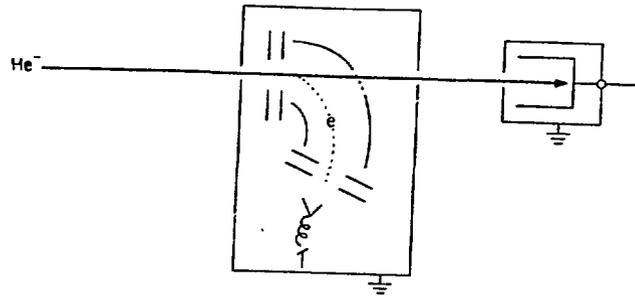


Fig. 5. Experimental sketch of double focusing hemispherical electron energy analyzer arrangement used to measure autodetached and collisionally detached electrons from He^- ion beams.

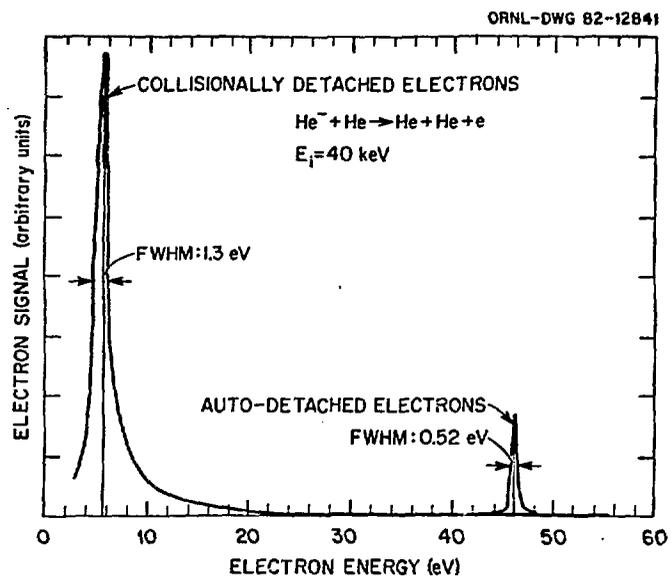
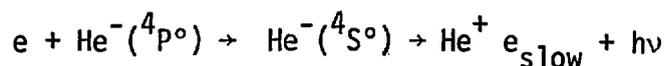


Fig. 6.

spread than the peak produced by collisional detachment. This peak is due in part to photodetachment by room temperature blackbody radiation. The spread in energy and observed count rate is close to that calculated assuming a blackbody distribution convoluted with the known experimental⁴⁹ and theoretical⁵¹ cross sections.

Nicolaides et al.⁷⁹ have recently studied bound states and decay mechanisms of He^- . They conclude that He^- has only two bound states $2p^3\ ^4S^\circ$ and $1s2s2p\ ^4P^\circ$. Both $^4S^\circ$ and $^4P^\circ$ autodetach to the adjacent continuum via spin-dependent forces. They describe two other decay mechanisms: nonrelativistic radiative autodetachment for $^4S^\circ$ and relativistic radiative autodetachment for $^4P^\circ$. Figure 7 shows the autodetachment schemes involved. The outgoing electron energy is expected to be low and the photon takes away most of the excitation energy. Nicolaides et al.⁷⁹ calculate a probability of radiative autodetachment of the $^4S^\circ$ state of $1.14 \times 10^{10} \text{ s}^{-1}$. Nicolaides and Komminos⁸⁰ have suggested that it may be possible to construct a tunable (over a narrow energy range) laser based upon radiative autodetachment of $\text{He}^- (^4S^\circ)$ at $\lambda \approx 323 \text{ \AA}$. The primary obstacle is a mechanism for population of $^4S^\circ$. One possibility is that an intense He^- ion beam (70 m amp pulses) could be passed through an intense electron beam and rely upon electron collisions to populate the $^4S^\circ$ state.



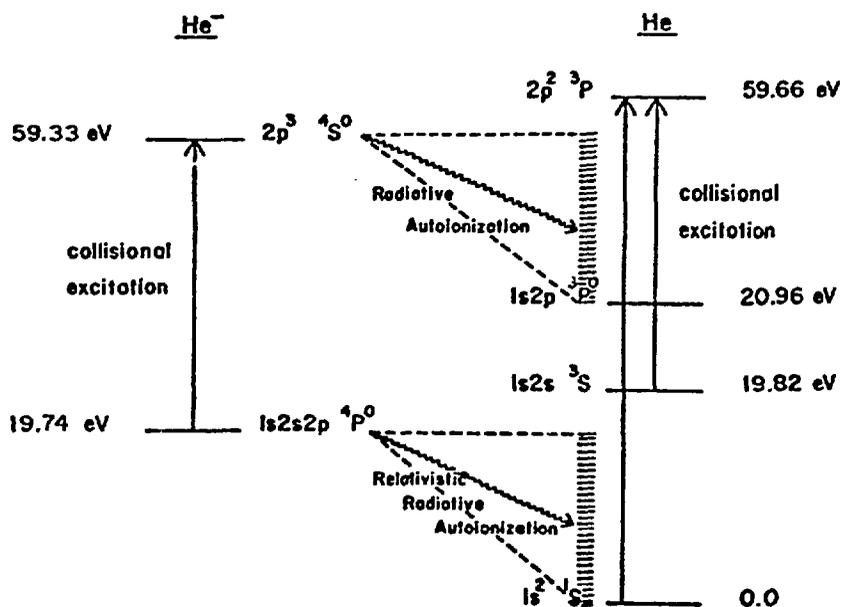
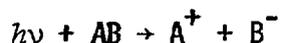


Fig. 7. Energy levels of He⁻ ($^4S^0$) and He⁻ ($^4P^0$) relative to the ground $1s2s \ ^3S$ and $2p^2 \ ^3P$ states of neutral helium. He⁻ $^4S^0$ can decay only to the He $1s2p \ ^3P^o$ continuum with a maximum photon energy of 38.64 eV. The $^4P^0$ state can undergo relativistic radiative autoionization to the He $1s^2 + e^- + h\nu$ continuum by mixing with the $1s^2 \ ^1P$ and $1s2s2p \ ^2P^o$ continuum via spin-dependent interactions. Helium $2p^2 \ ^3P$ can also decay to the He⁺ $1s + e^- + h\nu$ continuum. However, its main decay channel is to the lower discrete $1s2p \ ^3P^o$ level.⁸⁰

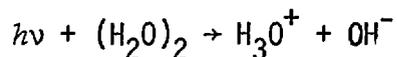
PRODUCTION OF NEGATIVE IONS BY PHOTON REACTIONS

The formation of ion-pairs by photon absorption, i.e.



is sometimes referred to as polar dissociation. This process can be particularly important in cases where the ion-pair limit lies below the ionization potential. The halogens I_2 and Br_2 are classic examples (e.g., the $I^+ + I^-$ limit is 0.49 eV below $I_2^+ + e$). In these cases large cross sections are observed below the ionization limit, however, once the photon energy approaches and exceeds the ionization limit the ion-pair cross section decreases dramatically. Figure 8 shows the experimental data of Morrison et al.⁸¹ for I_2 .

It is interesting to consider the polar dissociation of molecular clusters by photons. Although such experiments have not yet been reported, it is instructive to examine the energetics of such reactions. Let us use as an example the important case of photodissociation of water clusters into ion pairs. The energy required to ionize a single water molecule is 12.51 eV and the ionization potential for the dimer is 11.21 ± 0.09 eV.⁸² A recent value for the threshold for photoelectron emission from liquid water is 10.06 eV.⁸³ On the other hand the threshold for the polar dissociation of the dimer is 9.81 eV



$$\begin{aligned} E &= D(H_2O \cdot H_2O) + D(H-OH) - D(H^+ - H_2O) - EA(OH) + IP(H) \\ &= 0.17 + 5.113_6 - 7.18 - 1.89 + 13.6 = 9.81 \text{ eV} \end{aligned}$$

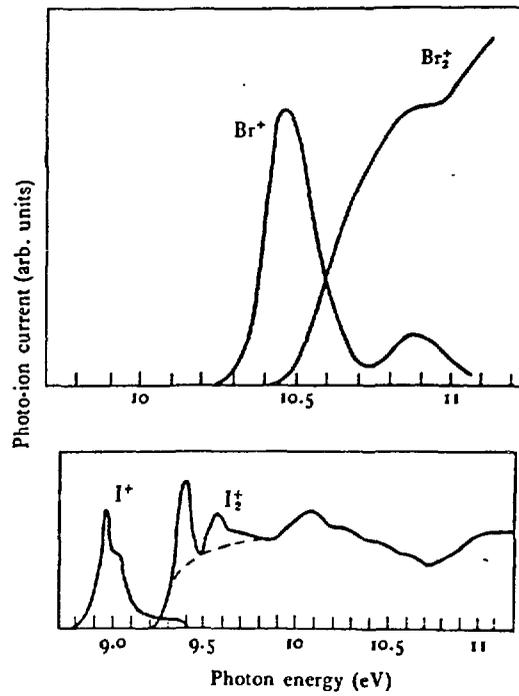
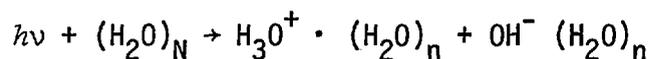


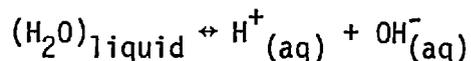
Fig. 8. Relative cross sections for $\text{Br}^+ + \text{Br}^-$ and Br_2^+ ($\text{I}^+ + \text{I}^-$ and I_2^+) produced from photon collision with Br_2 (I_2) as observed by Morrison et al.⁸¹

The significant lowering of energy primarily comes from the rather large proton affinity of water (7.18 eV).⁸² Also, since the ion-dipole interaction energies are generally greater than the van der Waals interactions we would expect the energy for the polar dissociation reaction to continue to decrease as the cluster size increases. Figure 9 shows an approximate plot of photodissociation energy versus cluster size for the case of symmetric fission, i.e.,



where $N = 2n + 2$.

Dissociation energies for $\text{OH}^- (\text{H}_2\text{O})_n$ were taken from Kebarle and co-workers^{84,85} and for $\text{H}_3\text{O}^+ (\text{H}_2\text{O})_n$ from Lau et al.⁸⁶ The major uncertainty in the data plotted in Fig. 9 is the neutral bond dissociation energies. The important point to note from Fig. 9 is that photodissociation of $(\text{H}_2\text{O})_N$ for $N=12$ could occur for photons with energies of $\lesssim 4$ eV. The proton transfer reaction in liquid water, i.e.,



exhibits a low ΔH (0.628 eV) due to the effective solution and dielectric shielding of product ions in water. Natzle et al.⁸⁷ have recently studied dissociative ionization of water induced by single-photon vibrational excitation. The quantum yield for production of $\text{H}^+_{(\text{aq})}$ and $\text{OH}^-_{(\text{aq})}$ increases from 2×10^{-9} to 4×10^{-5} for energies between 0.94 and 2.25 eV. Figure 10 shows the data taken from Ref. 87.

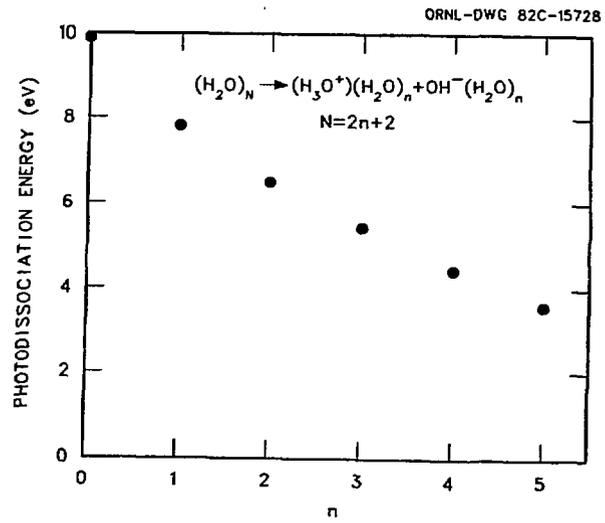


Fig. 9

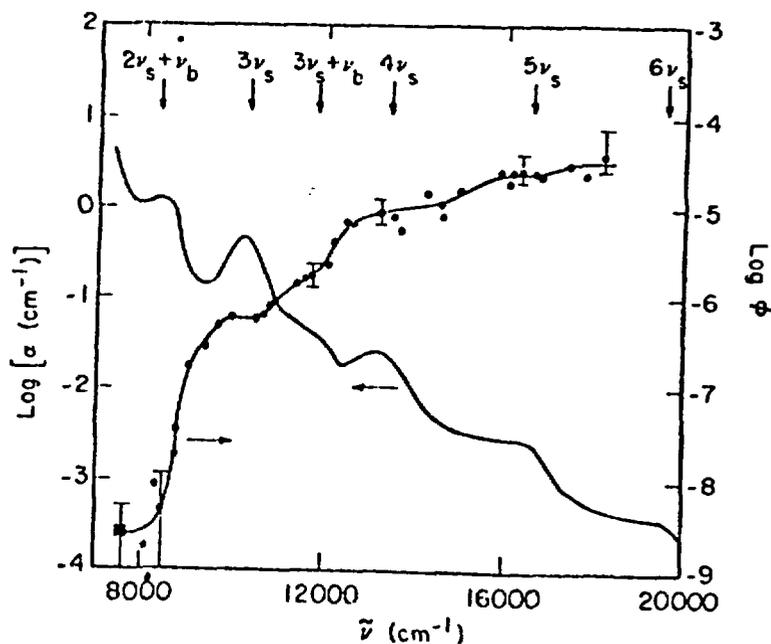


Fig. 10. Quantum yield (ϕ) for photoionization of water at 283 ± 1 K as a function of photon energy ($\tilde{\nu}$). A line is drawn through experimental points with estimated errors from this study (\bullet). The point (\blacksquare) was taken with the iodine laser. The absorption spectrum of water is shown as the dependence of the natural absorption coefficient (α) on wave number ($\tilde{\nu}$). [$I/I_0 = \exp(\alpha)$.] Band assignments are shown with subscripts b and s representing bending and stretching modes, respectively.⁸⁷

The quantum yield is seen to rise rapidly at the onset of a vibrational band and is relatively constant at $\sim 10^{-5}$ - 10^{-6} through the band center. Given the photon intensities in present dye lasers and the ability of producing large molecular water clusters from nozzle beams, it is possible to study the production of ion pairs in water clusters for various cluster sizes. It may also be possible to obtain information on the minimum energy to produce an ion pair for various cluster sizes, thereby accurately reproducing and extending the approximate data shown in Fig. 9.

COLLISION OF HIGH RYDBERG ATOMS WITH ELECTRON ATTACHING MOLECULES AND THE POSSIBLE INFLUENCE OF DIPOLE BOUND STATES

The Rydberg electron in a highly excited Rydberg state can be viewed as almost free and slow. That is, the excited electron and the ion core are sufficiently separated so that when a molecule collides with a Rydberg atom the molecule can be viewed as reacting with either the electron or ion core separately. Fermi⁸⁸ used data on ultra-low energy elastic electron scattering to analyze successfully the observed pressure shift of the high Rydberg series absorption spectra of an alkali metal atom perturbed by a foreign gas atom. Since Fermi's original contribution, there has been a considerable body of theoretical^{89,90} and experimental⁹¹⁻⁹³ evidence to suggest that the rate constant for transfer of a loosely bound Rydberg electron to a target molecule should be equal to the attachment rate for free electrons of the same energy. Perhaps the best experimental evidence for this equivalence comes from the unpublished data of Chupka.⁹⁴ Figure 11 displays the electron charge transfer rate from Rydberg excited argon atoms to some hexafluoride

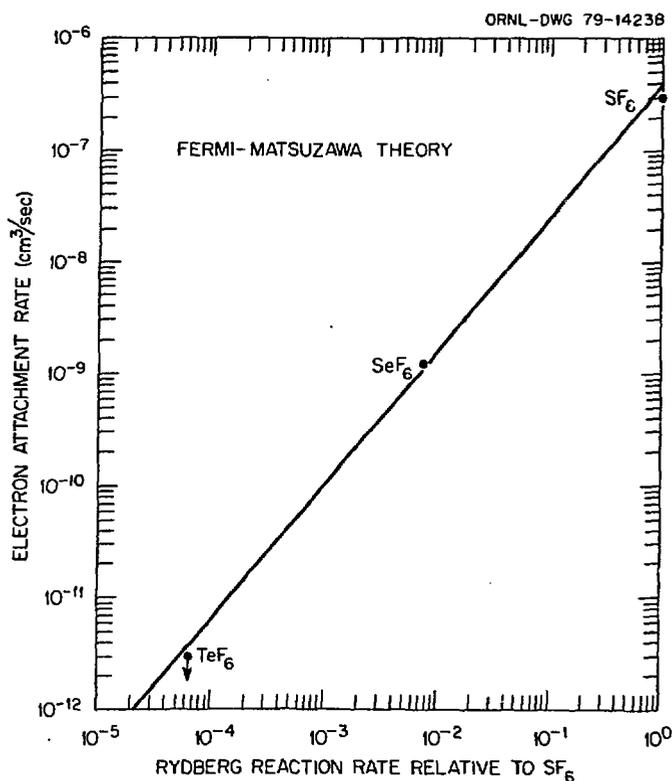
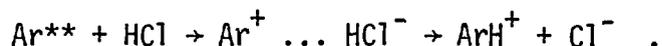


Fig. 11. Rydberg reaction rate leading to negative ions for various hexafluoride molecules relative to SF₆ as measured by W. A. Chupka (unpublished results) versus the thermal electron attachment rate as determined by Davis et al.⁹⁵ The Fermi-Matsuzawa model predicts a straight line as shown. 88-90

molecules as measured by Chupka, versus the thermal electron attachment rate for the same hexafluorides as determined by Davis et al.⁹⁵ The solid line through the data points is the Fermi-Matsuzawa prediction of equivalence between Rydberg reaction rates and slow electron attachment rates. The data not only confirm the Fermi-Matsuzawa model but the ions observed by Chupka are in fact identical to those found in slow electron attachment experiments (i.e., $\text{SF}_6^-/\text{SF}_6$, $\text{SeF}_5^-/\text{SeF}_6$, $\text{TeF}_5^-/\text{TeF}_6$).

The Rice University group of Stebbings, Dunning, and colleagues has presented some equally compelling evidence for the free-electron model. The thermal electron attachment rate for perfluoromethylcyclohexane (C_7F_{14}) is known to increase with electron energy.⁹⁵ Hildebrant et al.⁹⁶ have actually observed an analogous increase of the ionization rate with *decreasing* n when xenon atoms in high Rydberg states collide with C_7F_{14} . Thus, the equivalence of both the magnitude, energy dependence, and ion products for Rydberg charge exchange rates and thermal attachment rates seems to be well founded. We should hasten to point out, however, that the positive ion core of the Rydberg state can play a role in the collision other than simply bringing up the slow electron. For example, we know that thermal electrons attach to CH_3NO_2 to produce a short-lived CH_3NO_2^- ion with a lifetime of less than 10^{-6} s. However, the CH_3NO_2^- formed through Rydberg charge exchange is stable,⁸⁸ indicating that the recoiling positive ion relaxes vibrations initially excited in the negative ion. The very presence of the ion core can also make certain reactions possible which are apparently not available for slow electrons. For example, Chupka (unpublished results) has found that the reaction $\text{Ar}^{**} + \text{HCl} \rightarrow \text{ArH}^+ + \text{Cl}^-$ proceeds. Such a reaction would not be

predicted from the model of free electron attachment since the thermal electron attachment rate to HCl is less than $3 \times 10^{-12} \text{ cm}^3/\text{s}$ and may well be zero.⁹⁵ Thus, HCl is an example where the Rydberg core must play a critical role and, in fact, the reaction is only possible because of the $\text{ArH}^+ + \text{Cl}^-$ channel. But does the Rydberg electron transfer to HCl^- and then the Ar^+ core react to abstract a hydrogen atom? If so, we must postulate a potential energy surface for HCl^- that lies very close to the ground state. Such states have been postulated by Rohr and Linder⁹⁷ to explain their low-energy electron scattering data for the case of the hydrogen halides. The negative ion surface is believed to exist due to the dipole field of the molecule. Such negative ion states do not show up in limited basis set valence type calculations. However, the properties of the dipole field are such that we are assured of bound states if the dipole moment of a molecule is greater than ~ 2 Debye.^{98,99} The dipole moment of HCl is only 1.08 Debye, less than the critical moment, but virtual states of the dipole field could provide a mechanism for electron transfer in the reaction



Under this proposal the Fermi-Matsuzawa model would again apply. However, one could make an equally convincing argument that the Ar^+ core of Ar^{**} reacts with HCl to form ArH^+ and the Cl^- takes away the electron. Clearly, more experimental and perhaps theoretical work is necessary to solve this riddle.

There is a further example in which the thermal electron attachment rate does not approximate the Rydberg reaction rate. Namely, highly

excited rare gas Rydberg atoms (excited by electron impact) react rapidly^{91,100} with acetonitrile (CH_3CN) to produce CH_3CN^- , whereas the thermal energy electron attachment rate constant for CH_3CN is $\leq 1.25 \times 10^{-14} \text{ cm}^3/\text{s}$. This, incidentally, is the lowest upper limit which has been placed on an electron attachment rate. Acetonitrile, like HCN, is a "closed shell" molecule, and the valence-type empty orbitals would be high in energy, and no valence-type bound states are expected. The dipole moment of CH_3CN is 3.92 Debye and well exceeds the minimum dipole moment required to form a bound state.^{98,99} The dipole states are very fragile due to the low binding energy and would not survive the collisions inherent in an electron swarm experiment. Thus, it is not surprising that the attachment rate is unmeasurably small. We should mention that the Rydberg reaction rate estimated by Stockdale et al.⁹¹ was not as large as that reported by Sugiura and Arakawa.¹⁰⁰ A possible explanation is that Stockdale et al.⁹¹ did not detect all of the CH_3CN^- produced. In this connection, Odom and Hill (unpublished results) have reacted sodium high Rydberg states with CH_3CN and see *no* CH_3CN^- negative ions. They do observe a large cross section for collisional ionization producing a free electron. More experiments are definitely required to resolve the discrepancy. In resolving the discrepancy perhaps we will learn more about dipole states of the electron-molecule system.

The production and detection of dipole bound negative ion states offer a real challenge to experimentalists. The problem is to gently place the electron on the dipole and then detect the ion without ejecting the electron in the process of detection. Table IV represents a list of molecules that are assured of weakly bound dipole states. These compounds

have vapor pressures that are suitable for use in mass spectrometer experiments. We have studied fast alkali collisions with each of these molecules and observe parent negative ions only in the case of nitromethane, which has a bound state due to an empty valence orbital ($EA = 0.44 \pm 0.2$ eV).¹⁰¹ In this case the dipole state should be considered as the excited state of $CH_3NO_2^-$.

Finally, we should mention that Matsuzawa¹⁰² has suggested the use of high Rydberg atoms to obtain information on electron-molecule resonance at ultra-low energies. Resonances in elastic electron molecule scattering would cause an oscillation in the n dependence of the pressure shift. As an example, if one could detect oscillations of 0.005 cm^{-1} in the pressure shift at low pressures where one can avoid multiple scattering effects, then the high-Rydberg atom could be used to detect resonances with widths of 10^{-3} eV.

NEGATIVE IONS OF MOLECULAR CLUSTERS

The clustering of neutral molecules to ions is a broad subject. Various techniques have been employed to study the interactions of an ion and a molecule which lead to clustering; the flowing and stationary afterglow, ion cyclotron resonance, and high pressure mass spectroscopy. These studies are directed toward understanding the nature of the forces affecting cluster stability. In many cases the ion and clustering ligand have been systematically varied in order to separately access individual ionic or neutral properties such as ion size, polarizability, etc. In some cases, the cluster ions themselves have been studied via collisional-dissociation, photodetachment, or photodissociation reactions.

TABLE IV. SOME MOLECULES WITH DIPOLE MOMENTS SUFFICIENTLY
LARGE TO PERMANENTLY BIND AN ELECTRON

Molecule	Dipole Moment (Debye)
Cyanomethane H_3CCN (acetonitrile)	3.92
Formamide H_2NCOH	3.25
Nitromethane H_3CNO_2	3.46
Cyanamide H_2NCN	4.27
Dimethyl sulfoxide $(\text{CH}_3)_2\text{SO}$	3.96
Vinylene carbonate $\text{C}_3\text{O}_3\text{H}_2$	4.5

During the past few years C. E. Klots and R. N. Compton have taken a different approach to cluster ion studies by examining electron attachment to preexisting clusters of molecules. A supersonic nozzle expansion is employed to prepare the molecular cluster so that it was possible to study electron attachment to ultracold ($T_{\text{trans}} \approx 1^\circ\text{K}$, $T_{\text{rot}} \approx 2^\circ\text{K}$, $T_{\text{vib}} \approx 20\text{-}30^\circ\text{K}$) molecules and molecular clusters. We will briefly discuss some of these studies below.

ELECTRON ATTACHMENT TO ULTRACOLD MOLECULES AND MOLECULAR CLUSTERS

The cross section for electron attachment to molecules can be especially sensitive to thermal effects. Henderson, Fite, and Brackman¹⁰³ found, for example, that the maximum in the cross section for the process $e + \text{I}_2 \rightarrow \text{O}^- + 0$ shifts to lower energy and increases in magnitude upon heating the O_2 . Also, the energy onset for O^- from CO_2 is temperature dependent; at room temperature the threshold is 0.25 eV below the expected thermodynamic threshold.¹⁰⁴ The most dramatic effect of internal energy upon electron attachment cross sections is found in the case of N_2O . For N_2O , at room temperature, a separate O^- peak appears at ~ 0.5 eV.¹⁰⁵ Chantry¹⁰⁵ attributes this dramatic temperature effect to thermal excitations of bending modes of N_2O . Such excitations would yield good Franck-Condon overlap with the bent configuration of the N_2O^- ground electronic state.

Klots and Compton^{106,107} have largely eliminated these artificial thresholds by employing sonic nozzle expansions to adiabatically cool the gas. For example, Fig. 12 shows the O^- signal from the reaction $e + \text{N}_2\text{O} \rightarrow \text{O}^- + \text{N}_2$ as a function of electron energy. The prominent peak

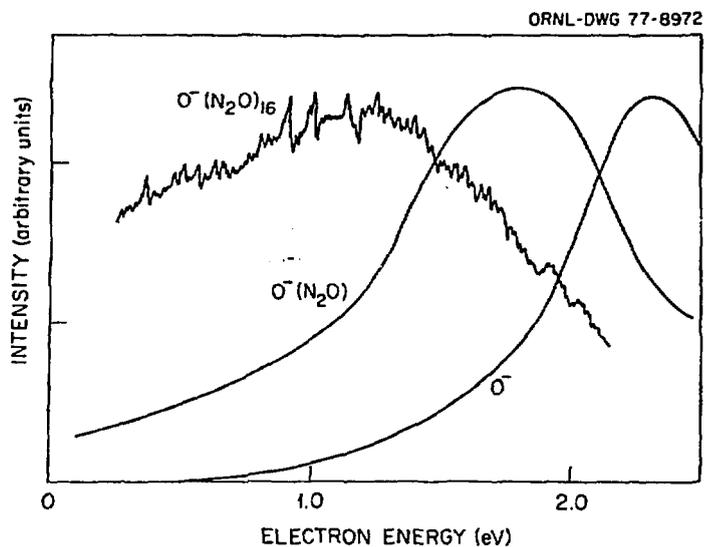


Fig. 12. A few of the negative ions observed from electron attachment to supersonic molecular beams of nitrous oxide as a function of the electron energy. Ions with the formula $O^-(N_2O)_n$ with $0 \leq n \leq 3$ are observed.¹⁰⁷

at ~ 0.5 eV in the room temperature data is absent in the nozzle experiment. Similarly, the onset for O^- from CO_2 shown in Fig. 13 occurs at the proper thermodynamic threshold. Electron beam experiments employing sonic nozzle expansions offer a number of advantages: (1) rotational ($\sim 1^\circ K$), vibrational ($\sim 20-50^\circ K$), and translational ($\sim 1^\circ K$) cooling, (2) translational cooling greatly reduces the Doppler profile from the energy dependence of a resonance or threshold, (3) increased molecular density for a given collision chamber pressure.

Van der Waals polymers can also be produced in sonic expansions. We have studied electron attachment to polymers of CO_2 ,^{106,107} N_2O ,¹⁰⁷ and H_2O .¹⁰⁸ In the case of CO_2 , the most intense cluster ions occur with general formula $O^-(CO_2O)_n$ with $0 \leq n \leq 6$ (see Fig. 13). Long-lived ions with charge-to-mass ratios corresponding to $(CO_2)_n^-$ with $2 \leq n \leq 6$ were detected. Carbon dioxide is linear whereas CO_2^- is bent at about 135° . For bond angles less than $\sim 140^\circ$, the CO_2^- curve lies below that for CO_2 . The experimental vertical¹⁰⁹ and adiabatic¹¹⁰ EA of CO_2 are -3.8 and -0.6 ± 0.2 eV, respectively. Linear CO_2^- autodetaches in $\sim 10^{-15}$ s. However, due to poor Franck-Condon factors between the bent CO_2^- and linear CO_2 , the lifetime of ground state CO_2^- is ~ 90 μs . The $(CO_2O)_n^-$ ions appear to be stable ($\tau > 10^{-3}$ s). Rossi and Jordan¹¹¹ have employed the Hartree-Fock method to predict that the adiabatic EA of $(CO_2)_2$ is small but positive. Their most stable configuration consisted of a bent CO_2^- "solvated" by a nearly linear CO_2 (C_s symmetry). If this turns out to be true, these experimental results will provide the first observation of a solvated electron in the gas phase. Solvation energies can be large [e.g., >0.6 eV in the case of $(CO_2)_2^-$] and could provide

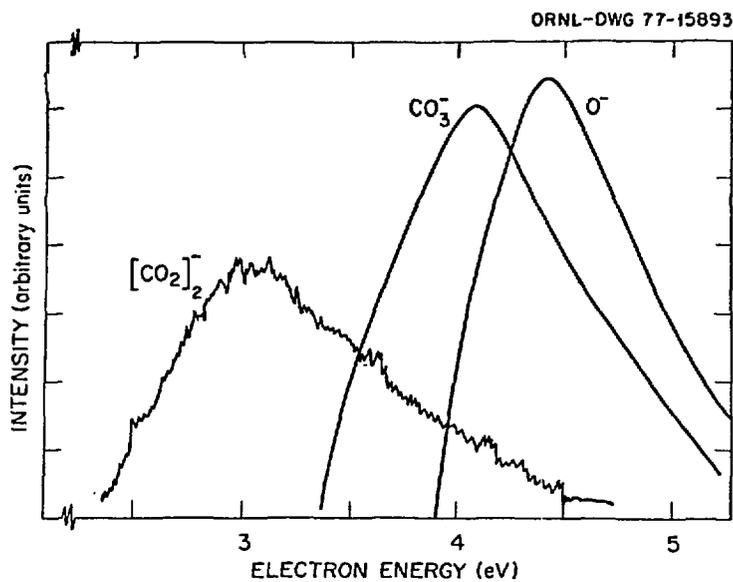


Fig. 13. A few of the negative ions observed from electron attachment to supersonic molecular beams of carbon dioxide as a function of the electron energy. Ions with the formula $(\text{CO}_2)_n^-$ with $0 \leq n \leq 6$ are observed. Larger ion clusters were most likely present.¹⁰⁷

stability for a large number of anions. In this connection Klots¹¹² has mixed H_2O and CO_2 in a nozzle expansion to produce the $(\text{CO}_2 \cdot \text{H}_2\text{O})^-$ ion.

The formation of CO_2^- ions from CO_2 clusters is an example of "evaporative electron attachment." It is a particularly good illustration of collisional stabilization by a built-in third body. The attachment of low-energy electrons to an O_2 molecule has usually been envisaged in terms of a classical three-body mechanism; an electron is captured by an oxygen monomer. Collision with a third body can stabilize the ion if the collision occurs before autodetachment takes place. We have found that an O_2^- can be formed with high efficiency from a single-step attachment to a preexisting oxygen dimer.¹⁰⁷ Spurred by these observations, Shimamori and Fessenden¹¹³ have reexamined the mechanisms of electron attachment to oxygen in the gas phase. They find that electron attachment to oxygen at low-temperature occurs much faster than predicted by the classical three-body mechanism. The estimated rate constants for attachment to van der Waals molecules are nearly two orders of magnitude larger than for O_2 itself. This does not imply that the cross section for attachment is necessarily smaller, however. The cross section for attachment to a single O_2 molecule exhibits strong maxima (actually double maxima due to fine structure splittings) at the vibrational levels of O_2^- . On the other hand O_2^- from $(\text{O}_2)_2$ is a dissociative process and could show a rather broad energy dependence depending upon the potential energy surfaces involved.

As a further example of stabilization by collisions, let us consider the attachment of low-energy electrons to carbon tetrachloride. Thermal electron attachment to CCl_4 yields almost entirely Cl^- . Yet when CCl_4 is bound initially to CO_2 in a van der Waals molecule, one obtains CCl_4^- in a good yield.¹⁰⁶

As a final example of electron attachment to van der Waals molecules, let us consider the case of methyl iodide, CH_3I .¹¹⁴ In the low-pressure mass spectrometer, a methyl iodide molecule captures only electrons of near-zero energy to form I^- ions. When the molecule is part of a van der Waals molecule this is no longer the case. Figure 14 shows the signal of $\text{I}^- \cdot \text{CH}_3\text{I}$ for electron energies above 3 eV together with the SF_6^- scavenger spectrum. The scavenger spectrum is a measure of the inelastic scattering cross section for excitation of electronic excited states of methyl iodide. The close similarity of the two spectra have prompted us to argue¹¹⁴ that this should be viewed as involving an *intermolecular Feshbach resonance*. This is an incident electron excites one moiety of the cluster to an electronically excited state and the resulting slow electron is captured elsewhere in the cluster.

We originally began these cluster experiments in order to search for the "hydrated" electron in the gas phase. Thus far, we have been unsuccessful.¹⁰⁸ The large dipole moment of $(\text{H}_2\text{O})_2$ ($>2.4 \text{ C}$)¹¹⁵ assures us that $(\text{H}_2\text{O})_2$ is bound. However, the dipole moment of $(\text{H}_2\text{O})_3$ is probably very small. Thus, unless $(\text{H}_2\text{O})_2^-$ can be further solvated by water molecules any connection with the hydrated electron is tenuous. Very recently, Armbruster, Haberland, and Schindler¹¹⁶ have detected

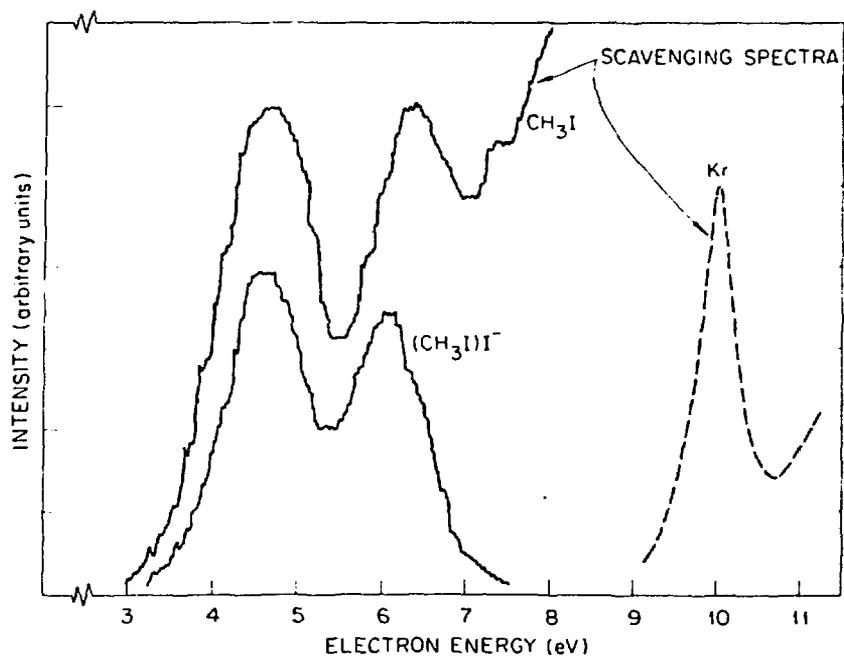


Fig. 14. Scavenging spectrum of methyl iodide monomer, and product of self-scavenging in the trimer, as function of electron energy. The scavenger spectrum is essentially the spectrum of excited states produced by electron impact excitation.¹¹⁴

negatively charged water cluster ions, $(\text{H}_2\text{O})_n^-$ for $n \geq 8$, in the gas phase. They expanded steam and free electrons through a supersonic nozzle expansion and observed $(\text{H}_2\text{O})_n^-$ with $n \geq 8$. For $(\text{H}_2\text{O})_{11}^-$ the signal is larger than the $\text{OH}^- \cdot (\text{H}_2\text{O})_{10}$ signal. These studies represent a breakthrough in the quest for studies of the hydrated electron in the gas phase.

ACKNOWLEDGMENTS

Research is sponsored by the Office of Health and Environmental Research, U.S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

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