LOW ENERGY ELECTRON ATTACHMENT TO POLYATOMIC MOLECULES AND NEGATIVE ION LIFETIMES

P. M. Collins, L. G. Christophorou, and J. G. Carter

(Thesis)
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P. M. Collins, L. G. Christophorou, and J. G. Carter

Submitted by Patrick Marc Collins as a dissertation to the Graduate School of The University of Tennessee in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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ABSTRACT

Nondissociative and dissociative low energy (≤ 15 eV) electron attachment processes have been studied in polyatomic molecules using a time-of-flight mass spectrometer. The first variation with incident electron energy of the mean autoionization lifetime of a long-lived parent negative ion has been found. Examples of this behavior are the negative ions of p-benzoquinone (C_{6}H_{4}O_{2}) and 1,4-naphthoquinone (C_{10}H_{6}O_{2}). Mean autoionization lifetimes have been measured also for the negative ions of azulene (C_{10}H_{8}), cinnamaldehyde (C_{6}H_{5}CH:CHCHO), o-, m-, and p-nitrotoluene (o-, m-, and p-C_{6}H_{4}CH_{3}NO_{2}), sulfur hexafluoride (SF_{6}), and hexafluoroacetone (C_{3}F_{6}). Electron attachment cross sections for the formation of C_{6}H_{4}O_{2}^{-}, C_{10}H_{6}O_{2}^{-}, and C_{10}H_{8}^{-} have been measured. Estimates of the electron affinities in both the ground and excited states have been made for C_{6}H_{4}O_{2} and C_{10}H_{8}, and in the ground state for C_{10}H_{6}O_{2}. Dissociative electron attachment processes have been studied in the alkyl bromides n-C_{N}H_{2N+1}Br where N = 2,3,4,5,6,7,8, and 10, azulene, and acetaldehyde (CH_{3}CHO). Experimental data are presented which indicate certain diatomic-like characteristics of dissociative electron attachment to the n-C_{N}H_{2N+1}Br systems.
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CHAPTER I

INTRODUCTION

I. STUDIES OF LOW ENERGY ELECTRON ATTACHMENT TO MOLECULES

Fundamental Importance of Low Energy Electron Attachment to Molecules

Low energy electron attachment to molecules is of fundamental physical and biological importance. Of primary interest is the usefulness of electron attachment processes in studying molecular structure. Basic physical properties of molecules that can be determined through low energy electron attachment studies include electron affinities of molecules, bond dissociation energies, electron attachment cross sections, mean autoionization lifetimes of long-lived negative ion states, and shapes and positions of molecular and negative ion potential energy functions.

The interactions of large numbers of low energy electrons produced when ionizing radiation interacts with matter are still poorly understood. A number of intermediate reactions between initial radiation action and the final effects are the subject of intense study by radiation physicists. Certain normal and beneficial biological processes proceed via electron transport. Other abnormal or harmful processes such as carcinogenesis and toxicogenesis may be related to electron transport properties of molecules and negative ion structure. A correlation between carcinogenicity and electron transport properties of molecules has been attempted by many workers and reviewed by Blaunstein and Christophorou (1968a) and Christophorou (1970). The biological
importance of energy transfer via electron transport in molecules has been discussed in several books [see, e.g., Szent-Györgyi (1960, 1968), Pullman and Pullman (1963), and Christophorou (1970)].

Practical Application of Low Energy Electron Attachment to Molecules

The electron accepting capacity of molecules might be utilized to great advantage in controlling large numbers of free electrons. Some electron attaching molecules have high dielectric strengths which make them good insulators. Nuclear explosions, ionization in rocket exhausts, and ionization around space vehicles reentering the earth's atmosphere create large numbers of free electrons, which might be removed by strong electron attaching gases. The negative ions of atoms and small molecules have been used in high energy accelerators, and their presence in the upper atmosphere and nebulae have also made them important in the fields of geophysics [Dalgarno (1968)] and astrophysics [Branscomb (1968)].

II. MOLECULAR ELECTRON ATTACHMENT PROCESSES

The capture of a free electron by a molecule may proceed via several channels which have been summarized by Christophorou (1970) as follows:

\[
\begin{align*}
AX + e & \rightarrow AX^- + \text{energy,} \\
AX + e & \rightarrow AX^* \\
AX^* & \rightarrow A (or A^*) + X^- \quad (I-1)
\end{align*}
\]
where AX represents a molecule composed of the atoms (or groups of atoms) A and X, AX$^{-*}$ represents an excited compound negative ion, $\sigma_o$ is the cross section for the formation of AX$^{-*}$, $p_{ai}$ is the probability that AX$^{-*}$ will autoionize, $\sigma_{ai} (= \sigma_o p_{ai})$ is the cross section for autoionization, $p_{da}$ is the probability that AX$^{-*}$ will dissociate, $\sigma_{da} (= \sigma_o p_{da})$ is the cross section for dissociation, $p_{st}$ is the probability that AX$^{-*}$ will be stabilized, and $\sigma_{st} (= \sigma_o p_{st})$ is the cross section for stabilization. The formation of the initial compound negative ion state through which autoionization, dissociation, and stabilization may proceed is dependent upon the molecule AX and the energy of the incoming electron.

The process of autoionization, represented by

$$AX + e \xrightarrow{\sigma_o} AX^{-*} \xrightarrow{p_{ai}} AX \text{ (or } AX^* \text{)} + e,$$

is studied for the molecules presented in Chapters IV and V which capture thermal and epithermal energy electrons for lifetimes $> 10^{-6}$ sec. These systems can decay from the state AX$^{-*}$ to the original neutral molecular state AX or to a vibrational or an electronic excited state AX$^*$. The terms autoionization and autodetachment will be used interchangeably in this study. Autodetachment is a more restrictive term than autoionization of the negative ion. In the initial step of negative ion formation the metastable negative ion (compound system) is in an autoionizing state, such as a superexcited atom or molecule. Many systems, referred to as long-lived parent negative ions, have mean autoionization lifetimes long enough to allow their study in time-of-flight mass spectrometers TOFMS (see Chapter III).
Dissociative electron attachment, represented by

\[ AX + e \xrightarrow{\sigma_0} AX^{*} \xrightarrow{P_{da}} A(\text{or } A^{*}) + X^{-} \text{ (or } X^{*-} \), \]  

is studied for several molecules presented in Chapter VI. In dissociative electron attachment the kinetic energy from the incoming electron plus the electron affinity of the molecule (\( e + EA \), where EA is defined in Chapter II) combine to break one or more bonds. This results in the formation of fragments, one of which attaches the electron. Only two fragments are shown in the representation (I-3). However, for large molecules more than two fragments may be formed. Dissociative electron attachment competes with autoionization and possibly stabilization and can be studied in both electron swarm and electron beam experiments (see Chapter III).

Permanent negative ions may be formed through stabilization of \( AX^{-*} \). This stabilization process is represented by

\[ AX + e \xrightarrow{\sigma_0} AX^{*} \xrightarrow{P_{st}} AX^{-} + E, \]  

where \( E \) is the excess energy of attachment equal to \( e + EA(AX) \). This stabilization of the negative ion occurs through collisions in high pressure experiments (see Chapter III) or, to a lesser extent, by emission of radiation. Stabilization is not an important process in the TOFMS used in this study (the mean free path for molecular collisions is much greater than the distance a molecule travels while in the collision chamber under the conditions described in Chapters IV and V).
Radiative attachment is represented by

\[
AX + e \rightarrow AX^- + h\nu,
\]

where \(h\nu\) is a quantum of radiation whose emission stabilizes the negative ion. This process has a very small probability of occurrence.

Ion pair production is not detailed here because it is not a resonance capture process. The incoming electron provides the energy necessary for the dissociation of a molecule into a positive and a negative ion. The energy at which this process occurs is also generally above the energy range studied (\(< 15\) eV) in this investigation. The electron attachment processes described here and negative ion formation in general have been discussed in a number of books and articles [see, e.g., Christophorou (1970), McDaniel (1964), Massey and Burhop (1969), Massey (1950, 1969), Branscomb (1957), Field and Franklin (1957), Prasad and Craggs (1962), Loeb (1956, 1960), Buchel'nikova (1960), Craggs and Massey (1959), and Hasted (1964)].

Three groups of negative ions have been distinguished [Chaney et al. (1970)] on the basis of the magnitude of the negative ion lifetime \(\tau\).

1. Extremely short-lived ions with \(\tau\) in the interval \(10^{-15} \leq \tau \leq 10^{-13}\) sec. These processes are observed as resonances in electron scattering experiments or in dissociative attachment studies.

2. Moderately short-lived ions with \(\tau\) in the interval \(10^{-13} \leq \tau \leq 10^{-6}\) sec. Collisonal stabilization can occur in this time interval at high pressures, and such processes can be observed in high pressure swarm experiments (see Chapter III).
3. Long-lived negative ions for which \( \tau > 10^{-6} \text{ sec} \). The lifetimes of many of these processes can be determined directly under single collision conditions with a TOFMS (see Chapter III).

III. OBJECTIVES OF THE PRESENT INVESTIGATION

The objectives of this study of low electron energy (\( \leq 15 \text{ eV} \)) electron attachment to polyatomic molecules are the following:

1. Using a TOFMS, identify the masses of long-lived negative ions formed at low energies. Measure the mean autoionization lifetimes of these ions, and search for possible energy dependences of these lifetimes. Investigate the relation between lifetime and molecular degrees of freedom. Combine relative ion yields as a function of incident electron energy measured in the TOFMS with attachment rates measured by others in swarm experiments [Chaney and Christophorou (1969), Christodoulides and Christophorou (1969)] to determine electron attachment cross section functions and electron affinities in both the ground and excited-electronic states.

2. Identify the masses of fragment ions and measure their yields as a function of electron energy.

3. Perform a comprehensive study of the dissociative electron attachment processes in the brominated hydrocarbons \( n-C_{N}H_{2N+1}Br \) where \( N = 2,3,4,5,6,7,8, \) and 10 through the use of a TOFMS. Identify the shapes and widths of the \( Br^- \) resonances from \( n-C_{N}H_{2N+1}Br \). In cooperation with A. A. Christodoulides and using capture rates measured by Christodoulides and
Christophorou (1969), perform swarm-beam combinations to determine the electron attachment cross sections and the energy scale calibrations for the formation of Br\(^-\) from the \(n-C_\text{H}_{2N+1}\text{Br}\) molecules. Compare the electron attachment cross sections and the Br\(^-\) resonance widths for the molecules of the series to determine what, if any, isotope effects due to diatomic-like behavior of the molecules exist.

4. Investigate possible relationships between the electron attachment properties of the molecules studied in the gas phase and their biological activities (e.g., toxicity).
CHAPTER II

THEORETICAL BACKGROUND AND ANALYTICAL PROCEDURES

I. INTRODUCTION

General Comments

Unimolecular electron capture has been treated through the use of the Bloch-Bradbury mechanism and through resonant electron scattering theory. These theories have been used successfully to describe diatomic molecules, but their results have not, in general, been directly applicable to large molecular systems. However, some characteristics of dissociative electron attachment, predicted for diatomic molecules, have been found in large chain molecules (see Chapter VI). These results indicate that certain large molecules exhibit diatomic-like dissociative electron attachment behavior. However, the complexity of polyatomic molecules and the negative ions of the parent molecules and fragments has precluded any substantial quantitative theoretical treatments of nondissociative electron attachment processes in the systems discussed in this study. A simple model is presented later in this chapter that relates the electron attachment cross section, the mean autoionization lifetime, and the electron affinity for long-lived parent negative ions formed at low incident electron energies. This allows reasonable estimates of the EA of complex molecules through the present measurements of lifetimes and cross sections.
Bloch-Bradbury Mechanism

Bloch and Bradbury (1935) presented the first theoretical treatment of unimolecular electron capture. This treatment considers the mechanism in which a negative ion disposes the excess energy of formation (incident electron kinetic energy plus molecular electron affinity) through excitation of the molecular vibration and rotational energy levels. Electron capture, that is, transition from a free electron plus neutral molecule state to a bound molecular state, is possible through a weak coupling between the electron motion and the nuclear motion of the molecule. Bloch and Bradbury found the transition probability from a free to a bound electronic state and the lifetime of the resulting vibrationally and rotationally excited negative ion state. This treatment was restricted to diatomic molecules.

Some years later Massey (1950) treated electron capture by using the nuclear kinetic energy operator as the perturbation causing electron capture. Stanton (1960) has followed up these two basic studies with a consideration of the selection rules involved in electron capture by the Bloch-Bradbury mechanism. Chen (1963, 1966), has used this approach to calculate the cross section for dissociative attachment in \( \text{H}_2 \) and to give an exact description of dissociative attachment processes by a finite set of coupled equations.

Resonant Electron Scattering

Electron attachment by molecules has recently been investigated through the approach of resonance scattering theory. Bardsley, Herzenberg, and Mandl (1964a, 1964b, 1966), O'Malley (1966, 1967),
Chen (1966, 1967, 1969), and Chen and Peacher (1967) have contributed to the development of this more recent approach to electron capture theory. Bardsley and Mandl (1968) and Burke (1968) have reviewed the resonant theory of electron-molecule collisions. The term resonance, as applied to electron capture, refers to a state in which an electron is temporarily captured by a molecule thereby forming a compound metastable system. Most of resonant scattering theory is formulated by using the Born-Oppenheimer separation and treating electron capture as an electronic transition from a continuum to a discrete electronic state. When the final discrete state is degenerate with the continuum, one has a resonance.

Resonances examined in the present study have lifetimes which are long compared to the transit time of an electron traversing a molecule. During the long lifetime of the complex negative ion, the incident electron and the nuclei of the molecule exchange energy. Following electron attachment, autoionization, stabilization, and dissociation (when energetically possible) are competing processes.

Bardsley and Mandl (1968) have classified resonances [see also Feshbach (1958, 1962)] according to the manner in which the electron is trapped to form a negative ion.

**Shape Resonances**

Shape resonances characterize those situations in which the electron is trapped inside a potential barrier. The electron experiences an attractive potential close to the molecule, and this region of attraction is surrounded by a region of repulsion. An α particle, for example,
is bound to a radioactive nucleus in a shape resonance. Shape resonances can exist for molecules in which the electronic motion is affected, that is, electronic excitation, followed by temporary binding of the electron to the molecule. However, the additional electron must possess enough energy to be detached from the molecule even though it has lost some energy through electronic excitation.

**Electron-Excited Feshbach Resonances**

When an incident electron loses energy through electronic excitation of the target and the electron then has insufficient energy to escape the target, an electron-excited Feshbach resonance is formed. Before the electron can be emitted it must reabsorb energy from the target. Christophorou, Carter, and Christodoulides (1969) have reported the first observation of a long-lived parent molecular negative ion formed via an electron-excited Feshbach resonance. Variation with incident electron energy of the mean negative ion lifetime for this electron-excited Feshbach resonance in p-benzoquinone (BQ) is presented in Chapter IV.

**Nuclear-Excited Feshbach Resonances**

Nuclear-excited Feshbach resonances are resonances in which the incident electron loses energy to the target, and this energy is transferred solely to the nuclear motion of the target molecule. Such resonances have been observed in many large molecules, and the lifetimes of the negative ions formed have been found in a number of cases to be $> 10^{-6}$ sec. However, all of the previously reported long-lived negative ion resonances have had constant lifetimes $\tau$. Some resonances of this
type are discussed in Chapter V. In addition, the first reported variation of \( \tau \) with incident electron energy is presented in Chapter IV for a nuclear-excited Feshbach resonance in 1,4-naphthoquinone (NQ). Mean negative ion lifetime measurements, relative negative ion yields as a function of incident electron energy, and electron attachment cross sections are presented in Chapters IV and V for nuclear-excited Feshbach resonance processes in NQ and other molecules.

II. LONG-LIVED PARENT NEGATIVE ION RESONANCES

Potential Energy Diagram

A schematic potential energy diagram for nondissociative electron attachment to diatomic molecules is shown in Figure 1. The potential energy curves in Figure 1 are replaced by \( 3n-6 \) dimensional potential energy surfaces for polyatomic molecules of \( n \) atoms. These surfaces are, of course, impossible to describe in two-dimensional space. Yet, Figure 1 is a useful schematic for discussing the low energy parent negative ion resonances, some of which are presented in Chapters IV and V. For molecules with positive electron affinities (EA), as shown in Figure 1, the negative ion potential energy curve \( A^{\ast}X \) lies below the neutral molecule potential energy curve \( AX \). The electron affinity of a molecule is defined as the difference in energy between a neutral molecule and an electron at rest at infinity and the molecular ion when both the neutral molecule and the negative ion are in the ground electronic, vibrational, and rotational states. Molecular electron affinities have been reviewed by Pritchard (1953), Briegleb (1964), and Moisewitsch (1965). Two recent books which have tables of molecular electron
Figure 1. Schematic potential energy diagram for nondissociative electron attachment to diatomic molecules with positive EA's.
affinities are by Page and Goode (1969) and Christophorou (1970). The latter work has the most complete annotated table of EA values in existence at this time.

Electron Attachment Cross Sections

Christophorou et al. (1965) have presented a method which combines swarm and beam techniques to obtain absolute electron attachment cross sections as a function of electron energy. This procedure, called the swarm-beam combination, also yields an independent energy scale calibration.

Beam experiments often provide a very close approximation to the shape of the electron attachment cross section \( \sigma_a \) because they utilize nearly monoenergetic electrons. However, absolute measurements of the magnitude of \( \sigma_a \) are difficult to make using beam experiments. Swarm experiments have entirely different characteristics. The electron energy distributions are broad, and this results in a poor energy resolution at all but thermal and epithermal energies. Swarm experiments yield accurate determinations of the absolute electron attachment rates averaged over the swarm energy distribution. Fortunately the assets of each type of experiment, the \( \sigma_a \) shape from the beam, and the absolute attachment rate from the swarm, can be combined by the use of a swarm-beam combination.

The method of the swarm-beam combination is as follows. The electron attachment rate \( \alpha (E, P) \) with \( \frac{E}{P} \), where \( \frac{E}{P} \) is the pressure-reduced electric field, is measured in the swarm experiment. The attachment cross section as a function of electron energy \( \sigma_a (E) \) and the electron attachment rate are related by
\[ \alpha \left( \frac{E}{P} \right) \sim \frac{E}{P} = N_o \left( \frac{E}{m} \right)^{\frac{1}{2}} \int_{0}^{\infty} \varepsilon^{\frac{3}{2}} \sigma_a(\varepsilon) f(\varepsilon, \frac{E}{P}) \, d\varepsilon, \]  

(II-1)

where \( N_o \) is the number density of attaching molecules per torr at room temperature, \( m \) is the electron mass, \( \varepsilon \) is the electron energy, and \( f(\varepsilon, \frac{E}{P}) \) is the electron energy distribution function. If \( \alpha_{i_{1}} \) is the measured rate of attachment for the \( i^{th} \) value of \( \frac{E}{P} \), \( \sigma_{a_{j}}(\varepsilon) \) is a trial function for the attachment cross section, and \( (\alpha)_{i_{j}} \) is the calculated (from Equation II-1) \( \alpha \) for the \( i^{th} \) value of \( \frac{E}{P} \) and the \( j^{th} \) specification of the trial function, then for each trial function a best fit to the experimental data is found by satisfying the requirement,

\[ \sum_{i} \left[ (\alpha_{i_{j}}) - \alpha_{i_{1}} \right]^2 = M_j = \text{minimum}. \]  

(II-2)

The quantity \( \sigma_a(\varepsilon) \) is expressed in terms of the negative ion current function \( I(\varepsilon) \) obtained from the beam experiment as follows:

\[ \sigma_{a_{j}} = K_{j} T_{j} I(\varepsilon), \]  

(II-3)

where \( K_j \) is a multiplication factor that changes \( I(\varepsilon) \) from experimentally determined relative units to absolute electron attachment cross section units, and \( T_j \) is a translation operator that shifts \( I(\varepsilon) \) along the energy axis. Now Equations (II-1) and (II-3) can be substituted into Equation (II-2). The result is
Equation (II-2) may be written as follows,

$$\frac{dM_j}{dT_j} = 0. \quad (II-5)$$

Equations (II-5) and (II-4) are solved for $M_j$ and $K_j$ using a particular $T_j$. For the best value of $T_j$, a minimum exists for $M_j$. This calculation is performed by a computer, and the best values of $K_j$ and $T_j$ are printed out. These values are substituted into Equation (II-3) in order to obtain an independent energy scale calibration and the absolute electron attachment cross section.

Although the swarm-beam combination is an accurate method of determining $\sigma_a$ and the energy scale for low energy electron attachment processes, experimental swarm data alone can be used to find the mean cross section for electron attachment. For example, they can easily yield the mean velocity-weighted attachment cross section $\langle \sigma_a \rangle_v$ defined by the relation

$$\langle \sigma_a \rangle_v = \frac{\omega w}{N_o (2/m)^{3/2} \langle \varepsilon \rangle^{3/2}}, \quad (II-6)$$

where $N_o$ is the number density of attaching molecules per torr, $m$ is the mass of the electron, $\varepsilon$ is the electron energy, and $\omega w$ is the two body electron attachment rate at $\varepsilon$. Equation (II-6) has been found to
give a good approximation to the true cross section for $\epsilon \leq 0.5$ eV by Blaunstein and Christophorou (1968b). The disadvantage of this calculation is that $\sigma_a$ is obtained as a mean velocity-weighted cross section. Christophorou (1970) has discussed a relation that could be used to satisfactorily determine exact attachment cross sections as a function of $\epsilon$, rather than mean velocity-weighted attachment cross sections. In a recent paper, Christophorou, McCorkle, and Carter (1970) have presented a semiempirical relation for determining the magnitude and shape of the electron attachment cross section for subthermal ($< \frac{3}{2}$ kT) peaking resonances from swarm data alone. They have made the following approximation to the attachment cross section:

$$\sigma_a(\epsilon) = A \sqrt[\gamma]{\epsilon}, \quad (II-7)$$

where $\sigma_a(\epsilon)$ is the electron attachment cross section, $\epsilon$ is the incident electron energy, and $A$, $\gamma$ are constants determined for the particular molecule studied from the measured attachment rates as a function of $\frac{E}{F}$ and the known electron energy distribution functions.

Mean Autoionization Lifetimes

Since the observation by Edelson, Griffiths, and McAfee (1962) that the mean autoionization lifetime $\tau$ for $SF_6^{-*}$ was of the order of $\mu$secs, many such long-lived parent negative ions have been observed for large molecules at low energies. Several molecules which form similar long-lived parent negative ions upon electron impact have been investigated in this study. Lifetime measurements for nuclear-excited Feshbach
resonances are presented in Chapter V for the negative ion resonances of sulfur hexafluoride (SF\(_6\)), o-, m-, and p-nitrotoluene (o-, m-, and p-C\(_6\)H\(_4\)CH\(_3\)NO\(_2\)), azulene (C\(_{10}\)H\(_{14}\)), and cinnamaldehyde (C\(_6\)H\(_5\)CH:CHCHO). For these molecules, \(\tau\) was not found to vary with \(e\). However, in Chapter IV data are presented which clearly show the variation of \(\tau\) with energy across a nuclear-excited Feshbach resonance in 1,4-naphthoquinone (NQ) and the variation of \(\tau\) with energy across an electron-excited Feshbach resonance in p-benzoquinone (BQ). These data provide the first experimental evidence that \(\tau\) for long-lived parent negative ions can be energy dependent.

A simple model relating \(\tau\), the electron attachment cross section \(\sigma_a\), and the electron affinity of the molecule EA has been given by Compton et al. (1966a, 1966b) for nuclear-excited Feshbach resonances. This model has been used in the present study to determine the EA of some of the molecules mentioned above once \(\tau\) and \(\sigma_a\) have been measured. A derivation of the relation describing \(\tau\), \(\sigma_a\), and EA is as follows.

One assumes that the following reaction takes place,

\[
\begin{align*}
\text{AX}^{*-1} & \xrightarrow{\sigma_a} \text{AX} + e, \\
\end{align*}
\]

(II-8)

that is, a low energy electron \(e\) is attached to a polyatomic molecule AX. The resulting negative ion \(\text{AX}^{*-1}\) decays from the metastable state with a mean autoionization lifetime \(\tau\) to the original neutral molecule plus a free electron state. Following attachment the excess energy of negative ion formation (incident electron kinetic energy \(e\) plus EA) is assumed to be distributed into all the vibrational modes of the ion.
The quantities $\tau$ and $\sigma_a$ are assumed to be related through the principle of detailed balance:

$$\tau = \frac{\rho^-}{\rho_0} \frac{1}{\nu \sigma_a},$$  \hspace{0.5cm} (II-9)

where $\rho^-$ is the density of the negative ion states, $\rho_0$ is the product of the density of states for the incident electron and the neutral molecule, and $\nu$ is the incident electron velocity. The density of final states is the product of the number of neutral molecular states, one, and the density of states of the free electron $\rho_e$. The quantity $\rho_e$ is taken from Schiff (1955) to be

$$\rho_e = \frac{2 \nu}{\pi \hbar^3}.$$  \hspace{0.5cm} (II-10)

A semiclassical energy density expression for large molecules, where the molecule is regarded as a set of $n$ (= number of atoms) weakly coupled harmonic oscillators, has been modified from the work of Marcus and Rice (1951) by Whitten and Rabinovitch (1963). This expression, given by Equation (II-11), is used to approximate $\rho^-$

$$\rho^- = \frac{[\epsilon_{T} + (1 - \beta \omega') \epsilon_{Z}]^{N}}{\Pi(N) \frac{N}{\Pi} \hbar \nu_{i}}.$$  \hspace{0.5cm} (II-11)

Here $\epsilon_{Z}$ is the zero point vibrational energy, $\epsilon_{T}$ is the energy of the ion in excess of $\epsilon_{Z}$ (the sum $\epsilon$, EA, and the vibrational energy of the original molecular system above $\epsilon_{Z}$), $N$ is the number of internal (or
vibrational) degrees of freedom (= $3n-6$ for nonlinear molecules) [see, e.g., Barrow (1962)], and $1-\beta$ is an empirical correction factor. The quantity $\beta$, termed the modified dispersion parameter by Whitten and Rabinovitch (1963), is determined from

$$\beta = \frac{(N-1) \langle \nu^2 \rangle}{N \langle \nu \rangle^2}, \quad (II-12)$$

where $\langle \nu^2 \rangle$ is the mean square of the molecular vibration frequencies, and $\langle \nu \rangle^2$ is the square of the mean of the molecular vibration frequencies. The parameter $w'$ is a function of $\epsilon' = \epsilon / \epsilon_z$ and can be taken from Figure 2. The spin degeneracy of the negative ion is assumed to be two.

Equations (II-10) and (II-11) are substituted into Equation (II-9) to obtain the following expression relating $\tau$, $\sigma_a$, and $EA$:

$$\tau = \frac{2\pi^2 \hbar^3 \left[ \epsilon_{pN} + (1 - \beta w') \epsilon_z \right]^{N-1}}{m^2 \nu \Pi(N) \prod_i \nu_{i} \sigma_a(v)} \quad (II-13)$$

In this form calculations are restricted to ion decay to the single original neutral molecular state as shown by Equation (II-8). Another factor must be taken into account when the incident electron energy is above one or more of the excited vibrational levels of the ion. After electron capture and energy distribution among the $n$ weakly coupled harmonic oscillators, the system may decay to vibrationally excited neutral molecular states. In this case, the number of available neutral molecular states to which the ion can decay is increased from one (the
Figure 2. Correction factor $x'$ versus $\varepsilon'$. 
ground state) to one plus the number of possible sums of vibration overtones below $\varepsilon$. Some of the molecules may be in excited vibrational states prior to electron attachment as a result of source temperatures. This would also increase the number of available neutral molecular states to which the ion could decay. If this number is designated as $K$, and $v_i$ and $v_0$ are the velocities of the incident and outgoing electrons, Equation (II-13) may be modified as follows:

$$
\tau(\varepsilon) = \frac{2\pi^2}{Km^2v_0^2} \frac{\sum_{i=1}^{N} \frac{(1 - \beta_{i})\varepsilon_{i}}{\nu_{i}^{2} \sigma_{i}(\nu_{i})}}{\prod_{i=1}^{N} \nu_{i}^{2} \sigma_{i}(\nu_{i})} .
$$

Equation (II-14) predicts a very pronounced drop in $\tau$ with increased $\varepsilon$ because of the many vibration overtones of large molecules which are accessible at energies slightly above thermal.

Several limitations should be considered before using Equations (II-13) and (II-14).

1. The lifetime $\tau$ is obviously very dependent upon incident electron energy distribution and ion source temperature. Measurements of $\tau$ are presently being taken in beam experiments where radiation from a hot filament just a few centimeters from the collision chamber can excite molecules and ions. Also, the incident electron energy distribution is broad compared to vibrational energy level spacing.

2. It is assumed that all vibrational modes share the excess energy available from negative ion formation. That this energy is distributed to all the vibrational degrees of freedom may depend on negative ion geometry.
3. Equilibrium conditions are not satisfied for $\tau$ measurements in beam experiments, and for this reason Equation (II-13) yields only lower limits for $EA$ [see, e.g., Compton et al. (1966a) and Klots (1967)].

4. The negative ion vibrational frequencies are assumed to be the same as the neutral molecule vibrational frequencies. This is a good approximation because of the large size of the ions to which these equations apply.

5. The empirical correction factor $1 - \beta u'$ [Whitten and Rabinovitch (1963)] introduces very little error in calculations.

Two of the findings in this study give qualitative support to Equation (II-14).

1. Values for $EA$ calculated from Equation (II-14) are in fair agreement with $EA's$ determined by other means (see Chapters IV and V).

2. The decrease in $\tau$ with electron energy for 1,4-naphthoquinone (see Chapter IV) is predicted by Equation (II-14).

III. DISSOCIATIVE ELECTRON ATTACHMENT

General Comments

Dissociative electron attachment has been treated using both the Bloch-Bradbury mechanism [see, e.g., Bloch and Bradbury (1935), Massey (1950), Stanton (1960), and Chen (1963, 1966)] and resonant scattering theory [see, e.g., Bardsley, Herzenberg, and Mandl (1964a, 1964b, 1966), O'Malley (1966, 1967), Chen (1967, 1968), Chen and Peacher (1967), Bardsley (1968), and Bardsley and Mandl (1968)]. Recently Christophorou
(1970) has given a treatment of dissociative attachment which emphasizes, among other aspects of dissociative attachment, the isotope effects that are most pertinent to this study.

Resonance dissociative electron attachment can be represented as follows:

\[ AX + e \rightarrow AX^{*-} \rightarrow A \ (or \ A^*) + X^- \ (or \ X^{*-}). \]  

(II-15)

The complex negative ion state is formed quickly (~ \(10^{-15}\) sec) so that the separations and velocities of the nuclei remain constant during the capture process, that is, the Born-Oppenheimer approximation holds.

Potential Energy Diagram

Following the formation of \(AX^{-*}\), the complex negative ion state dissociates into the fragments as shown in Equation (II-15). Figure 3 shows the schematic potential energy diagram for dissociative attachment in which the potential energy curve for \(AX^{-*}\) is purely repulsive. This diagram is for diatomic and diatomic-like molecules. The EA of X is shown as the difference between the asymptotes of the A + X and the A + X^- curves. Also shown is the dissociation energy of AX[D(A-X)], the difference in energy between the asymptote of the A + X curve and the zero point energy \(e_z\) of AX. Significant positions of internuclear separation are shown in Figure 3. The region \(R = R_L\) to \(R = R_C\) is the "autoionization region," and in this region the negative ion is unstable toward electron ejection. As mentioned in Chapter I, dissociation and autoionization are in competition, and this is the region (shown by vertical lines) in which this competition takes place. Points \(R_L\) and
Figure 3. Schematic potential energy diagram for dissociative electron attachment where the potential energy curve for AX⁻ is purely repulsive.
$R_2$ are the classical turning points for the molecule in the ground vibrational level. Point $R_c$ is the crossing point of the negative ion and neutral molecule potential energy curves. Beyond $R_c$ only dissociation can take place. Point $R_e$ is the position of the potential minimum for AX or the equilibrium position on the AX potential curve. Energies $E_1$ and $E_2$, as measured from the ground vibrational level of the neutral molecule, are the energy limits at the boundaries of the Franck-Condon region. That is, $E_1$ and $E_2$ determine the energy width in which vertical transitions occur from the ground state of the neutral molecule to the complex negative ion state. The Franck-Condon region is designated by horizontal lines in Figure 3.

The Morse Function

The potential of a diatomic or diatomic-like molecule both near the equilibrium position and for large internuclear separations has been given by Morse (1929) and described by Herzberg (1950). Although this function is not very satisfactory for describing electron molecule interactions, it provides a neutral molecule potential energy function that is very useful for illustrating mechanisms of electron attachment. The Morse function is given as follows:

$$U(R - R_e) = D_e (A - X) \left[ 1 - e^{-\beta'(R - R_e)} \right]^2,$$  \hspace{1cm} (II-16)

where $D_e(A - X)$ is the dissociation energy with reference to the minimum of the neutral molecule potential curve, that is, $D[A - X] + \epsilon_z$. The quantity $\beta'$ is given by
\[
\beta' = \sqrt{\frac{2\pi^2 \mu}{\hbar (A-X) N}} u_x,
\]  

(II-17)

where \( \mu \) is the reduced mass of the diatomic or diatomic-like system, \( c \) is the velocity of light, \( \omega_x \) is the lowest vibration frequency of the A-X vibration mode, and \( N \) is Avogadro's number. The Morse functions for the molecules \( n-C_1H_9Br \), \( n-C_7H_{11}Br \), and \( n-C_9H_{13}Br \) are given in Chapter VI in connection with dissociative electron attachment to these molecules and the formation of \( Br^- \) from them.

Isotope Effects

The probability that the negative ion \( AX^- \) will dissociate without autodetachment has been introduced in a very straightforward way by Holstein (1951). He proposed that the cross section for dissociative electron attachment \( \sigma_{da} \) can be given by the product of the cross section for the formation of \( AX^- \), \( \sigma_o \), and the probability \( e^{-\tau_s/\tau_a} \) that \( AX^- \) will dissociate without autodetachment as follows:

\[
\sigma_{da} = \sigma_o e^{-\tau_s/\tau_a},
\]

(II-18)

where \( \tau_a \) is the autodetachment lifetime, and \( \tau_s \) is the time required for the nuclei to reach the crossing point \( R_c \) shown in Figure 3, page 25.

More recent treatments of dissociative electron attachment give an explicit expression for \( \sigma_o \) in Equation (II-18). Moreover, the form of \( \sigma_{da} \) derived from resonant scattering theory predicts several types of mass or isotope effects. A convenient form for describing these effects
in dissociative attachment has been given by O’Malley (1966, 1967). O’Malley’s expression is given by Equation (II-19), where electron attachment is assumed to take place with the molecule initially in the ground vibrational state

\[
\sigma_{da} = \frac{4\pi \hbar^3/2}{k_i^2} \frac{\Gamma_a}{\Gamma_d} e^{-\frac{1}{2} \left( \frac{\Gamma_a}{\Gamma_d} \right)^2} \left( \frac{E_0 - \varepsilon}{\hbar \omega} \right)^2 e^{-\rho(\varepsilon)}. \tag{II-19}
\]

Here \(\varepsilon\) is the incident electron energy, \(k_i^2 = (2m/\hbar^2) \varepsilon\) (\(k_i\) is the incident electron’s wave number), \(\bar{g}\) is a statistical factor involving the weight factors for rotational and electronic angular momentum and relative spin multiplicity, \(\Gamma_a\) is the partial autoionization width, \(\Gamma_d\) is the total autoionization width, \(\Gamma_d\) is the experimentally determined dissociative attachment cross section width, \(E_0 = E_0 + \frac{1}{2} \hbar \omega\), \(E_0\) is the electron energy at the peak of \(\sigma_{da}(\varepsilon)\), \(\frac{1}{2} \hbar \omega\) is the zero point energy associated with the bond that is broken when the ion dissociates, and \(e^{-\rho(\varepsilon)}\) is the survival probability term. The form of \(\rho(\varepsilon)\) is given by O’Malley (1966) as follows:

\[
\rho(\varepsilon) = \frac{\Gamma_a(R)}{\hbar} \frac{dR}{v(R)}, \tag{II-20}
\]

where \(R_\varepsilon\) is the internuclear separation at which incident electrons of energy \(\varepsilon\) are captured, \(R_c\) is the internuclear separation at the crossing point shown on Figure 3, page 25, and \(v(R)\) is the relative separation velocity of the nuclei.

Isotope effects are predicted due to the mass dependence of Equation (II-19) and a similar expression for \(\sigma_{da}\) given by Bardsley and
Mandl (1968). Some of the discussions of isotope effects upon $\sigma_{da}$ are by O'Malley (1966), Bardsley and Mandl (1968), and most recently by Christophorou (1970). The mass dependence of Equation (II-19) will now be discussed by following the treatment of O'Malley (1966).

Both $\Gamma_d$ and $\rho(\epsilon)$ are mass dependent quantities. The quantity $\Gamma_d$ is given as follows by O'Malley (1966):

$$\Gamma_d = \frac{2v'}{\left(\frac{\hbar}{\mu \omega}\right)^{\frac{3}{2}}} \tag{II-21}$$

where $V'$ is the force acting to separate A and X$^-$ at $R_c$, $\omega$ is the frequency of oscillation of the A-X mode, and $\mu$ is the reduced mass of the AX$^-$ system. The relative velocity of separation of the nuclei is proportional to $\mu^{-\frac{3}{2}}$. Therefore, the time $\tau_s$ required for the nuclei to separate to $R_c$, the point beyond which the ion is stable against auto-ionization, is proportional to $\mu^{\frac{3}{2}}$, that is,

$$\rho \propto \mu^{\frac{1}{2}} \tag{II-22}$$

In Equation (II-19) a $\Gamma_d$ factor appears in the denominator, and this factor results in a $\sigma_{da} \propto \mu^{\frac{1}{2}}$ mass dependence. As pointed out by O'Malley (1966), if $\rho$ is small and $\epsilon \approx E_0$, this will be the only significant mass dependence of $\sigma_{da}$. This type of isotope effect has been classified the small inverse isotope effect. It has been observed by Sharp and McDowell (1967) for CH$_4$ and CD$_4$, and also in this study for n-C$_N$H$_{2N+1}$Br where $2 \leq N \leq 6$. 
The \((\Gamma_d)^2\) in the denominator of the exponent of Equation (II-19) results in a \(\mu^\frac{1}{\nu}\) dependence of the exponent on the reduced mass. This mass dependence in the Gaussian factor makes the Gaussian factor narrower with increased \(\mu\), which causes a narrowing of the \(\sigma_{da}\) peak width, generally without significantly affecting the peak value of \(\sigma_{da}\). That is, for cases other than vertical onset, the peak value of \(\sigma_{da}\) is not affected much by the mass dependence of \(\Gamma_d\) in the Gaussian, but the tail of the Gaussian is very dependent upon this \(\Gamma_d\). For the case of vertical onset, that is, when dissociation is not energetically possible for all internuclear separations in the Franck-Condon region, the peak value for \(\sigma_{da}\) will be very dependent upon \(\mu\), and \(\sigma_{da}\) at threshold will be much greater for lighter isotopes. Probable examples of this isotope effect are the 14 eV peak for \(H_2\) [Rapp and Briglia (1965), Rapp, Sharp, and Briglia (1965)] and the 3.7 eV peak in \(H_2\) [Schulz and Asundi (1965)].

The mass dependence of \(\rho\), given by Equation (II-22), is often referred to as the mass dependence of the survival probability term. This dependence has the same form as the Gaussian factor, which is e\(const\,\mu^{\frac{1}{\nu}}\). If \(\rho\) is small \((\tau_s < \tau_a\)\), this survival probability factor's mass dependence is small. This results in a small direct isotope effect. This type of isotope effect has been observed in \(H_2O, D_2O\) [Compton and Christophorou (1967)]. It has also been observed in \(HCl, DCl, HBr, DBr\); and \(HI, DI\) [Christophorou, Compton, and Dickson (1968)].
CHAPTER III
EXPERIMENTAL APPARATUS AND PROCEDURE

I. INTRODUCTION

Two types of experiments, beam experiments and swarm experiments, have been widely used to study electron attachment in gases. In beam experiments a narrow energy distribution of electrons is focused into a collision chamber in which gases at low pressures \((10^{-7} - 10^{-3} \text{ torr})\) are studied under single collision conditions. Swarm experiments utilize a broad, and in certain cases, known distribution function of electrons to study attachment in gases at high pressures, often in the range 200-1000 torr under multiple collision conditions. Emphasis will be placed on beam studies, specifically using the TOFMS. Swarm data will be combined with beam data in Chapters IV, V, and VI in order to obtain electron attachment cross sections and independent energy scale calibrations.

TOFMS’s, Lozier tubes, and total collection methods are the most widely used beam experiments. These types of experiments have been discussed in books by Christophorou (1970), McDaniel (1964), Massey and Burhop (1969), and Massey (1950, 1969). Review articles that describe the type of TOFMS used in the present study include those by Christophorou et al. (1965) and Joy (1967). A detailed description of the TOFMS used in obtaining the data presented in Chapters IV, V, and VI will now be given, and this will be followed by a brief description of the steady state swarm method.
II. TOFMS

A linear non-magnetic type mass spectrometer of the design initially described by Stephens (1946) was used in this study. This TOFMS was constructed at the Oak Ridge National Laboratory on the basis of the Bendix model 14-206 mass spectrometer. A schematic diagram of the geometry of the TOFMS is shown in Figure 4. The following is a discussion of the TOFMS used in this study. The electron source will be discussed in Section III.

A 1 μsec pulse of electrons is focused through the electron gun every 100 μsec. Electrons from this pulse are attached to neutral molecules in the collision chamber, and parent and/or fragment negative ions are formed. A backing plate pulse of about -150 V forces these negative ions into the flight tube ~0.5 μsec after the electrons are pulsed through the gun. At the entrance of the flight tube the negative ions are given a fixed energy which can vary from 1 to 4.5 kV. Ions of different mass enter the flight tube at approximately the same time. The velocities $v$ of these ions in the flight tube are inversely proportional to the square roots of their respective masses $m$ [see, e.g., Wiley and McLaren (1955)] according to the equation

$$v = \sqrt{\frac{2E}{m}}, \quad (III-1)$$

where $E$ is the ion acceleration energy determined by the voltage applied to the flight tube linear (see Figure 4). Therefore, ions of different mass become separated in time of flight $t$ as they traverse the flight
Figure 4. Geometry of the TOFMS (dimensions not to scale).
tube. This \( t \) is given by

\[
t = L \sqrt{m/2E} ,
\]

(III-2)

where \( L \) is the length of the flight tube.

These pulses of ions traversing the flight tube can be focused or deflected by the horizontal and vertical focusing or deflecting plates (see Figure 4) inside the flight tube liner. The ions can also be focused and retarded by the ion lens (see Figure 4) farther along the flight path. Any neutral molecules formed by electron detachment from negative ions will be unaffected by potentials applied to the deflection plates and the ion lens.

A block diagram of the TOFMS is shown in Figure 5. At the end of the flight tube both negative ions and neutral molecules are detected by a Bendix M306 electron multiplier (EM). Upon impact with the cathode of the EM, the bunches of ions and neutrals produce electrons that are set free from the cathode. Several permanent magnets spaced close to a coated glass dynode strip cause the electrons from the cathode to spiral down this strip. The electrons undergo many collisions along this strip thereby producing other (secondary) electrons. At the end of the strip \( \sim 10^6 \) electrons arrive for every electron that initially started down the strip from the cathode. Negative voltage signals from the EM are amplified by a factor of 100 by a pulse amplifier. A wide band amplifier further increases the signals by an adjustable factor of from 3 to 10. At this point signals corresponding to different mass peaks are, in general, not of the same amplitude or current magnitude. The output of
Figure 5. Block diagram of the TOFMS.
the wide band amplifier is then fed into a discriminator-pulse shaper (DP) [Ward and York (1963)]. The DP removes all negative signals of amplitude below an adjustable value of 1 to 10 V. All signals from the EM and the amplifiers are negative. Signals larger than 1 V in magnitude entering the DP are shaped into 5 V positive signals by the DP. Although output signals are of uniform voltage magnitude, the signal strength (current magnitude) is still, in general, different for each signal. The width of the signals out of the DP can be varied from 10 to 500 nsec.

These signals are then fed into a time-to-amplitude converter (TAC). Here a ramp voltage is superimposed upon signals from the DP. Signals arriving at different times in the TAC (corresponding to different masses in the flight tube) are increased by different amplitudes through the addition of the ramp voltage. The output of the TAC is comprised of signals of different amplitude which can be counted and stored in different channels of a multichannel analyzer. The ramp pulse used by the TAC is small enough so that no signal is generated for output without the addition of a gate pulse. This gate is positioned coincident in time with the mass signal of interest, and it is made narrow enough in time to allow only this signal to pass through the TAC. Signals from the TAC are fed into either a multichannel analyzer or a count rate meter to which a Brown recorder is connected. The master pulser (see Figure 5) triggers the ramp pulse, the gate pulse, and the scope which is used to monitor all signals and pulses.

The background pressure of the instrument is $\sim 1 \times 10^{-7}$ torr as measured by a Bayard-Alpert type ionization gauge located at the sample
end of the instrument. Sample pressures range from $5 \times 10^{-7}$ torr to $1 \times 10^{-4}$ torr. These pressures depend upon the type of experiment performed (e.g., measurement of lifetimes or measurement of energy dependences of electron attachment resonances) and also upon the vapor pressure of the material under study. The system is pumped with a six inch oil diffusion pump. A liquid nitrogen trap and a freon baffle are located between the flight tube and the diffusion pump.

Up to three samples, initially in solid, liquid, or gas phases, can be simultaneously or individually metered into the collision chamber. Solids with low vapor pressures are sometimes heated by a heat gun, a water bath, or a heater tape in order to increase the sample pressure in the system. Care is always taken to keep sample temperatures below the sample decomposition temperature. Heater tapes are wound around all inlet tubing and the flight tube in order to prevent sample condensation in the system.

III. ELECTRON SOURCE

The purpose of the electron source is to produce a constant current of low energy electrons of known energy with a narrow energy spread. The electron source in the mass spectrometer is a five-electrode source. It is usually operated using the retarding potential difference (RPD) technique. This technique [Fox et al. (1955)] provides a means of obtaining an electron beam of width $\sim 0.1$ eV by the subtraction of two low resolution electron energy distributions. The RPD method has been employed by many workers. However, little appears in the literature about the operation of the RPD electron gun at low energies ($< 1$ eV).
Gordon, Haarhoff, and Krieg (1969) and Anderson and Eggleton (1967) have recently discussed the theoretical operation of the RPD technique.

An illustration of the potentials on each electrode of the electron gun during RPD operation is shown in Figure 6. A tungsten filament 1 is normally operated at 1.5 to 2.0 amps. Electrons from the filament are normally biased out of the gun by a negative potential of 4 to 5 V on the anode 2. The anode is pulsed every 100 μsec by a 7 V positive 1 μsec duration pulse. Thus, for this 1 μsec interval, the electron gun is on. Electrodes 3 and 5, which are at filament potential, provide a uniform field at the retarding electrode 4. The retarding electrode is operated at a potential of about -0.5 V with respect to the filament so that only the high energy half of the electron energy distribution can pass this electrode. By biasing this electrode less negative by a small amount ΔV, an additional central portion of the electron energy distribution of width ΔV is allowed to pass the retarding electrode. The difference (in) ion current formed for the two retard settings is due to attachment by electrons in the energy distribution which are not allowed to pass the retarding electrode for the first voltage setting, but which pass the retarding electrode when the retarding potential is increased by ΔV for the second voltage setting. The energy of the electrons passing through the gun is determined by the potential of the retarding electrode with respect to ground. A schematic diagram of the RPD electron source is shown in Figure 7. In this figure the relative positions of the source electrodes 1,2,3, and 4, collector 6, collector shield 5, collision chamber 9, grid 8, and backing plate 7 are shown.
Figure 6. Illustration of the source electrode potentials for the RPD method.
Figure 7. Schematic diagram of the RPD electron source.
Some anomalous effects have been observed by several workers operating a RPD electron source. Negative difference ion currents, caused by improper retard electrode potential, have been reported by Burns (1964) and Fox et al. (1955). Frost and McDowell (1955) have found spurious maxima in the ionization efficiency curves. This problem was caused by poor source magnet alignment. Anderson, Eddleton, and Kessing (1967) have also considered the effect of source magnetic field on the RPD source. Marmet (1964) has treated space charge effects in the RPD source.

One basic criterion for dependable operation of a RPD source is constant electron current as a function of energy. Several factors can cause the electron beam current not to be constant with energy, such as:

1. The electron current always drops sharply to zero at zero electron energy. The electron current in the collision chamber for energies close to 0 eV cannot be accurately measured. At these energies the electrons pass through the chamber more as a diffuse cloud than as a narrow beam. Collection of these electrons by the collector is very inefficient.

2. Periodic defocusing can occur due to spiraling of electrons in the source magnetic field. Two precautions were taken to insure elimination of this magnetic field problem. The source magnets were adjusted so that the source magnetic field was fixed at about 70 gauss, and the electron collector (trap) current $I_2$ in Figure 7 was kept constant with energy above the region of sharp increase slightly above zero energy.
3. Focusing by the gun electrodes, most often the anode electrode, could cause electron transmission to be energy dependent.

Many factors can give rise to a poor energy resolution also, such as:

1. Broadening of the electron energy distribution from the filament will always be a factor limiting resolution. This is believed to be caused primarily by the potential gradient along the filament.

2. Thermal broadening is always present. Decreasing the filament current (temperature) decreases thermal broadening.

3. Poor alignment of the source magnetic field can seriously broaden, skew, or in other ways distort the electron energy distribution. Extreme care is always taken to align this magnetic field.

4. Poor filament or electrode slit alignment causes electron scattering by the source surfaces. When replacing a filament, it is sometimes necessary to try several filaments before proper alignment is attained. While assembling the source after cleaning, guide pins are placed through the electrodes to assure proper slit alignment.

5. Any penetration into the gun of the electric field due to the high accelerating voltage on the flight tube liner will seriously affect electron energies in the gun. A gold shield around the collector and two grids between the collision chamber and the flight tube liner minimize this field penetration.

6. Surface potentials on the electrodes of the gun, the backing plate, the collector shield, the collector, or the grid will
affect the electron energy distribution. These potentials are sometimes caused by molecular deposit on or reactions with the surfaces listed above. Electroplating platinum black on the collector and collector shield is found to decrease both electron scattering by the surfaces and the effect of these potentials on the collector and collector shield.

7. Interaction of the sample gas with the filament surface is sometimes a problem with highly electronegative samples or sample fragments. If the filament is permanently poisoned by the sample, it must be replaced.

8. Space charge effects, which become more important with increasing electron beam current, can affect the electron energy distribution. Electron current is always kept as low as other operating conditions will allow.

9. Any potential on the backing plate while electrons are passing through the collision chamber drastically affects the electron energy. By pulsing the backing plate about 0.5 μsec after the electrons are pulsed through the gun, the effect of the backing plate pulse on the electrons is minimized. In addition, a bias is applied to the backing plate to nullify the effect of any overshoot of this backing plate pulse at the time the electrons are passing close to the backing plate. Although the RPD method remains basically unchanged almost twenty years after its development by Fox et al. (1951), two recent developments allow automation of the technique. The use of lock-in amplifiers makes possible automatic pulsing of the retard electrode and also
direct readout of the difference ion current. Chantry (1969) has presented a technique of sweeping through an energy spectrum quickly and repeatedly and then storing counts in a multichannel scalar.

IV. MASS IDENTIFICATION

Identifying the masses of all ions formed upon electron impact is the first step in a negative ion study using a TOFMS. Upon entering the flight tube, ions of a different mass will be accelerated along the axis of the flight tube with different velocities according to Equation (III-1). Masses $m_1$ and $m_2$ will have different times of flight, $t_1$ and $t_2$, given by

$$\sqrt{m_1/m_2} = t_1/t_2.$$  \hspace{1cm} (III-3)

Thus, by knowing the mass of one or more ions in the flight tube and by measuring $t_1$ and $t_2$, one can determine the masses of other ions present through Equation (III-3).

In order to obtain best mass resolution, the adjustment of the magnitude of the backing plate pulse was found to be most critical [see, e.g., Sanzone (1970)]. This adjustment was made to minimize the effect caused by the creation of ions in different parts of the collision chamber. In the TOFMS used in this study a $C_{10}H_7^-$ signal of 127 a.m.u. was separated from the parent ion $C_{10}H_8^-$ signal of 128 a.m.u. (see Chapter V). These signals appeared at different energies, and thus could not be observed simultaneously. Also the $C_{10}H_7^-$ signal was very weak, which made time-of-flight resolution difficult. It would be possible to
resolve peaks from heavier ions differing by 1 a.m.u. if the two mass signals were both of high intensity.

V. NEGATIVE ION LIFETIMES

Mean autoionization lifetimes \( \tau \) of negative ions in the interval \( 1 \leq \tau \leq 500 \mu s \) can be measured with the TOFMS. These measurements are made by separating the ions from the pulse of ions and neutrals a known distance along the flight tube. Since the acceleration energy of the ions is known, one can determine the time required for the packet of ions and neutrals to reach the separation point.

All ions for which \( \tau \) was determined in this study were assumed to obey an exponential decay law. That an exponential decay law is obeyed for the negative ions investigated in this study is shown in Chapter IV. Thus, \( \tau \) can be determined from the following equation,

\[
\tau = - \frac{t}{\ln \frac{N}{N_0}},
\]

(III-4)

where \( \tau \) is the mean negative ion lifetime, \( N^- \) is the number of negative ions which have not autoionized in time \( t \), and \( N_0 \) is the total number of metastable negative ions at \( t = 0 \). The quantity \( \tau \) can then be determined using Equation (III-4) in two ways.

First, one can always calculate \( \tau \) directly from Equation (III-4) by substituting \( t, N^- \), and \( N_0 \) for a particular ion acceleration energy. This method is satisfactory when the known lifetime of a negative ion, which has approximately the same charge to mass ratio \( q/m \) can be reproduced before and after the unknown lifetime measurement is taken. To
To ensure proper spectrometer operation in this study, SF$_G^*$ was often used in this manner.

The second method of determining $\tau$ is referred to as the slope method, first used by Compton et al. (1966a, 1966b) and later employed by Naff, Cooper, and Compton (1968, 1970) and Compton and Huebner (1969a). If one knows $t$, $N^-$, and $N_o$ for several acceleration energies, $\tau$ can be determined from the plot of $-d\ln\frac{N^-}{N_o}$ vs $t$. The lifetime is the inverse of the slope of a straight line through the points $-d\ln\frac{N^-}{N_o}$ and the origin. All measurements presented in Chapter V could be plotted in this manner. Ions for which $\tau$ is found to vary with electron energy, which are presented in Chapter IV, cannot be plotted in this manner. Although the ions of p-benzoquinone and 1,4-naphthoquinone studied in Chapter IV obey an exponential decay law, the broad exciting electron energy distribution results in a broad distribution in $\tau$ for the ions created. In this case, since the incident electrons of energy $\varepsilon$ are not monoenergetic, $\tau(\varepsilon)$ is not the same for all ions formed.

Determinations of $\tau$ can be made using two means of separating the ions from the neutrals in the pulse. By applying a potential to the ion lens shown in Figure 4, page 33, one can separate the ions in time of flight from the neutrals in the pulse. A count with the ion lens at flight tube liner potential gives $N_o$. A count with the ion lens negative with respect to the liner separates (retards) the ions from the neutrals and gives a count of the neutrals. Since the ion lens also focuses the ion beam, a count of the ions $N^-$ cannot be used in determining $\tau$. 
The negative ion lifetime \( \tau \) can also be measured by deflecting the ions out of the pulse. Horizontal deflection plates shown in Figure 4, page 33, are used to remove the ions in this case. A voltage of 500 V positive or negative with respect to the liner applied to the horizontal deflection plates has been found to remove all ions from the pulse for acceleration energies from 1500 to 4500 eV and masses up to 158 a.m.u. Periodic checks showed that lifetimes taken by retarding and deflecting the ion pulse were in agreement.

Consideration must be given to the following possible sources of error in lifetime measurements:

1. Electron detachment by the grids along the ion pulse path.
   The spectrometer used in this study had two such grids along the ion pulse path, and detachment by grids has been shown to be negligible in similar spectrometers having three similar grids [Compton et al. (1966a)].

2. Spontaneous or collision-induced dissociation of the parent negative ions in the flight tube must be negligible. All ions which dissociate in times short with respect to the time the ions remain in the collision chamber (\(< 1 \mu\text{sec}\)) have times of flight corresponding to the masses of the dissociation fragments. No ions have been observed to dissociate spontaneously with lifetimes \(> 1 \mu\text{sec}\). Collision-induced dissociation is negligible for the pressures used for \( \tau \) measurements (\(\sim 10^{-5}\) torr) and the ordinary times of flight to the separators (\(\sim 10 \mu\text{sec}\)).
3. Counting efficiency by the EM must be the same for both ions and neutrals which have the same kinetic energy. The fulfillment of this condition has been accomplished through single pulse counting techniques for both ions and neutrals.

4. Collisional detachment and charge transfer cannot take place in the flight tube. Collisional detachment does not occur at the pressures used in this study, $1 \times 10^{-7} \text{ torr} < P < 1 \times 10^{-4} \text{ torr}$, as verified by the independence of $\tau$ with respect to $P$ in this range. This is also verified by the fact that permanent negative ion signals, such as $\text{SF}_5^-$, possess no neutral component as observed in the spectrometer. Charge transfer would require collisions within the ion pulse which as stated in consideration 2 above, are unlikely for the operating conditions used.

If any of the above sources of error were present during a lifetime measurement, $\tau$ from the slope technique $\tau_{\text{slope}}$ and $\tau$ from direct calculation $\bar{\tau}$ would not agree. Also, a straight line for determining $\tau$ from the slope technique would be impossible to obtain or would not pass through the origin. Values of $\tau_{\text{slope}}$ (with straight line passing through the origin) and $\bar{\tau}$ are in good agreement for the molecules studied in Chapter V.

VI. SWARM EXPERIMENT

Swarm experiments employ a broad, and in certain cases, known electron energy distribution function to form negative ions under multiple collision conditions. The electron energy distribution functions for a
particular set of carrier gases, for example, \text{N}_2, \text{Ar}, \text{C}_2\text{H}_4 [\text{see, e.g., Christophorou (1970), Ritchie and Whitesides (1961), Carleton and Megill (1962), and Englehardt, Phelps, and Risk (1964)}], depend upon the pressure reduced electric field $\frac{E}{F}$ [\text{see, e.g., Christophorou, Chaney, and Christodoulides (1969)}]. Swarm experiments provide absolute electron attachment rates $\alpha_w$ as a function of electron energy [\text{Christophorou and Compton (1967)}]. Detection of ions with intermediate lifetimes (see Chapter I) is also possible through the use of swarm experiments. Complete stabilization of ions of both long and intermediate lifetimes is reasonable in view of the high pressures employed in the swarm experiments [\text{Christophorou and Compton (1967)}]. The swarm method used by Chaney and Christophorou (1969) and Christodoulides and Christophorou (1969) to study many of the molecules which have also been investigated by the electron beam method in this study was first described by Bortner and Hurst (1958).

A swarm-beam combination [\text{Christophorou et al. (1965)}] can be performed through the use of both the electron swarm and electron beam techniques (see Chapter IV). This procedure accurately establishes the energy scale and the electron attachment cross section for an attachment process. This is done by combining the shape of the resonance, usually best established by the beam experiment, with the attachment rate, measured by the swarm experiment and the known electron swarm energy distribution function. A computer program determines the best fit of the electron beam data and the electron swarm data [\text{Christophorou et al. (1965)}].
CHAPTER IV

ENERGY DEPENDENCE OF THE ELECTRON ATTACHMENT CROSS SECTION AND THE TRANSIENT NEGATIVE ION LIFETIME FOR NUCLEAR-EXCITED AND ELECTRON-EXCITED FESHBACH RESONANCES IN POLYATOMIC MOLECULES

I. GENERAL INTRODUCTION

Physical Importance

Many long-lived parent negative ions formed via nuclear-excited Feshbach resonances have been reported for polyatomic molecules. These reported observations have been characterized by sharp, subthermal peaking electron attachment cross section functions. Also, the mean auto-ionization lifetimes $\tau$ for the parent negative ions have been constant with energy across the resonances previously reported. Several other nuclear-excited Feshbach resonances of this type are discussed in Chapter V. Moreover, of greater importance to this study, a nuclear-excited Feshbach resonance has been observed in 1,4-naphthoquinone (NQ). This resonance possesses a high energy tail that may be associated with electron capture and simultaneous excitation of higher molecular skeletal deformation modes. Also, $\tau$ for NQ-$^*$ is found to have a drastic variation with incident electron energy.

Until recently no long-lived parent negative ions formed via electron-excited Feshbach resonances had been reported. Christophorou, Carter, and Christodoulides (1969) have reported the observation of a long-lived parent negative ion of p-benzoquinone (BQ) formed via an
electron-excited Feshbach resonance. This resonance has been further investigated in this study, with emphasis on the τ of BQ−*, which has also been found to vary with incident electron energy.

**Biological Importance**

The quinones, including p-benzoquinone, 1,4-naphthoquinone, and 2-methyl 1,4-naphthoquinone, are present in plants, animals, and microorganisms and are of extreme biological importance. It is particularly relevant to this study that many quinones, especially naphthoquinones, play an important role in electron transport in the body [see, e.g., Mahler and Cordes (1966), Brodie (1965), Ramasarma (1968), Russell and Brodie (1961), Martius (1961), Green (1961), Redfearn (1961), and Chance (1961)]. The naphthoquinones, including 1,4-naphthoquinone [Subirana et al. (1960)] and 2-methyl 1,4-naphthoquinone (vitamin K3), are known to enhance blood clotting, thereby reducing bleeding time. The effect of p-benzoquinone on plant metabolism has been studied [see, e.g., Schmidt and Flaig (1962)], and light induced electron transfer has been observed in a three-body system including chlorophyll and p-benzoquinone [Tollin and Green (1963)].

**II. P-BENZOQUINONE**

**Negative Ion Yield**

A strong parent negative ion current appears in BQ at approximately 1.9 eV incident electron energy in the TOFMS. This BQ−* ion current and the ion current for Br− from C6H5Br are shown in Figure 8, which is taken from Christophorou, Carter, and Christodoulides (1969). Br− from C6H5Br was used to calibrate the energy scale. BQ−* is shown in Figure 8
Figure 8. $Br^{-}/C_6H_5Br$ current as a function of electron energy.
with C\textsubscript{6}H\textsubscript{5}Br (full line with data points) and without C\textsubscript{6}H\textsubscript{5}Br (full line without data points) in the system. Measurements taken in the present study confirm both the shape and the energy scale calibration of this BQ\textsuperscript{*} resonance. No ions other than C\textsubscript{6}H\textsubscript{4}O\textsubscript{2}\textsuperscript{-} were observed in the mass spectrometer at low energies. No metastable dissociation fragments, for example, C\textsubscript{6}H\textsubscript{3}O\textsubscript{2}\textsuperscript{*-}, can be formed at 2.1 eV since these can be ruled out on energetic grounds.

**Electron Attachment Cross Section**

The electron attachment cross section for the electron-excited Feshbach resonance in BQ has been determined through the use of a swarm-beam combination [Christophorou et al. (1965)]. Also, the swarm-beam technique was employed to determine the energy scale that best fits the swarm and beam data. The results of the swarm-beam combination are presented in Figure 9. The electron attachment process has a peak cross section value of 6.7 x 10\textsuperscript{-17} cm\textsuperscript{2} and is attributed to electron capture in the field of the lowest triplet state T\textsubscript{1}, which results from an n \textarrowleft π* transition at 2.31 eV [McClure (1968)]. The energy of the peak value for the cross section in Figure 9 is 2.1 eV.

The electron attachment rate as a function of mean electron energy for BQ is shown in Figure 10. These swarm data were taken by Christodoulides and Christophorou (1969). The carrier gases used are C\textsubscript{2}H\textsubscript{4}, N\textsubscript{2}, and Ar, as shown in the figure, and there is good agreement between the attachment rates measured in different carrier gases [Christophorou, Chaney, and Christodoulides (1969)]. When the thermal value of \( \omega \) (= 1.2 x 10\textsuperscript{5} sec\textsuperscript{-1} torr\textsuperscript{-1}) was used, the mean velocity-weighted thermal attachment cross section was calculated from
Figure 9. Electron attachment cross section for the formation of Bq- as a function of electron energy.
Figure 10. Electron attachment rate $\alpha \omega$ as a function of mean electron energy $\langle \varepsilon \rangle$ for BQ$^\cdot$. 
Equation (II-6) to be $3.5 \times 10^{-19}$ cm$^2$. The thermal attachment process is associated with capture in the benzene ring of BQ.

**Negative Ion Lifetime**

The mean autoionization lifetime $\tau$ for $\text{BQ}^{-*}$ is plotted in Figure 11. A continuous variation of $\tau$ from 50 µsec at 1.7 eV to 8 µsec at 3.2 eV has been found. The value of $\tau$ plotted in Figure 11 is the average of four consistent runs for which the ion accelerating voltage is 2.5 keV. The lifetime was independent of BQ pressure ($1 \times 10^{-5}$ to $1 \times 10^{-4}$ torr) and filament current (1.6 to 2.5 amps). Each lifetime measurement for $\text{BQ}^{-*}$ was preceded by a $\tau$ measurement for $\text{SF}_6^{-*}$. This procedure, as described in Chapter III, was performed in order to ensure proper operation of the TOFMS. Prior to all $\tau$ measurements in this study, the $\tau$ for $\text{SF}_6^{-*}$ was taken as a function of electron energy and was consistently found to be independent of energy. Special care was taken to ensure that this condition held for the measurements of $\tau$ for $\text{BQ}^{-*}$ and $\text{NQ}^{-*}$.

The data plotted in Figure 11 were taken without using the RPD method, as were all lifetime data presented in this study. Because of the relatively intense $\text{BQ}^{-*}$ signal, a lifetime measurement was taken as a function of electron energy for $\text{BQ}^{-*}$ with the RPD method. This measurement gave results consistent with the results shown in Figure 11. The decrease in $\tau$ over the high energy side of the resonance for $\text{BQ}^{-*}$ is the result of the excess energy of the captured electron, which enhances autoionization. This enhancement is probably due to the availability of more neutral molecular states to which the excited negative ion $\text{BQ}^{-*}$ can decay.
Figure 11. Negative ion lifetime $\tau$ as a function of electron energy for $\text{D}_2^-$.
The thermal energy attachment process in BQ, evidenced in the swarm results of Figure 10, page 55, was not detected in the TOFMS. This could be due to the low electron attachment cross section \(3.5 \times 10^{-19} \text{ cm}^2\) for this process, to a low efficiency of producing thermal electrons in the electron beam source, or to a lifetime of the state which is short (< \(10^{-6}\) sec) compared with the detection limit of the TOFMS.

**Electron Affinity**

A rough estimate of the EA for BQ in the excited state \(T_1\) can be made by subtracting the negative ion peak energy (2.1 eV) from the peak energy of the triplet state, which is 2.31 eV [McClure (1968)]. This results in a value of \(\sim 0.2\) eV for the EA of BQ in the excited state \(T_1\).

Through the use of Equation (II-13) and vibrational frequencies for BQ given by Anno and Sado (1960), and EA of \(\sim 0\) eV has been obtained for BQ in the ground state for a thermal attachment cross section equal to \(3.5 \times 10^{-19} \text{ cm}^2\), a \(\tau = 35\) μsec, and an incident electron energy of 0.05 eV. However, if \(\tau < 10^{-6}\) sec, EA is even smaller. This is in disagreement with EA values of 1.37 and 0.77 eV for the ground state of BQ reported by Farragher and Page (1966) and Briegleb (1964). Since we have estimated EA for BQ in the excited state \(T_1\) to be 0.2 eV and EA of the ground state to be < 0 eV, it appears that in this case

\[(\text{EA})_{\text{excited state}} > (\text{EA})_{\text{ground state}}.\]

**III. 1,4-NAPHTHOQUINONE**

**Negative Ion Yield**

The parent negative ion yield as a function of electron energy \([I(e)]\) for 1,4-naphthoquinone (NQ, \(1,4-C_6\text{H}_2\text{O}_2\)), measured in the TOFMS,
possesses a high energy tail. For this reason it is much more significant than the I(\epsilon) for ions of any other previously reported long-lived nuclear-excited Feshbach resonance, which includes the resonances reported in Chapter V. The ion yield for NQ^*, taken from a typical run, is shown in Figure 12 along with the I(\epsilon) for SF_6^*, taken under identical conditions. A high energy tail in the NQ ion current is evident, and this tail may be associated with electron capture and simultaneous excitation of higher skeletal deformation modes. Sixteen consistent I(\epsilon) curves were taken for NQ. These runs were performed under different operating conditions for the TOFMS. Filament current during these runs ranged from 1.7 amps to 2.4 amps. Except for some broadening of the I(\epsilon) curves (see Chapter III) in the high filament current runs, all of these curves exhibited strikingly similar shapes.

Stamatovic and Schulz (1968) have found that the width of the SF_6^* resonance at thermal energies is < 0.02 eV, which is approximately an order of magnitude narrower than the electron beam width used while taking the data in Figure 12. For this reason, the ion yield for SF_6^* gives, to a first approximation, the shape of the electron current energy distribution function at thermal energies which is used to obtain I(\epsilon) for NQ^*.

**Electron Attachment Cross Section**

The absolute electron attachment rate \omega is plotted as a function of mean electron energy \langle \epsilon \rangle in Figure 13. These data were taken by Chaney and Christophorou (1969) by the electron swarm method. It is noted that good agreement between measurements made in different carrier
Figure 12. Comparison of negative ion current as a function of electron energy for $\text{SF}_6^-$ and $\text{N}_2^-$.
Figure 13. Electron attachment rate $\alpha \omega$ as a function of mean electron energy $\langle \varepsilon \rangle$ for $\text{N}_2^-$. 
gases is found (Figure 13). Also, the electron swarm data in Figure 13 are in good agreement with the electron beam data in Figure 12. Through the use of Equation (II-6), \( \langle \sigma_a \rangle_v \) was calculated to be \( 6.17 \times 10^{-15} \text{ cm}^2 \) at thermal energies.

**Negative Ion Lifetime**

The mean autoionization lifetime \( \tau \) for \( \text{NQ}^{-*} \) was found to have a form very different from that of any of the previously reported long-lived parent ions that result from nuclear-excited Feshbach resonances. All previously reported long-lived parent negative ion resonances at thermal energies have constant lifetimes, that is, they exhibit no variation of \( \tau \) with energy across the resonance. Some ions of this type are reported in Chapter V. In contrast to \( \tau \) for these negative ions, the average autoionization lifetime for \( \text{NQ}^{-*} \) exhibits a drastic variation with electron energy.

The lifetimes for both \( \text{SF}_6^{-*} \) and \( \text{NQ}^{-*} \) are plotted in Figure 14 as a function of electron energy. The incident electron energy distribution (not using the RPD method) is approximated by \( I(e) \) for \( \text{SF}_6^{-*} \). The ion current for \( \text{NQ}^{-*} \) exhibits a slight high energy tail. The lifetime for \( \text{SF}_6^{-*} \) is shown as a function of energy in the lower part of Figure 14. At each electron energy, the lifetime for \( \text{SF}_6^{-*} \) is the average of all \( \tau \) measurements which were taken before and after each \( \tau \) measurement of \( \text{NQ}^{-*} \). Two points should be noted concerning \( \tau \) for \( \text{SF}_6^{-*} \).

1. The lifetime is constant with electron energy across the \( \text{SF}_6^{-*} \) resonance.

2. The average of twelve measurements of the \( \tau \) for \( \text{SF}_6^{-*} \) at the energies shown in Figure 14 is \( 30.8 \pm 1.7 \mu\text{sec} \). This is
Figure 14. Negative ion current as a function of electron energy for SF6\(^{-}\) and NO\(^{-}\)\(^{-}\) and negative ion lifetime as a function of electron energy for SF6\(^{-}\) and NO\(^{-}\)\(^{-}\).
almost identical to the $\tau$ for SF$_6^-$ of 32 $\mu$sec from the slope technique as presented in Chapter V.

The latter data for SF$_6^-$ were taken about one year after the former data were taken. This indicates that the TOFMS was operating properly while measuring the NQ lifetimes. Since the masses of the SF$_6^-$ (146 a.m.u.) and the NQ$^-$ (158 a.m.u.) are approximately the same, the charge to mass ratios of SF$_6^-$ and NQ$^-$ are approximately the same. Therefore, the requirement that must be fulfilled for determining lifetimes by the direct calculation method (see Chapter III) is met.

The curve displaying $\tau$ for NQ$^-$ as a function of energy shown in Figure 14 is the average of six consistent runs. These were taken for the two ion acceleration energies 1.5 and 2.5 keV. The filament current was kept as low as possible (1.6 to 1.9 amps) during these measurements, and the NQ pressure was $\sim 5 \times 10^{-7}$ torr over a background pressure of $1 \times 10^{-7}$ torr. The error in $\tau$ for NQ$^-$ varies from $\sim 20$ percent for the high count rates on the central portion of the curve to $\sim 40$ percent for the low count rates on the low and high energy tails of the curve. Due to the low counting rates, resulting mainly from the low vapor pressure of NQ, the RPD method could not be employed in measuring $\tau$. It is believed, however, that the variation of $\tau$ is more drastic than indicated in Figure 14.

The sharp decrease in $\tau$ for NQ$^-$ from $\sim 350$ $\mu$sec at thermal energies to $\sim 15$ $\mu$sec at 1.3 eV is attributed to the increase in excess vibrational energy of the negative ion. This allows decay of the ion to a number of neutral molecular states (see Chapter II). Note that for SF$_6^*$, which has a sharper resonance and no skeletal structure, $\tau$ does not vary with energy.
The small decrease in $\tau$ at low energies is attributed to experimental factors. A constant background of neutral counts could cause such an effect. Additionally, an apparent decrease in $\tau$ would be observed if, as the electron energy is decreased, the portion of the electron energy distribution function that overlaps the ion resonance changes shape in such a way that an increasing portion of the captured electrons form shorter-lived ions. Since in all the measurements the background was essentially zero, the latter effect is considered more probable.

**Electron Affinity**

Through the substitution of the vibrational frequencies of NQ given by Singh and Singh (1968) into Equation (II-13), the EA for the ground state NQ molecule was calculated to be 0.6 eV. This value is in fair agreement with the value of 0.7 reported by Briegleb (1964) from charge transfer studies. However, it is in disagreement with a theoretical value of 1.70 eV [Kunii and Kuroda (1968)].

**IV. SUMMARY**

The data presented in this chapter for BQ and NQ are summarized in Table I. The quantities $\tau$, $\sigma$, and EA are presented in this table for BQ and NQ for the energies specified. These results are of significant physical value toward understanding the molecular structure of NQ and BQ and the low energy electron attachment processes (see Chapter I) that occur in polyatomic organic systems. In particular, it is of great physical interest to find a system (BQ) with as much as 2 eV of
### TABLE I
DATA SUMMARY FOR NQ AND BQ

<table>
<thead>
<tr>
<th></th>
<th>Peak Cross Section (cm²)</th>
<th>Lifetime (µsec)</th>
<th>Electron Affinity (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-benzoquinone</td>
<td>6.7 x 10⁻¹⁷ at 2.1 eV</td>
<td>48 at 1.7 eV to 8 at 3.2 eV</td>
<td>0.2 eV for first triplet state</td>
</tr>
<tr>
<td></td>
<td>3.5 x 10⁻¹⁹ at ~0 eV</td>
<td>~0 for ground state</td>
<td></td>
</tr>
<tr>
<td>1,4-naphthoquinone</td>
<td>6.17 x 10⁻¹⁵ at ~0 eV</td>
<td>350 at ~0 eV to 15 at 1.3 eV</td>
<td>0.60 eV for ground state</td>
</tr>
</tbody>
</table>
excess energy that can survive autoionization for $\sim 10^8$ times the vibration time. In addition, this study of BQ and NQ is of great biological significance in that these are systems which play an important role in electron transport in the body and in metabolism. Finally, this study provides a quantitative physical account of some of the electron accepting properties of BQ and NQ in the gas phase.
CHAPTER V
NONDISSOCIATIVE ELECTRON ATTACHMENT
TO POLYATOMIC MOLECULES

I. AZULENE

General Comments

Azulene (C_{10}H_{8}), which is a chemical isomer of naphthalene, has two carbon rings, one of seven members, the other of five members. The most widely known of azulene's many physically interesting properties is its anomalous fluorescence corresponding to the S_2 → S_0 transition [Beer and Longuet-Higgins (1955)]. This behavior is considered anomalous [Seybold and Gouterman (1965), Sponer (1959), and Jortner and Bixon (1969)] because of Kasha's empirical rule: "The emitting level of a given multiplicity is the lowest excited level of that multiplicity" [Kasha (1950)]. Since the observation of this anomaly in azulene, emission from the second excited singlet state has been observed in other molecules in both the gas phase [see, e.g., Poole and Dhingra (1969) and Geldof, Rettschnick, and Hoytink (1969)] and the liquid phase [Easterly et al. (1970)]. Among azulene's many biologically interesting properties is its inflammation inhibitive action [Maksimenko (1964)], which is used in the treatment of ulcers.

Azulene has been extensively studied using optical methods [see, e.g., Beer and Longuet-Higgins (1955) and Viswanath and Kasha (1956)]. It has also been studied by the electron beam method [Compton and Huebner (1968, 1969) and van Brunt and Wacks (1964)] and by the "pulse sampling technique" [Wentworth, Chen, and Lovelock (1966) and Wentworth
and Steelhammer (1968)]. In the present study the electron attachment properties of azulene have been investigated in the gas phase with both the electron swarm and the electron beam techniques.

**Negative Ion Yield**

A sharp long-lived negative ion resonance has been observed in the electron beam experiment for the parent negative ion at thermal energies. The negative ion yield as a function of electron energy $I(e)$ is shown in Figure 15. Here $I(e)$ for $C_{10}H_8^-$ is plotted along with $I(e)$ for $SF_6^-$. When $SF_6$ and $C_{10}H_8$ were in the TOFMS at the same time, the $C_{10}H_8^-$ and $SF_6^-$ peaks coincided energy wise. This coincidence of the $C_{10}H_8^-$ and $SF_6^-$ resonances does not necessarily imply that the $C_{10}H_8^-$ resonance peaks at zero energy. Schulz (1960) and Christophorou et al. (1965) have pointed out that the energy scale calibration based on a zero energy attachment resonance has often been found to be underestimated because the potential along the path of the electron beam is sometimes positive with respect to the measured potential of the entrance electrode of the collision chamber. However, this $C_{10}H_8^-$ resonance appears lower in energy than the $SF_6^-$ resonance from $SF_6$ (see Chapter VI) as measured in the electron beam experiment. The attachment rates measured by the electron swarm method, which are shown in curve A of Figure 16, confirm that there is a subthermal peaking process in azulene. The $SF_6^-$ signal was approximately three times more intense than the $C_{10}H_8^-$ signal as observed in the beam experiment. This relative intensity of $SF_6^-$ to $C_{10}H_8^-$ is in good agreement with the ratio between the absolute electron attachment cross section of $SF_6^-$ [$1.17 \times 10^{-14}$ cm$^2$; Christophorou, McCorkle, and Carter (1970)] and $C_{10}H_8^-$ ($3.5 \times 10^{-15}$ cm$^2$; this study)].
Figure 15. Comparison of negative ion current as a function of electron energy for $\text{SF}_6^-$ and $\text{C}_{10}\text{H}_8^*$. 

$\text{SF}_6^-$ (○)
$\text{C}_{10}\text{H}_8^*$ (○) × 3
Figure 16. Electron attachment rate $\alpha W$ for $C_{10}H_8$ as a function of $\langle \epsilon \rangle$. 
About twenty consistent measurements of $I(e)$ for $C_{10}H_{8}$ were taken for the thermal electron attachment process, and the full width at half height of $I(e)$ was always $\geq 0.20$ eV. The $C_{10}H_{8}^{-*}$ resonance was always slightly broader than the $SF_{6}^{-*}$ resonance. The narrowest width observed for the $SF_{6}^{-*}$ resonance was 0.12 eV. It should be noted, as mentioned in Chapter IV, that Stamatovic and Schulz (1968) have found that the width of $SF_{6}^{-*}$ is instrumental even for an energy resolution of 0.02 eV.

Electron Attachment Cross Section

The absolute electron attachment rate $\alpha \omega$ (sec$^{-1}$ torr$^{-1}$) for azulene is plotted as a function of mean electron energy $\langle e \rangle$ in curve A of Figure 16. These data were taken by Chaney and Christophorou (1969). The temperature during these measurements ranged from $423^\circ$ to $488^\circ$K, but no change in attachment with temperature was detected. These $\alpha \omega(\langle e \rangle)$ data are strikingly different in one way from $\alpha \omega(\langle e \rangle)$ curves for other aromatic molecules that have been found to attach electrons nondissociatively at thermal energies [Christophorou and Compton (1967) and Christophorou and Blaunstein (1969)]. The subthermal peaking attachment rates for these other aromatic molecules decrease more rapidly with increasing $\langle e \rangle$ than the decrease for azulene shown in curve A of Figure 16. This unusual behavior can be the result of either a single electron attachment process that peaks at energies greater than, but close to thermal energies, or two processes, one peaking at subthermal energies and the other peaking above thermal energies. The following procedure was employed to determine which of the above two explanations best fits the data and also to find the peak value of $\sigma_a$ for the process or processes involved. The thermal value of $\alpha \omega$, shown in curve A of
Figure 16, page 71, was substituted into Equation (II-6) to determine \( \langle \sigma_a \rangle \) for the thermal attachment process observed in the beam experiment. The value of \( \langle \sigma_a \rangle \) was found to be equal to \( 3.5 \times 10^{-15} \text{ cm}^2 \), and this was taken as the peak electron attachment cross section. The shape of the cross section at thermal energies was approximated by \( I(\varepsilon) \) from the beam experiment. Then, \( \omega \) was calculated from Equation (II-1), where \( f(\varepsilon, \frac{E}{P}) \) was taken from Engelhardt, Phelps, and Risk (1964). The results of this calculation are shown as curve B of Figure 16. This curve is typical of the \( \omega \) curves for other aromatic molecules which have been found to attach thermal energy electrons nondissociatively [Christophorou and Compton (1967) and Christophorou and Blaunstein (1969)]. Yet when curve A is compared to curve B of Figure 16, it is obvious that a large portion of the measured attachment rates above thermal energies cannot be accounted for by one process peaking at subthermal energies. Subtraction of curve B from curve A yields curve C, which is a measure of this portion of the attachment rate not accounted for by the subthermal peaking process observed in the electron beam experiment.

With the apparent attachment rate for the process not seen in the beam experiment known, only the shape of \( \sigma_a \) for this process was needed to apply the swarm-beam combination. The shape of the 2.1 eV process in BQ, which was Gaussian and given in Figure 9, page 54, was assumed for the process responsible for the attachment rates given by curve C of Figure 16. The swarm-beam combination (see Chapter II) was then applied with \( f(\varepsilon, \frac{E}{P}) \) for \( \text{N}_2 \) [Engelhardt, Phelps, and Risk (1964)] used in the calculations. The resulting cross section peaked at 0.3 eV,
and changing the width of the trial cross section function from 0.1 to 0.4 eV did not change the peak energy. The width did affect the peak cross section value, and a width of 0.2 eV resulted in a peak cross section value of $1 \times 10^{-15}$ cm$^2$. Through the use of the swarm-beam combination, curve C of Figure 16, page 71, could be reproduced with the cross sections determined to within 5 percent over the center portion of the curve and to within 15 percent over the low and high energy tails of the curve. It is thus shown by this analysis that the measured $\alpha \omega$ (curve A, Figure 16) can be made up of one process that peaks at subthermal energies and another that peaks at $\sim 0.3$ eV. No possible width or peak energy could be found for a single process that would give a good fit to the experimental $\alpha \omega$ data shown as curve A of Figure 16. A computational analysis, which employs the swarm-beam method, has been carried out in an attempt to find a single process. Using $I(e)$ for $C_1 e^{-e/\Delta}$, plotted in Figure 15, page 70, as the assumed shape and widths varying from 0.1 to 0.8 eV, the $\alpha \omega$ calculated from Equation (II-1) always resulted in a very poor fit to curve A of Figure 16. The best fit obtained with this procedure occurred when a width of 0.2 eV and a peak energy of 0.12 eV was assumed. The peak cross section value was $3.9 \times 10^{-15}$ cm$^2$. When this cross section was substituted into Equation (II-1), the calculated $\alpha \omega$ values from Equation (II-1) were found to be a very poor fit to the experimental $\alpha \omega$ plotted in curve A of Figure 16.

The shape of the electron attachment cross section could be very different from the assumed shape shown in Figure 15. For example, it might be argued that $\sigma_a$ has a shape similar to $\sigma_a$ for NO described in Chapter IV. This is unlikely for two reasons:
1. The experimental \( \omega \) curve for azulene is very different from the experimental \( \omega \) curve for NQ. The curve for NQ (shown in Figure 13, page 61) drops off much faster with increasing energy than the curve for azulene (curve A in Figure 16, page 71).

2. No variation in \( \tau \) with energy was detected for azulene. Therefore, it may be concluded that azulene attaches electrons via two processes:

1. A sharp subthermal peaking process, the width of which is instrumental in the beam experiment. The thermal electron attachment cross section for this process is \( 3.5 \times 10^{-15} \text{ cm}^2 \).

2. A weaker process which peaks at \( \approx 0.3 \text{ eV} \) and has a peak electron attachment cross section of \( \approx 1 \times 10^{-15} \text{ cm}^2 \) and a \( \tau < 10^{-6} \text{ sec} \). The \( \tau \) for the subthermal peaking process is given below.

Mean Autoionization Lifetime

The mean autoionization lifetime for the subthermal peaking cross section process in azulene has been measured in the TOFMS. The value of \( \tau \) for SF\(_6^*\) was measured before each \( \tau \) measurement for azulene to ensure proper operation of the TOFMS (see Chapter II). The ions C\(_{10}H_8^*\) (mass = 128 a.m.u.) and SF\(_6^*\) (mass = 146 a.m.u.) have charge to mass ratios that are not very different. Therefore, their behavior in the TOFMS is not expected to be drastically different. The value of \( \tau \) for C\(_{10}H_8^*\) was found to be \( 7 \pm 1 \mu\text{sec} \) for 12 runs. Each run consisted of from two to twelve individual \( \tau \) measurements. The value of \( \tau \) was constant with electron energy across the resonance. Acceleration voltages of 1.5, 2.0, and 2.5 keV were used during these measurements, and filament currents
ranged from 1.8 to 2.1 amps. The $C_{10}H_8$ pressures ranged from $1 \times 10^{-5}$ to $2 \times 10^{-5}$ torr. The value of $\tau$ for $C_{10}H_8^*$ of 8.13 $\mu$s reported by Compton and Huebner (1969) is in good agreement with the value in this study.

**Electron Affinity**

When $\tau (= 7 \mu$s), $\sigma_a (= 3.5 \times 10^{-15} \text{ cm}^2)$, and the vibrational frequencies given by van Tets and Günthard (1963) are substituted into Equation (II-13), an EA value of 0.46 eV is calculated for the ground state of azulene. This value is in fair agreement with the values of 0.59 eV and 0.66 eV reported by Wentworth, Chen, and Lovelock (1966). However, 0.46 eV is in disagreement with a value of 0.052 eV reported by Ehrenson (1962) and a value of 0.92 eV reported by Hoyland and Goodman (1962).

Rentzepis (1969) has observed the emission spectrum of azulene in methyl cyclohexane at 77°K excited by an intense laser beam. The spectrum, which is attributed to phosphorescence from the lowest triplet state ($T_1$) of azulene, has a 0-0 transition at $\sim 1.3$ eV and a peak at 1.11 eV. The value of $T_1 \sim 1.3$ eV agrees reasonably with the estimate of Lamola et al. (1965) of $T_1 \geq 1.36$ eV from triplet energy transfer experiments and with Pariser's (1956) calculated value of $T_1 = 1.47$ eV. The heavy-atom-induced emission, originally attributed by Robinson and Frosch (1963) to a triplet-triplet transition in azulene, was subsequently found to be due to a naphthalene impurity [Robinson (1969)], thus invalidating their estimate of $T_1 \leq 0.74$ eV. If the capture process observed in this study at $\sim 0.3$ eV is associated with electron
attachment in the field of the first excited triplet state of azulene, then the spectroscopic data [Renzephis (1969)] indicate an electron affinity in T₁ of ~0.8 eV, which is much higher than that of 0.46 eV for the ground state.

II. CINNAMALDEHYDE

Cinnamaldehyde (C₆H₅CH:CHCHO;CIN) has been observed to form a long-lived negative ion at thermal energies. The ion has been identified as the parent (158 a.m.u.), and the shape of the resonance was observed to be similar to that of the SF₆ resonance. Wentworth and Chen (1967) have determined the EA of CIN to be 0.82 eV by means of the common intercept method, and the σ₀ to be 2.0 x 10⁸ sec⁻¹ torr⁻¹ by the "pulse sampling" method [see, e.g., Wentworth, Chen, and Lovelock (1966) and Wentworth, Hirsch, and Chen (1967)]. In the present study the mean auto-ionization lifetime τ of CIN⁻ has been accurately measured in the TOFMS by means of both the slope method (τ_slope = 11.9 μsec) and the direct calculation method (τ = 12.0 μsec) (see Chapter III). The value of τ was constant with electron energy across the resonance.

Figure 17 shows a plot of the negative logarithm of N⁻ divided by N₀ versus time of flight (t) of the CIN⁻ before separation of N⁻ from N₀ + N⁻ in the beam experiment. The quantities N⁻ and N₀ are the number of ions and neutral molecules in the pulse after a time t. Initially, N₀ ions are formed at t = 0. The t's plotted in Figure 17 correspond to the seven acceleration voltages, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 keV. The lowest acceleration voltage corresponds to the longest t. The value of τ is equal to the inverse of the slope of the straight line in
Figure 17. $-\ln(N/N_0)$ versus time of flight $t$ for CIN$^-$ lifetime determination.
Figure 17. Also, $\tau$ can be calculated directly from Equation (III-4) after substituting $N^-$, $N_0$, and $t$ corresponding to each acceleration voltage. This calculation is shown as $\overline{\tau}$ in Figure 17, and $\tau$ from the slope technique is designated $\tau_{\text{slope}}$.

Several factors should be mentioned concerning Figure 17:

1. A straight line through the data points also passes through the origin. This criterion must be met in order to ensure an accurate $\tau$ from the slope method.

2. The points plotted are average values of four consistent runs.

3. The $\tau_{\text{slope}}$ is in very good agreement with $\overline{\tau}$.

4. The $\tau_{\text{slope}}$ and the $\tau$ of SF$_6$ were periodically measured between CIN$^-*$ runs to check the operation of the TOFMS.

5. The straight line drawn in the figure is a least squares fit of the data points with zero intercept.

During the $\tau$ measurements, the filament current was $\approx 1.8$ amps and CIN pressure was $\approx 1 \times 10^{-5}$ torr.

III. o-NITROTOLUENE

$o$-Nitrotoluene ($o$-NT; $o$-C$_6$H$_4$CH$_3$NO$_2$) has been observed to form a long-lived parent negative ion at thermal energies. The shape of the parent negative ion resonance and the shapes of the NO$_2^-$ dissociative electron attachment resonances at 0.62 and 3.22 eV have been given by Christophorou et al. (1966). A comprehensive study of $\tau$ for the thermal energy parent negative ion process has been performed. Figure 18 shows a plot of $\frac{\Delta m}{N^+}$ versus $t$ for times of flight corresponding to the acceleration voltages 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 keV. The value of $\tau$ was found to be constant with energy across the resonance.
Figure 18. \(-\ln(N^+ / N_0)\) versus time of flight \(t\) for \(\text{o-NITROTOLUENE}^*\) lifetime determination.
The conditions of a good \( \tau \) measurement that are mentioned for CIN\(^*\) are also satisfied for the o-NT\(^*\) measurement. As can be seen from Figure 18, \( \tau_{\text{slope}} \) and \( \tau \) are both found to be 13.1 \( \mu \text{sec} \). This figure is the average of three consistent runs. Filament current was about 1.8 amps and o-NT pressure was about \( 1 \times 10^{-5} \) torr.

IV. m-NITROTOLUENE

m-Nitrotoluene (m-NT; \( \text{m-C}_6\text{H}_4\text{CH}_3\text{NO}_2 \)) has also been found to form a long-lived parent negative ion at thermal energies. Christophorou et al. (1966) have measured the shape of this resonance and the shapes of the \( \text{NO}_2^- \) dissociative attachment resonances at 1.06 and 3.50 eV. The value of \( \tau \) for the parent ion has been measured (\( \tau_{\text{slope}} = 18.8 \mu\text{sec} \) and \( \tau = 18.7 \mu\text{sec} \)) in the present study, and \( \tau \) was found to be constant across the resonance. Figure 19 is a plot of \( \frac{N^-}{N} \) versus \( t \) for \( t \)'s corresponding to 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 keV. This figure is the average of three consistent runs. The conditions of a good \( \tau \) measurement which are satisfied for CIN\(^*\) and o-NT\(^*\) are also satisfied for the \( \tau \) measurement of m-NT\(^*\). Filament current was about 1.8 amps, and pressure about \( 1 \times 10^{-5} \) torr during these measurements.

V. p-NITROTOLUENE

p-Nitrotoluene (p-NT; \( \text{p-C}_6\text{H}_4\text{CH}_3\text{NO}_2 \)) has been found to form a long-lived parent negative ion at thermal energies upon electron impact. The shape of this resonance was observed to be similar to that of the SF\(_6^-\) resonance. A plot of \( \frac{N^-}{N} \) versus \( t \) for \( t \)'s corresponding to 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 keV is shown in Figure 20. Three consistent
Figure 19. $-\ln \left(\frac{N}{N_0}\right)$ versus time of flight $t$ for m-NITROTOluene lifetime determination.

m-NITROTOluene

$\tau_{slope} = 18.8 \mu$sec

$\bar{\tau} = 18.7 \mu$sec
Figure 20. $-\ln \left( \frac{N}{N_0} \right)$ versus time of flight $t$ for p-NT$^*$ lifetime determination.
runs are averaged to make up this figure. The value of $\tau_{\text{slope}}$ is found to be 13.8 $\mu$sec and $\bar{\tau}$ is found to be 14.0 $\mu$sec. The conditions of a good $\tau$ measurement that are enumerated for CIN\textsuperscript{*} are also present for the measurements taken for p-NT\textsuperscript{*}. The value of $\tau$ was also constant with electron energy across the resonance. The filament current was kept at about 1.8 amps, and p-NT pressure was maintained at about $1 \times 10^{-5}$ torr for these measurements.

VI. SULFUR HEXAFLUORIDE

General Comments

Many groups have studied electron attachment to SF\textsubscript{6}. Compton et al. (1966a) have found the EA for SF\textsubscript{6} to be 1.4 eV, and Kay and Page (1964) have found this EA to be 1.49 eV. Christophorou, McCorkle, and Carter (1970) have found $\omega$ at thermal energies to be $9 \times 10^9$ sec\textsuperscript{-1} torr\textsuperscript{-1}, and $\sigma_a$ at 0.05 eV to be $1.17 \times 10^{-14}$ cm\textsuperscript{2} for SF\textsubscript{6}.

The resonance in SF\textsubscript{6}\textsuperscript{*} at thermal energies was used often in this study. The shape, intensity, and energy of this resonance were continuously employed as references for resonances in other molecules at thermal energies. The value of $\tau$ for SF\textsubscript{6}\textsuperscript{*} was also used as a reference in lifetime measurements, as mentioned throughout this study.

Negative Ion Yield

The yield of SF\textsubscript{6}\textsuperscript{*} as a function of electron energy is shown in Figure 21. This resonance was taken over one hundred times during the course of this study. The shape and the energy dependence of this resonance are in good agreement with the work of others [see, e.g.,
Figure 21. Negative ion current as a function of electron energy \( \epsilon \) for SF\(_6^*\).
Negative Ion Lifetime

The lifetime of $\text{SF}_6^-$ was measured many times throughout this study. These measurements were undertaken in order to ensure proper operation of the TOFMS (see Chapter III). Figure 22 shows a plot of $\frac{\phi_p N^-}{N_0}$ versus $t$ for $\text{SF}_6^-$. This plot is the average of eight consistent runs, taken periodically during $\tau$ measurements for $\text{CIN}^-$, $\text{o-NT}^-$, $\text{m-NT}^-$, and $\text{p-NT}^-$. The $t$'s shown on this figure correspond to acceleration voltages of 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, and 4.5 keV. All the conditions of a good $\tau$ measurement mentioned earlier in this study apply to these measurements. The conditions in the spectrometer during the measurements shown in Figure 22 were a filament current of about 1.8 amps and a pressure of about $1 \times 10^{-5}$ torr. This value of $\tau = 32 \, \mu\text{sec}$ is slightly larger than the value of 26 $\mu\text{sec}$ measured by Compton et al. (1966a).

VII. HEXAFLUOROACETONE

Harland and Thynne (1969) found that the parent negative ion was formed for hexafluoroacetone ($\text{C}_3\text{F}_6$; HFA) at thermal energies in a TOFMS. They have also arrived at an estimate of the electron attachment cross section for HFA by a comparison of the intensity of the $\text{SF}_6^-$ signal in the TOFMS to the intensity of the HFA$^-$ signal. They found this relative intensity to be 58.9. By taking $\sigma_a(\text{SF}_6^-)$ to be $3.6 \times 10^{-15}$ cm$^2$ [Compton et al. (1966a)] they have estimated $\sigma_a(\text{HFA}^-)$ to be $6.1 \times 10^{-17}$ cm$^2$ at thermal energies. This estimate is probably low by
Figure 22. $-\ln \left( \frac{N}{N_0} \right)$ versus time of flight $t$ for $\text{SF}_6^*$ lifetime determination.
a factor of three because the $\sigma_a(SF^-)$ assumed is a factor of three lower than the presently accepted value of $1.17 \times 10^{-14}$ cm$^2$ [Christophorou, McCorkle, and Carter (1970)]. In the present study, $\tau$ for HFA$^-$ was measured to be $\sim 60$ $\mu$sec. The $\tau$ was not found to be a function of electron energy across the resonance.

VIII. MOLECULES IN WHICH A PARENT NEGATIVE ION WAS NOT OBSERVED

Acetaldehyde

No long-lived parent negative ion was found to be formed in acetaldehyde (CH$_3$CHO; ACET). Dissociative electron attachment in ACET is discussed in Chapter VI.

Benzaldehyde

Benzaldehyde (C$_6$H$_5$CHO) has been reported to have a positive EA by Kunii and Kuroda (1968) and Wentworth and Chen (1967). Several dissociative electron attachment peaks were observed in benzaldehyde in the present study. However, no long-lived parent negative ion was observed.

2-Methyl 1,4-Naphthoquinone

2-Methyl 1,4-naphthoquinone (C$_6$H$_4$CH$_3$O$_2$) was investigated because of the interesting findings for NQ presented in Chapter IV and because of its biological activity. The molecule C$_6$H$_4$CH$_3$O$_2$ is vitamin K$_3$, and it is a very effective blood clotting agent. However, no long-lived parent negative ion was found. Thus, the substitution of CH$_3$ for H in the two position of NQ decreases (or eliminates) the capacity of NQ to form a long-lived parent negative ion.
Nitropropane

Nitropropane \((\text{C}_3\text{H}_7\text{NO}_2)\) was investigated in the TOFMS. No long-lived parent negative ions were formed, but many fragments were seen at many different energies extending from just above thermal energies to 15 eV.

Tetranitromethane

Baltey and Lyons (1962) have reported an EA value of 1.78 eV for tetranitromethane \([\text{C(NO}_2]_4\)\]. A long-lived parent negative ion was not found in \([\text{C(NO}_2]_4\). This may be due to the symmetry of the molecule which results in the availability of only a small number of vibrational modes to share the excess energy of negative ion formation.

\[
\begin{align*}
n\cdot\text{C}_N\text{H}_{2N+1}\text{Br} & \quad (N = 2, 3, 4, 5, 6, 7, 8, \text{ and } 10) \\
\end{align*}
\]

Dissociative electron attachment processes in the molecules \(n\cdot\text{C}_N\text{H}_{2N+1}\text{Br}\) where \(N = 2, 3, 4, 5, 6, 7, 8, \text{ and } 10\) are discussed in detail in Chapter VI. However, none of these molecules were found to form long-lived parent negative ions.

Tetraethyl Lead

Tetraethyl lead \([\text{Pb(C}_2\text{H}_5]_4\]\), well-known as a fuel additive, was not found to form a long-lived parent negative ion. Some low energy fragment negative ions were observed in the TOFMS, but no effort was made to study these further.

Thymine

An attempt was made to study thymine \([\text{NHCONHCOC(CH}_3]_2\text{CH}]\) in the TOFMS. However, no negative ions were observed in the spectrometer.
The fact that no ions were seen is probably due to the vapor pressure of thymine, which was too low to allow a study of the thymine molecule in the TOFMS.

**Anthracene**

A relatively high thermal attachment rate of $1.5 \times 10^8$ sec$^{-1}$ torr$^{-1}$ has been reported for anthracene $[C_{6}H_{4}(CBr)_{2}C_{6}H_{4}]$ by Christophorou and Blaunstein (1969), and von Ardenne, Steinfeldler, and Tümmelr (1961) have observed a long-lived parent negative ion in anthracene. An attempt was made to introduce anthracene into the TOFMS. However, as was for the case of thymine, the vapor pressure of anthracene was too low to allow its study in the TOFMS.

**IX. SUMMARY**

The results presented in this chapter make a contribution toward understanding fundamental physical processes in complex molecules. In particular, the low-energy electron attachment process

$$AX + e \rightarrow AX^* \rightarrow AX + e$$

has been investigated in the physically and biologically interesting molecules azulene, cinnamaldehyde, o-, m-, and p-nitrotoluene, and sulfur hexafluoride. This process was not observed in acetaldehyde, benzaldehyde, 2-methyl 1,4-naphthoquinone, nitropropane, tetranitromethane, $n-C_{N}H_{2N+1}Br$ where $N = 2,3,4,5,6,7,8,$ and 10, and tetraethyl-lead. For the molecules in which the long-lived parent negative ion was observed,
\( \tau(\varepsilon) \) and \( \sigma_{\alpha}(\varepsilon) \), which are related to the molecular structure and EA, were measured. In all of the long-lived systems studied, a relatively large amount of energy remained in the negative ion for long times (\( \sim 10^8 \) times the molecular vibration time). These measurements on the electron transport properties of organic molecules could be of great value in understanding many of the problems in radiation physics, radiation biology, radiation chemistry, and the life sciences.
CHAPTER VI

DISSOCIATIVE ELECTRON ATTACHMENT IN POLYATOMIC MOLECULES

I. THE ALIPHATIC HYDROCARBONS OF THE FORM \( n-C_{N}H_{2N+1}Br \)

**General Comments**

The theoretical background of dissociative electron attachment to diatomic molecules was presented in Chapter II. The theoretical treatments discussed there have, as a rule, been applied to small molecules. In this study the chain molecules \( n-C_{N}H_{2N+1}Br \) where \( N \) equals 2(bromoethane), 3(bromopropane), 4(1-bromobutane), 5(1-bromopentane), 6(1-bromohexane), 7(1-bromoheptane), 8(1-bromoctane), and 10(1-bromodecane) were investigated at low pressure in a TOFMS. The negative ion dissociation fragments formed when electrons with energies \( \leq 3 \text{ eV} \) collided with these molecules were identified, and the negative ion yields as a function of electron energy from 0 to 3 eV were measured. Christodoulides and Christophorou (1969) have also studied these same molecules with a high pressure electron swarm technique. Absolute electron attachment rates measured by them have been combined with the results of this study to obtain the energy scale calibration and also the dissociative electron attachment cross section for the formation of \( Br^- \) from \( n-C_{N}H_{2N+1}Br \). The widths and the magnitudes of the dissociative electron attachment cross section functions for the formation of \( Br^- \) from \( n-C_{N}H_{2N+1}Br \) have been analyzed. Isotope effects (see Chapter III) due to diatomic-like behavior of the series \( n-C_{N}H_{2N+1}Br \) have been found. The toxicities of the molecules \( n-C_{N}H_{2N+1}Br \) have been analyzed to determine whether a relationship between the toxicities and the electron
accepting capacities (as determined by the dissociative electron attachment cross section for the formation of Br⁻ at energies below ~ 1 eV) of these molecules exists. Some of the molecules included in this study have important functions in metabolism [see, e.g., Bray and James (1958, 1960) and Thompson, Maw, and Young (1958)], and some are pollutants.

Dissociation Energies

It was suspected that the dissociation energy for the n-CₙH₂N₊₋Br molecules [D(n-CₙH₂N₊₋-Br)] might be independent of the number of carbon atoms N. Absorption spectra [Bentley, McDevitt, and Rozek (1964)] have shown that the C-Br vibration mode is independent of the rest of the chain in these molecules. Therefore, a review of the work on the dissociation energies for these systems was undertaken, and the results have been compiled in Table II. Column six in this table contains values of D(n-CₙH₂N₊₋-Br) calculated from

\[ D(n\text{-}C_{N+1}H_{2N+1}\text{-}Br) = \Delta H^\circ_f(C_{N+1}H_{2N+1}) + \Delta H^\circ_f(\text{Br}) - \Delta H^\circ_f(n\text{-}C_{N+1}H_{2N+1}\text{-}Br), \quad \text{(VI-1)} \]

where \( \Delta H^\circ_f(C_{N+1}H_{2N+1}) \) and \( \Delta H^\circ_f(n\text{-}C_{N+1}H_{2N+1}\text{-}Br) \) are the values shown in brackets in columns two and four. The value of \( \Delta H^\circ_f(\text{Br}) \) from Ref. e of Table II was used in these calculations. The \( \Delta H^\circ_f(C_{N+1}H_{2N+1}) \) and \( \Delta H^\circ_f(n\text{-}C_{N+1}H_{2N+1}\text{-}Br) \) are the heats of formation of CₙH₂N₊₋ and n-CₙH₂N₊₋Br, and \( \Delta H^\circ_f(\text{Br}) \) is the heat of formation of Br. Column seven lists values of D(n-CₙH₂N₊₋-Br) from the literature. The last column contains the average of the literature values (column 7) and the calculated value (column 6) for each molecule. It can be seen from the values in this last column, which are
<table>
<thead>
<tr>
<th>Mole</th>
<th>$\Delta H^0_{\text{f}}(\text{C}<em>n\text{H}</em>{2n+1})$ (kcal/mole)</th>
<th>Ref.</th>
<th>$-\Delta H^0_{\text{f}}(\text{n-C}<em>n\text{H}</em>{2n+1}\text{Br})$ (kcal/mole)</th>
<th>Ref.</th>
<th>$D(\text{n-C}<em>n\text{H}</em>{2n+1}\text{-Br})^a$ (eV)</th>
<th>Ref.</th>
<th>$D(\text{n-C}<em>n\text{H}</em>{2n+1}\text{-Br})^b$ (eV)</th>
<th>Ref.</th>
<th>$D(\text{n-C}<em>n\text{H}</em>{2n+1}\text{-Br})^c$ (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$Br</td>
<td>31.5</td>
<td>d</td>
<td>8.4</td>
<td>e</td>
<td>2.88</td>
<td>h</td>
<td>2.89</td>
<td>i</td>
<td>2.92</td>
<td>j</td>
</tr>
<tr>
<td>C$_2$H$_5$Br</td>
<td>24.5</td>
<td>d</td>
<td>15.42</td>
<td>e</td>
<td>2.82</td>
<td>l</td>
<td>2.99</td>
<td>o</td>
<td>3.01</td>
<td>n</td>
</tr>
<tr>
<td>n-C$_3$H$_7$Br</td>
<td>22</td>
<td>d</td>
<td>18.65</td>
<td>p</td>
<td>2.94</td>
<td>l</td>
<td>2.96</td>
<td>n</td>
<td>2.99</td>
<td>o</td>
</tr>
<tr>
<td>n-C$_4$H$_9$Br</td>
<td>19</td>
<td>d</td>
<td>25.7</td>
<td>q</td>
<td>2.92</td>
<td>l</td>
<td>[2.96]</td>
<td>n</td>
<td>2.99</td>
<td>o</td>
</tr>
</tbody>
</table>
TABLE II (continued)

<table>
<thead>
<tr>
<th>Mole.</th>
<th>$\Delta H_f^o(C_{N^2H2N+1})$ (kcal/mole)</th>
<th>Ref.</th>
<th>$-\Delta H_f^o(n-C_{N^2H2N+1}Br)$ (kcal/mole)</th>
<th>Ref.</th>
<th>$D(n-C_{N^2H2N+1}-Br)^a$ (eV)</th>
<th>Ref.</th>
<th>$D(n-C_{N^2H2N+1}-Br)^b$ (eV)</th>
<th>Ref.</th>
<th>$D(n-C_{N^2H2N+1}-Br)^c$ (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-C$<em>5$H$</em>{11}$Br</td>
<td>9.1</td>
<td>r</td>
<td>27.84</td>
<td>r</td>
<td>3.05</td>
<td>s</td>
<td></td>
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<td></td>
<td></td>
<td>2.83</td>
<td>(2.94)</td>
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</tr>
<tr>
<td>n-C$<em>6$H$</em>{13}$Br</td>
<td>4.2</td>
<td>r</td>
<td>35.4</td>
<td>q</td>
<td>2.88</td>
<td>(2.88)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>n-C$<em>8$H$</em>{17}$Br</td>
<td>-5.7</td>
<td>r</td>
<td>46.3</td>
<td>q</td>
<td>2.92</td>
<td>(2.92)</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

$^a$Present calculations using the values of $\Delta H_f^o$ shown in brackets in columns 2 and 4 and the expression $D(n-C_{N^2H2N+1}-Br) = \Delta H_f^o(C_{N^2H2N+1}) + \Delta H_f^o(\text{Br}) - \Delta H_f^o(n-C_{N^2H2N+1}Br)$. The $\Delta H_f^o(\text{Br}) = 26.74$ kcal/mole from Ref. e was used in all calculations.

$^b$Literature values.

$^c$Average of all literature values (column 7) and calculated value (column 6) for each molecule. The value of 2.93 eV is given for n-C$_4$H$_9$Br in place of 3.10 eV obtained from scant data because the average of the values for the six other molecules in this column is 2.93 eV.

TABLE II (continued)


m M. Szwarc, Chem. Rev. 47, 75 (1950).


s J. D. Cox, Tetrahedron 18, 1337 (1962).
plotted in Figure 23, that $D(n-C_{N-2N+1}H_{2N+1}-Br)$ where $N = 1, 2, 3, 4, 5, 6,$ and 8 is independent of $N$. For this reason the process

$$n-C_{N-2N+1}H_{2N+1}Br + e^{-} \rightarrow n-C_{N-2N+1}H_{2N+1}Br^* \rightarrow C_{N-2N+1}H_{2N+1} + Br^-$$ \hspace{1cm} (VI-2)

may be expected to occur at approximately the same incident electron energy independent of $N$. This is born out by the results for the molecules for which $2 \leq N \leq 6$. The average of the values for $D(n-C_{N-2N+1}H_{2N+1}-Br)$ plotted in Figure 23 is 2.93 eV, and this value is used to calculate the Morse functions for $n-C_4H_9Br$, $n-C_7H_{11}Br$, and $n-C_6H_{13}Br$. These three molecules were chosen as examples. The other molecules discussed here can be treated similarly.

Experimental Results on Dissociative Electron Attachment to $n-C_{N-2N+1}H_{2N+1}Br$

The yield of $Br^-$ as a function of electron energy from $n-C_{N-2N+1}H_{2N+1}Br$ has been measured with the aid of a TOFMS. Several ion current curves for the $Br^-$ from $n-C_{N-2N+1}H_{2N+1}Br$ were taken for each molecule to determine the approximate shapes of the dissociative attachment resonances and the full widths at half height. The widths of these resonances for each molecule are presented in Table III. The energy scale calibrations for these resonances have been determined from the swarm-beam combination described later in this section. The relative intensities of some of these resonances with the intensity of $n-C_{10}H_{21}Br$ normalized to one, as measured by the beam experiment, are presented in Table IV. These relative intensities do not yield as accurate a measure as the attachment cross sections obtained through the swarm-beam combination primarily
Figure 23. Dissociation energy $D(n-C_{N\,2N+1}\,Br)$ as a function of the number of carbon atoms $N$ for the molecules $n-C_{N\,2N+1}Br$. 
TABLE III
DATA SUMMARY FOR THE FORMATION OF Br$^-$ FROM $n$-C$_{N+1}$H$_{2N}$ Br VIA DISSOCIATIVE ELECTRON ATTACHMENT

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Reduced Mass</th>
<th>$\mu$</th>
<th>Br$^-$ Resonance Width (eV)</th>
<th>Average Br$^-$ Resonance Width (eV)</th>
<th>Average Reference SF$_5^-$ Resonance Width (eV)</th>
<th>Normalized Br$^-$ Resonance Width(a) (eV)</th>
<th>Br$^-$ Peak Energy(b) (eV)</th>
<th>Peak Cross Section(b) ($10^{-18} \text{ cm}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2H_5Br$</td>
<td>21.3</td>
<td>46,46,46,49,50,50,56,57</td>
<td>0.50 ± 0.04</td>
<td>0.35</td>
<td>0.51 ± 0.04</td>
<td>0.76</td>
<td>3.95</td>
<td></td>
</tr>
<tr>
<td>$n-C_3H_7Br$</td>
<td>28.0</td>
<td>48,50,50,52,55,58,58,60</td>
<td>0.54 ± 0.04</td>
<td>0.36</td>
<td>0.54 ± 0.04</td>
<td>0.74</td>
<td>4.14</td>
<td></td>
</tr>
<tr>
<td>$n-C_4H_9Br$</td>
<td>33.3</td>
<td>40,47,48,48,49</td>
<td>0.47 ± 0.03</td>
<td>0.33</td>
<td>0.51 ± 0.03</td>
<td>0.72</td>
<td>5.52</td>
<td>8</td>
</tr>
<tr>
<td>$n-C_5H_{11}Br$</td>
<td>37.6</td>
<td>40,42,47,47,48,48,52</td>
<td>0.46 ± 0.04</td>
<td>0.36</td>
<td>0.46 ± 0.04</td>
<td>0.70</td>
<td>6.14</td>
<td></td>
</tr>
<tr>
<td>$n-C_6H_{13}Br$</td>
<td>41.2</td>
<td>29,37,39,41,43,52</td>
<td>0.40 ± 0.07</td>
<td>0.34</td>
<td>0.42 ± 0.07</td>
<td>0.73</td>
<td>7.41</td>
<td></td>
</tr>
<tr>
<td>$n-C_7H_{15}Br$</td>
<td>44.2</td>
<td>35,40,41,42,42,43,44,50,53,54,54,57,58,58</td>
<td>0.49 ± 0.07</td>
<td>0.40</td>
<td>0.44 ± 0.07</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>$n-C_8H_{17}Br$</td>
<td>46.8</td>
<td>46,46,46,51,58</td>
<td>0.49 ± 0.05</td>
<td>0.35</td>
<td>0.50 ± 0.05</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>$n-C_{10}H_{21}Br$</td>
<td>51.0</td>
<td>52,53</td>
<td>0.52</td>
<td>0.36</td>
<td>0.52</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>
TABLE III (continued)

\[ ^{a}\text{Normalized to an average SF}_{5}^{-}\text{ resonance width (column 5) of 0.36 eV.} \]

\[ ^{b}\text{Obtained using the swarm-beam combination.} \]
<table>
<thead>
<tr>
<th>Molecule</th>
<th>Peak Intensity Ratio(^a)</th>
<th>Peak Cross Section Ratio(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_5\text{Br})</td>
<td>0.61</td>
<td>0.49</td>
</tr>
<tr>
<td>(\text{n-C}_4\text{H}_9\text{Br})</td>
<td>0.79</td>
<td>0.68</td>
</tr>
<tr>
<td>(\text{n-C}<em>6\text{H}</em>{13}\text{Br})</td>
<td>0.91</td>
<td>0.91</td>
</tr>
<tr>
<td>(\text{n-C}<em>6\text{H}</em>{17}\text{Br})</td>
<td>0.95</td>
<td>----</td>
</tr>
<tr>
<td>(\text{n-C}<em>{10}\text{H}</em>{21}\text{Br})</td>
<td>1.00</td>
<td>----</td>
</tr>
</tbody>
</table>

\(^a\) Ratio of the \(\text{Br}^-\) peak intensity from \(\text{n-C}_N\text{H}_{2N+1}\text{Br}\) to the \(\text{Br}^-\) peak intensity from \(\text{n-C}_{10}\text{H}_{21}\text{Br}\) obtained directly by the beam method.

\(^b\) Ratio of the peak electron attachment cross section for the formation of \(\text{Br}^-\) from \(\text{n-C}_N\text{H}_{2N+1}\text{Br}\) to the peak electron attachment cross section for the formation of \(\text{Br}^-\) from \(\text{n-C}_6\text{H}_{13}\text{Br}\) (taken as 0.91) obtained from cross section data in Table III, page 99.
because the relative current intensities are affected by poor and non-uniform ion collection efficiency of TOFMS's. The numbers in the second column of Table IV are, however, in agreement with the ratios of the absolute electron attachment cross sections determined by the swarm-beam combination, which are shown in the third column of Table IV.

Swarm-beam combinations (see Chapter III) were performed through the use of the Br⁻ resonance shapes from this study and the electron attachment rates of Christodoulides and Christophorou (1969). The peak electron attachment cross sections and the energy scale calibrations determined in this manner are presented in Table III for Br⁻ from C₂H₅Br, n-C₃H₇Br, n-C₄H₉Br, n-C₅H₁₁Br, n-C₆H₁₃Br, and n-C₇H₁₉Br.

The following Br⁻ resonances from C₂H₅Br, n-C₃H₇Br, n-C₄H₉Br, n-C₅H₁₁Br, n-C₆H₁₃Br, n-C₇H₁₉Br, n-C₈H₁₇Br, and n-C₁₀H₂₁Br were taken under similar experimental conditions. Filament current was about 1.7 amps and collector current was about 5 x 10⁻⁹ amps during all the runs. The temperature in the collision chamber was slightly above room temperature, and it was assumed that this collision chamber temperature was below the decomposition temperatures of all the molecules studied. The decomposition temperatures of all the molecules studied are above room temperature. Gosavi and Rao (1968) have found the decomposition temperatures of n-C₇H₁₅Br, n-C₈H₁₇Br, and n-C₁₀H₂₁Br to be 68°, 76°, and 84°C, respectively. The sample gas pressure was about 1 x 10⁻⁴ during the measurements.

1. C₂H₅Br: Figure 24 shows the yield of Br⁻ from C₂H₅Br as a function of electron energy. This curve is the average of eight consistent runs. The dissociative electron attachment
Figure 24. Br$^-$ current from C$_2$H$_5$Br as a function of electron energy $\varepsilon$. 
cross section for the formation of Br\textsuperscript{-} from C\textsubscript{2}H\textsubscript{5}Br was found to be equal to 3.95 x 10\textsuperscript{-18} cm\textsuperscript{2} at the peak energy 0.76 eV as determined by the swarm-beam combination.

2. n-C\textsubscript{3}H\textsubscript{7}Br: Figure 25 shows the yield of Br\textsuperscript{-} from n-C\textsubscript{3}H\textsubscript{7}Br as a function of electron energy. Eight consistent runs are averaged to make up this curve. The peak value of $\sigma_{da}$ for the formation of Br\textsuperscript{-} from n-C\textsubscript{3}H\textsubscript{7}Br was found to be 4.14 x 10\textsuperscript{-18} cm\textsuperscript{2} through a swarm-beam combination, and the energy of this peak was 0.74 eV.

3. n-C\textsubscript{4}H\textsubscript{9}Br: The Br\textsuperscript{-} yield from n-C\textsubscript{4}H\textsubscript{9}Br as a function of electron energy is shown in Figure 26. Here six consistent runs are averaged. In a preliminary study of this Br\textsuperscript{-} resonance from n-C\textsubscript{4}H\textsubscript{9}Br, five runs were taken three months prior to the time when the data presented in Figure 26 were taken. Both sets of data were in good agreement, and the full widths at half height were 0.50 eV for the average of the preliminary data and 0.48 eV for the data plotted in Figure 26. Thus, these curves were not only reproducible from day to day, as indicated by the good agreement among the curves used to make up Figure 26, but also reproducible after three months with a different source filament and different source cleanliness.

The dissociative attachment cross section for the formation of Br\textsuperscript{-} from n-C\textsubscript{4}H\textsubscript{9}Br was determined to be 5.52 x 10\textsuperscript{-18} cm\textsuperscript{2} at the resonance peak through a swarm-beam combination, and the energy at this peak was found to be 0.72 eV.
Figure 25. Br\textsuperscript{-} current from n-C\textsubscript{2}H\textsubscript{4}Br as a function of electron energy $\epsilon$. 
Figure 26. $\text{Br}^-$ current from $n$-$\text{C}_4\text{H}_9\text{Br}$ as a function of electron energy $\varepsilon$. 
4. \( n-C_{11}H_{11}Br \): The \( Br^- \) yield from \( n-C_{11}H_{11}Br \) as a function of electron energy is shown in Figure 27. This curve is the average of six consistent runs. From the swarm-beam combination the dissociative electron attachment cross section for the formation of \( Br^- \) from \( n-C_{11}H_{11}Br \) was found to be \( 6.14 \times 10^{-18} \) cm\(^2\) at the peak energy. The energy of this peak was found to be equal to 0.70 eV.

5. \( n-C_{13}H_{13}Br \): The yield as a function of electron energy for \( Br^- \) from \( n-C_{13}H_{13}Br \) is shown in Figure 28. Here six consistent runs are averaged. The dissociative electron attachment cross section for this process was determined to be \( 7.41 \times 10^{-18} \) cm\(^2\) at the peak energy found equal to 0.73 eV through the swarm-beam combination. Figure 29 shows the dissociative electron attachment cross section functions for the formation of \( Br^- \) from \( C_2H_5Br \), \( n-C_3H_7Br \), \( n-C_4H_9Br \), \( n-C_5H_{11}Br \), and \( n-C_6H_{13}Br \). These important results will be discussed in detail later in this chapter.

6. \( n-C_{15}H_{15}Br \), \( n-C_{17}H_{17}Br \), \( n-C_{21}H_{21}Br \): The \( Br^- \) resonances in these three molecules were recorded in a manner similar to the resonances for the other less massive alkyl bromides described above. The data taken on these resonances are compiled in Table III, page 99. Furthermore, it has been evidenced through a swarm experiment study [Christodoulides and Christophorou (1969)] that the \( Br^- \) dissociative electron attachment resonance in these molecules peaks at lower energies than the \( Br^- \) resonances discussed above. Because of limitations on the accuracy
Figure 27. Br\textsuperscript{-} current from n-C\textsubscript{11}H\textsubscript{21}Br as a function of electron energy $\varepsilon$. 
Figure 28. $\text{Br}^{-}$ current from $\text{n-C}_6\text{H}_{13}\text{Br}$ as a function of electron energy $\varepsilon$. 
Figure 29. Dissociative electron attachment cross section $\sigma_{da}(\epsilon)$ as a function of electron energy $\epsilon$ for $n$-C$_{N}$H$_{2N+1}$Br where $2 \leq N \leq 6$. 
of absolute energy scale determinations for these molecules, the study of Br\textsuperscript{−} from n-C\textsubscript{7}H\textsubscript{15}Br, n-C\textsubscript{9}H\textsubscript{17}Br, and n-C\textsubscript{10}H\textsubscript{21}Br was not carried further.

Christophorou and Stockdale (1968) have analyzed \( \sigma_{da} \) peak values versus peak energy for thirty molecules and discussed this energy dependence of \( \sigma_{da} \) within the framework of resonant scattering theory. The present data for n-C\textsubscript{N}H\textsubscript{2N+1}Br where \( 2 \leq N \leq 6 \), when analyzed in a similar fashion, are in agreement with the data plotted by Christophorou and Stockdale.

While measuring the yields of Br\textsuperscript{−} from all of the above molecules, a small amount of SF\textsubscript{6} (\( \approx 10^{-6} \) torr) was also introduced into the system. This SF\textsubscript{6} was placed in the system so that the SF\textsubscript{5}\textsuperscript{−} resonance at \( \sim 0.35 \) eV [Chen and Chantry (1969) and Christophorou, McCorkle, and Carter (1970)] could be used as a standard reference resonance. In some cases over two hours were necessary for conditions in the TOFMS to stabilize. Before stabilization was reached, both the SF\textsubscript{5}\textsuperscript{−} and the Br\textsuperscript{−} resonances were found to be broad and shifted in energy with respect to the resonances taken under stable conditions in the TOFMS. When the SF\textsubscript{5}\textsuperscript{−} resonance was stabilized to a constant width of \( \sim 0.36 \) eV, the Br\textsuperscript{−} resonances were taken. The width of the SF\textsubscript{5}\textsuperscript{−} resonance was periodically taken to check the conditions in the TOFMS. Almost as many SF\textsubscript{5}\textsuperscript{−} resonances were recorded as Br\textsuperscript{−} resonances while studying the Br\textsuperscript{−} resonances.

After initial stable conditions were achieved for each molecule, the widths of both the SF\textsubscript{5}\textsuperscript{−} and the Br\textsuperscript{−} resonances remained constant. The average widths of these reference SF\textsubscript{5}\textsuperscript{−} resonances, taken for each n-C\textsubscript{N}H\textsubscript{2N+1}Br molecule, are given in Table III, page 99. Christophorou,
McCorkle, and Carter (1970) have averaged fifteen of the SF\textsubscript{5} resonances from the present study and used the resulting shape to determine the dissociative electron attachment cross section for the formation of SF\textsubscript{5} from SF\textsubscript{6}. This cross section is shown in Figure 30, where the peak cross section value of $4.9 \times 10^{-18}$ cm\textsuperscript{2} and the peak energy of 0.37 eV are determined from a swarm-beam combination.

Discussion of Results

**Isotope effects based upon a diatomic molecule model.** The molecules $n$-C\textsubscript{N}H\textsubscript{2N+1}Br where $N = 2, 3, 4, 5, 6, 7, 8,$ and $10$ have been found to form Br\textsuperscript{-}, a permanent fragment ion, via a dissociative electron attachment process upon electron impact in the TOFMS. The energy of the peak of these resonances was approximately the same for the molecules where $2 \leq N \leq 6$, and this energy was 0.73 eV. As can be seen from Table III, page 99, this peak energy varied from 0.70 eV for $n$-C\textsubscript{7}H\textsubscript{15}Br to 0.76 eV for C\textsubscript{2}H\textsubscript{12}Br in the molecules $n$-C\textsubscript{N}H\textsubscript{2N+1}Br where $2 \leq N \leq 6$. The peak value of the cross section function for the formation of Br\textsuperscript{-} from $n$-C\textsubscript{N}H\textsubscript{2N+1}Br where $2 \leq N \leq 6$ is plotted as a function of $\mu^{1/4}$, the reduced mass to the one fourth power, in Figure 31. The quantity $\mu$, given by Equation (VI-3), is the reduced mass of the $n$-C\textsubscript{N}H\textsubscript{2N+1}-Br diatomic-like system. The two components of this system are taken to be C\textsubscript{N}H\textsubscript{2N+1} and Br

$$\mu = \frac{m_{C_nH_{2N+1}} m_{Br}}{m_{C_nH_{2N+1}} + m_{Br}}.$$  \hspace{1cm} (VI-3)

In Equation (VI-3), $m_{C_nH_{2N+1}}$ is the mass of C\textsubscript{N}H\textsubscript{2N+1}, and $m_{Br}$ is the mass of Br. The reduced mass $\mu$ is listed in column two of Table III.
Figure 30. $\text{SF}_5^-$ current from $\text{SF}_6$ as a function of electron energy $\epsilon$. 
Figure 31. Maximum dissociative electron attachment cross section \( \sigma_{da}(\varepsilon) \) as a function of \( \mu^4 \) for \( n-C_NH_{2N+1}Br \) where \( 2 \leq N \leq 6 \).
As discussed on page 29, if the effect of the Gaussian factor (small anyway) in Equation (II-19) is neglected, and the survival probability is large, that is, autoionization is slow compared to dissociation, then Equation (II-19) predicts that $\sigma_{da} \propto \mu^{1/4}$. It is apparent from Figure 31 that $\sigma_{da}$ does increase approximately with $\mu^{1/4}$ for these molecules. This increase is very likely the result of an inverse isotope effect due to diatomic-like behavior of these molecules.

The width of the resonance in the first five molecules, for which the peak cross section has been determined, decreases with increasing reduced mass. This could be accounted for by the narrowing of the Gaussian factor in Equation (II-19) with increasing $\mu$. This decrease in resonance width when $2 \leq N \leq 6$ is thought to be a genuine molecular effect rather than an experimental effect.

**Toxicities.** No correlation can be found between the peak dissociative electron attachment cross section values and the toxicities of the molecules $C_2H_5Br$, $n-C_3H_7Br$, $n-C_4H_9Br$, $n-C_5H_{11}Br$, and $n-C_6H_{13}Br$. When thermodynamic activity is used as the toxicity index, the toxicities of the series are related as follows:

\[
\left(\frac{P_s}{P_t}\right)_{CH_3Br} \gg \left(\frac{P_s}{P_t}\right)_{C_2H_5Br} > \left(\frac{P_s}{P_t}\right)_{n-C_3H_7Br} > \left(\frac{P_s}{P_t}\right)_{n-C_4H_9Br} \\
\approx \left(\frac{P_s}{P_t}\right)_{n-C_5H_{11}Br} > \left(\frac{P_s}{P_t}\right)_{n-C_6H_{13}Br},
\]

where $P_t$ is the pressure of the vapor of a substance at which a certain toxic effect is produced, and $P_s$ is the saturated vapor pressure at the temperature of the system. Ferguson and Pirie (1948) and Hassall (1957)
have discussed the toxicities of this series in the gas phase, and Moje (1963) has measured the toxicities in the liquid phase of the n-alkyl bromides relative to n-butylbromide (n-C$_4$H$_9$Br). Restricting discussion to the gas phase, one can interpret relation (VI-4) in the following way. In the vapor phase the thermodynamic activity of a substance at any concentration is the relative saturation of the vapor. The thermodynamic activity at which the substance causes the specific toxic effect is equal to $P_t/P_s$. Therefore, the toxicity, or the inverse of the thermodynamic activity, decreases with increasing $N$ in the series n-C$_N$H$_{2N+1}$Br where $1 < N < 6$ according to the relation (VI-4). Since the dissociative electron attachment cross section increases with increasing $N$ in the series n-C$_N$H$_{2N+1}$Br where $2 < N < 6$, no direct correlation can be seen between the dissociative electron attachment cross sections and the toxicities of the molecules in this series. The higher toxicities for the lower members of this series has been attributed to their higher chemical reactivity. It may, however, be inferred that if dissociative electron attachment is related to the toxicity of the molecules in the series n-C$_N$H$_{2N+1}$Br, then the increase in toxicity with increasing $N$ may reflect the toxic effect of radicals produced following dissociative attachment. In general, radicals become more toxic as $N$ increases.

**Potential energy curves.** The Morse functions for the neutral n-$C_{4}H_{9}$-Br, n-$C_{5}H_{11}$-Br, and n-$C_{6}H_{13}$-Br systems are shown in Figures 32, 33, and 34. The dissociation energy $D(n-C_{N}H_{2N+1}$-Br) was assumed to be 2.93 eV, and the vibration frequency of the C-Br mode was assumed to be 643 cm$^{-1}$ [Bentley, McDevitt, and Rozek (1964)] in the Morse function calculations for each molecule. The probability density function for the
Figure 32. Schematic potential energy diagram for \( n\text{-C}_4\text{H}_9\text{Br} \) and \( n\text{-C}_4\text{H}_9\text{Br}^* \).
Figure 33. Schematic potential energy diagram for \( n-C_{6}H_{11}Br \) and \( n-C_{6}H_{11}Br^- \).
Figure 34. Schematic potential energy diagram for n-C₆H₁₃Br and n-C₆H₁₃Br•.
ground state of each molecule, given by Equation (VI-5), has been found by squaring the absolute value of the ground state wave function

$$|\psi(R-R_e)|^2 = \psi^2(R-R_e) = \sqrt{\frac{\alpha}{\pi}} e^{-\alpha(R-R_e)^2}. \quad (VI-5)$$

In Equation (VI-5), \(R\) is the internuclear separation of \(C_{N}H_{2N+1}\) and \(Br\), \(R_e\) is the equilibrium separation, and \(\alpha\) is given by

$$\alpha = \frac{\hbar^2 \mu}{N_o c} \frac{\omega c}{h}, \quad (VI-6)$$

where \(\omega\) is the vibration frequency of the C-Br mode in wave numbers, \(c\) is the velocity of light, and \(N_o\) is Avogadro's number. An attempt to represent the \(n-C_{N}H_{2N+1}Br^{-}\) potential energy function has been made by correlating points on the \(\psi^2_o\) curve with points on the negative ion current yield which have the same intensity relative to the peak value of \(\psi^2_o\) and the peak value of the \(Br^{-}\) resonance. For example, the peak of the \(Br^{-}\) curve for \(n-C_{4}H_{9}Br\) occurs at 0.72 eV from Figure 26, page 106. Therefore, the position on the \(n-C_{N}H_{2N+1}Br^{-}\) potential energy function corresponding to this energy and peak intensity would be 0.72 eV above the ground state of the \(n-C_{4}H_{9}Br\) molecule and at the same internuclear separation as the \(\psi^2_o\) peak. It must be noted that this procedure for approximating the upper potential energy curves yields only a rough schematic representation of the actual potential energy surface. See, for example, O'Malley (1966) for a discussion of the precautions that must be taken when one interprets negative ion potential curves.
In Figure 32, page 117, a function $U(R)$, given by Equation (VI-7), is plotted to determine whether this function is in agreement with the experimentally determined complex negative ion function

$$U(R) = \frac{A}{R^2} + B.$$  \hspace{1cm} (VI-7)

It has been suggested by Chen (1963) that Equation (VI-7) is a good representation of the complex negative ion function. However, as can be seen from Figure 32, $U(R)$, where $R$ is the internuclear separation and $A$ and $B$ are constants, is not a good fit to the $n-C_{4}H_{7}Br^{-}$ potential curve determined by the procedure described above.

II. AZULENE

In addition to the two electron capture processes discussed in Chapter V for azulene, the dissociative electron attachment process

$$C_{10}H_{8} + e^{-} \rightarrow C_{10}H_{7}^{-} \rightarrow C_{10}H_{7}^{-} + H$$ \hspace{1cm} (VI-8)

was also studied. This process was extensively studied by the electron beam method because the $C_{10}H_{7}^{-}$ upon initial inspection appeared to be metastable. However, upon further investigation it was found that the neutral molecules that appeared to be the result of $C_{10}H_{7}^{-}$ autoionization were actually $C_{10}H_{8}$ molecules which had autoionized following the formation of $C_{10}H_{7}^{-}$ by electron scavenging. The $C_{10}H_{7}^{-}$ resonance was measured 14 times with the RPD method and 6 times without the RPD method. There was significant scatter in the points for spectra taken with the
RPD method because the $C_{10}H^{-}$ signal was ~ 500 times less intense than the $C_{10}H_8^-$ signal at thermal energies. However, the spectra taken without the RPD method, one of which is shown in Figure 35a, were consistent. The best resonance taken with the RPD method and the thermal parent ion process (dashed curve) are shown in Figure 35b. Both $C_{10}H_7^{-}$ spectra taken with the RPD method and without the RPD method show structure due to electronic excitation of the $C_{10}H^{-}$. The energy scales for Figures 35a and 35b were calibrated with the $CH_3^-$ and $O^-$ resonances from $CH_3CHO$ at 6.0 and 9.4 eV [Dorman (1966)] and $H^-$ from $H_2O$ at 6.4 and 8.6 eV [Compton and Christophorou (1967)]. The parent negative ion at thermal energies and the $C_{10}H_7^-$ dissociation fragment were the only negative ions of azulene seen in the TOFMS. The thermal process forms metastable parent ions, and the dissociative attachment process in the range 5.5 to 9.5 eV forms permanent $C_{10}H_7^-$ fragments. To verify that the process in the range 5.5 to 9.5 eV was the result of a single interaction and not the result of electron scavenging, the pressure dependence of the $C_{10}H_7^-$ current was measured. The $C_{10}H_8$ pressure versus the negative ion currents of $C_{10}H_8^-$ at thermal energies and $C_{10}H_7^-$ at 7 eV are plotted in Figures 36 and 37. Since these log-log plots form straight lines with slopes equal to one, the following processes are suggested:

$$C_{10}H_8 + e \text{ (thermal)} \rightarrow C_{10}H_8^- \rightarrow C_{10}H_8 + e \quad \text{(VI-9)}$$

$$C_{10}H_8 + e \text{ (~ 7 eV)} \rightarrow C_{10}H_8^- \rightarrow C_{10}H_7^- + H + e \quad \text{(VI-10)}$$
Figure 35. $C_{10}H_{7}^-$ current as a function of electron energy (a) not using the RPD method and (b) using the RPD method.
Figure 36. $C_{10}H_8^-$ current as a function of $C_{10}H_8$ pressure $P$. 
Figure 37. $\text{C}_{10}^7\text{H}_8^*$ current as a function of $\text{C}_{10}^7\text{H}_8$ pressure $P$. 

SLOPE $\approx 1$
III. ACETALDEHYDE

Acetaldehyde (CH$_3$CHO) is physically important because of the many dissociative electron attachment processes that take place upon low energy electron impact. It is also biologically important because it appears throughout the body, for example, in the breath and saliva [Larsson (1965)], in the urine [Said and Fleita (1965)], and in the blood [McCord and Gadsen (1964) and Baker, Alenty, and Zack (1969)]. Its presence in the blood affects arterial shrinkage in relation to arteriosclerosis, and CH$_3$CHO is a major metabolite of ethanol. Also, CH$_3$CHO is present as a pollutant in automobile exhaust [Barber and Lodge (1963)], treated waste water [Kuchumova, Verigo, and Mamontova (1963)], and cigaret smoke [Laurene, Lyerly, and Young (1964)]. Acetaldehyde is also present in many foods such as beef [Sanderson, Pearson, and Schweigert (1966)], chicken [Minor et al. (1965)], butter [Winter et al. (1963)], apples [Nishimura and Hirose (1964)], and bread [Rothe and Thomas (1963)].

As stated in Chapter V, no long-lived parent negative ion was found in acetaldehyde. However, the permanent fragment ions CH$_3^-$, O$^-$, CHCO$^-$, and CH$_3$CO$^-$ were found to form via dissociative electron attachment. Six measurements were taken of each of the O$^-$, CH$_3^-$, and CH$_3$CO$^-$ resonances, and five measurements were taken of the CHCO$^-$ resonance with the RPD method employed. Two measurements were taken of each of the above resonances without employing the RPD method. These measurements were all consistent, and the energy scale for each resonance was calibrated with the H$^-$ resonances at 6.4 and 8.6 eV from H$_2$O [Compton and
Christophorou (1967)]. The negative ion yields as a function of electron energy for \( 0^- \) and \( \text{CH}_3^- \) from \( \text{CH}_3\text{CHO} \) are shown in Figure 38. These data were taken with the RPD method. These same resonances, taken without the RPD method, are shown in Figure 39. Also shown in this figure are the results of Dorman (1966) for \( \text{CH}_3^- \) and \( 0^- \), which were taken not using the RPD method. The energy dependences of the negative ion yields are shown for \( \text{CH}_3\text{CO}^- \) and \( \text{CHCO}^- \) in Figure 40. These data were taken with the RPD method. In Figure 41 similar data are plotted, but for these, the RPD method was not employed. Also shown in Figure 41 are the results of Dorman (1966) for \( \text{CH}_3\text{CO}^- \) and \( \text{CHCO}^- \), taken without the RPD method. The relative intensities of \( \text{CH}_3^- \) to \( 0^- \) and \( \text{CH}_3\text{CO}^- \) to \( \text{CHCO}^- \), as shown in Figures 38, 39, 40, and 41 for the present work, are the experimentally determined relative intensities. In the present study the \( \text{CH}_3^- \) current was found to be approximately half as intense as that for \( 0^- \), and the \( \text{CH}_3\text{CO}^- \) and \( \text{CHCO}^- \) signals were approximately an order of magnitude less intense than the \( 0^- \) signal. The intensities of the work of Dorman (1966), shown in Figures 39 and 41, are arbitrary. The present study and the work of Dorman (1966) are in fair agreement with respect to both the resonance energies and shapes for \( \text{CH}_3^- \), \( 0^- \), \( \text{CH}_3\text{CO}^- \), and \( \text{CHCO}^- \) taken without the RPD method (see Figures 39 and 41). In addition to the \( \text{CH}_3^- \), \( 0^- \), \( \text{CH}_3\text{CO}^- \), and \( \text{CHCO}^- \) resonances shown in Figures 39 and 41, Dorman (1966) observed weaker resonances in \( \text{CHCO}^- \) at \( \sim 6 \) eV, \( \text{CH}_3\text{CO}^- \) at \( \sim 9 \) eV, \( \text{OH}^- \) at \( \sim 9 \) eV, \( \text{CH}_2^- \) at \( \sim 10 \) eV, and stronger resonances in \( \text{H}^- \) at \( \sim 6 \) eV and \( \sim 8 \) eV. These weaker resonances seen by Dorman (1966) were either too weak to be seen in the TOFMS used in the present study or masked by stronger resonances of approximately the same mass.
Figure 36. CH$_3^-$ and O$^-$ currents from CH$_3$CHO as a function of electron energy $\epsilon$ with the RPD method.
Figure 39. $\text{CH}_3^-$ and $\text{O}^-$ currents from $\text{CH}_3\text{CHO}$ as a function of electron energy $\epsilon$ without the RPD method.
Figure 40. \( \text{CH}_3\text{CO}^- \) and \( \text{CHCO}^- \) currents from \( \text{CH}_3\text{CHO} \) as a function of electron energy \( \epsilon \) with the RPD method.
Figure 41. CH$_3$CO$^-$ and CHCO$^-$ currents from CH$_3$CHO as a function of electron energy $\varepsilon$ without the RPD method.
and energy. The fact that no H⁻ was seen from CH₃CHO in the present study could be the result of deflection of the H⁻ ion beam by the source magnets in the TOFMS.

The bond dissociation energies in CH₃CHO are D(CH₃ - CHO) \approx 3.0 \text{ eV}, D(CH₃CO-H) \approx 3.4 \text{ eV} [Vedeneyev et al. (1966)], and D(0 = C) \approx 7.6 \text{ eV} [Cottrell (1958)]. As pointed out by Dorman (1966), the coincidences in energy of the CH₃ and CH₃CO⁻ resonances and the O⁻ and CHCO⁻ resonances indicate that CH₃⁻ and CH₃CO⁻ probably proceed via the same CH₃CHO⁻* state, and 0⁻ and CHCO⁻ probably proceed via the same CH₃CHO⁻* state.

IV. SUMMARY

The dissociative electron attachment process

\[ AX + e \rightarrow AX^- + P_{da} \rightarrow A(\text{or A}^*) + X^- \text{ (or X}^\text{*}) \]  \hspace{1cm} (I-3)

has been studied in several physically and biologically important molecules. The alkyl bromides n-CₙH₂₀₋₂N⁺Br where 2 \leq N \leq 6 have been found to exhibit diatomic-like characteristics which are reflected in the observed dependences of both the \( \sigma_{da} \) for the formation of Br⁻ under electron impact and the width of the Br⁻ resonances on \( \mu \), the reduced mass.

A broad, structured C₁₀H⁷⁻ resonance from 5.5 to 9.5 eV was found in azulene, and the dissociation fragments O⁻, CH₃⁻, CH₃CO⁻, and CHCO⁻ from acetaldehyde were studied. These processes are particularly interesting because of the functions of azulene and acetaldehyde in many
biological processes. The peak energies and the peak dissociative electron attachment cross sections for the formation of the fragment negative ions studied in this chapter are summarized in the next chapter.
CHAPTER VII

SUMMARY

I. LONG-LIVED PARENT POLYATOMIC NEGATIVE IONS

Long-lived parent negative ions have been found to form in
p-benzoquinone, 1,4-naphthoquinone, azulene, cinnamaldehyde, o-, m-, and p-nitrotoluene, sulfur hexafluoride, and hexafluoroacetone under low energy electron impact. No long-lived parent negative ions were
found to form in acetaldehyde, benzaldehyde, 2-methyl 1,4-naphthoquinone, nitropropane, tetranitromethane, tetraethyl-lead, and \( n-C_{N-2N+1}Br \) where \( N = 2, 3, 4, 5, 6, 7, 8 \), and 10. The inability of these molecules to form
long-lived parent negative ions is probably due to the availability of
only a small number of vibrational modes participating in the sharing of
the excess energy of negative ion formation. Most important among the
metastable parent negative ions observed are those formed via a nuclear-
excited Feshbach resonance in 1,4-naphthoquinone and those formed via
an electron-excited Feshbach resonance in p-benzoquinone. For the
systems that form long-lived parent negative ions, \( \sigma_a \) and \( \tau \) were mea-
sured and related through detailed balancing to \( N \). This allowed deter-
mination of approximate EA values for these molecules. The values of
\( \sigma_a(\nu) \), \( \tau(\varepsilon) \), and EA found for the nondissociative electron attachment
processes studied are summarized in Table V.

The electron-excited Feshbach resonance in p-benzoquinone is the
first long-lived electron-excited Feshbach resonance to be reported.
The variation of the mean autoionization lifetime from \( \sim 50 \mu \text{sec at 1.7 eV} \)

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### TABLE V

**SUMMARY OF NONDISSOCIATIVE ELECTRON ATTACHMENT PROCESSES**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Peak Cross Section (cm²)</th>
<th>Lifetime (µsec)</th>
<th>Electron Affinity (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-C₆H₄O₂</td>
<td>6.7 x 10⁻¹⁷ at 2.1 eV</td>
<td>48 at 1.7 eV to 8 at 3.2 eV</td>
<td>0.2 for first triplet state</td>
</tr>
<tr>
<td></td>
<td>3.5 x 10⁻¹⁹ at ~0 eV</td>
<td></td>
<td>~0 for ground state</td>
</tr>
<tr>
<td>1,4-C₁₀H₆O₂</td>
<td>6.17 x 10⁻¹⁵ at ~0 eV</td>
<td>350 at ~0 eV to 15 at 1.3 eV</td>
<td>0.60 for ground state</td>
</tr>
<tr>
<td>C₁₀H₈</td>
<td>3.5 x 10⁻¹⁵ at ~0 eV</td>
<td>7 at ~0 eV</td>
<td>0.46 for ground state</td>
</tr>
<tr>
<td></td>
<td>1 x 10⁻¹⁵ at ~0.3 eV</td>
<td>&lt; 1 at 0.3 eV</td>
<td></td>
</tr>
<tr>
<td>C₆H₅CH:CHCHO</td>
<td>12 at ~0 eV</td>
<td></td>
<td>0.82&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>o-C₆H₄CH₃NO₂</td>
<td>13 at ~0 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-C₆H₄CH₃NO₂</td>
<td>19 at ~0 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-C₆H₄CH₃NO₂</td>
<td>14 at ~0 eV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF₆</td>
<td>1.17 x 10⁻¹⁴ at ~0 eV</td>
<td>32 at ~0 eV</td>
<td>1.49&lt;sup&gt;c&lt;/sup&gt;, 1.4&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>C₃F₆</td>
<td>~6.1 x 10⁻¹⁷ at ~0 eV</td>
<td>~60 at ~0 eV</td>
<td></td>
</tr>
</tbody>
</table>
### TABLE V (continued)


to $\sim 8 \mu$sec at 3.2 eV for the electron-excited Feshbach resonance in p-benzoquinone provided the first evidence that $\tau$ for long-lived parent negative ion resonances is energy dependent. Following the investigation of p-benzoquinone, an equally interesting variation of $\tau$ from $\sim 350 \mu$sec at thermal energies to $\sim 15 \mu$sec at 1.3 eV was observed in 1,4-naphthoquinone. In addition to this $\tau(e)$ behavior, vibrational structure was evidenced in the 1,4-naphthoquinone resonance. The presence of this vibrational excitation is compatible with the decrease in $\tau$ with increased electron energy. As higher vibrational states are populated, the compound negative ion state $NQ^{-*}$ has more available neutral molecular states to which it can decay. This increase in states to which the excited ion can decay decreases the autoionization lifetime $\tau$ of the ion.

Both a subthermal peaking parent negative ion resonance and a capture process associated with electron attachment in the first triplet state of azulene were found. The similar systems o-, m-, and p-nitrotoluene are interesting because $\tau$ for o-NT and p-NT is approximately the same ($\tau_{o-NT} = 13 \mu$sec and $\tau_{p-NT} = 14 \mu$sec), but $\tau$ for m-NT has a significantly higher value of 19 $\mu$sec. This could be due to a higher electron attaching capacity for aromatic molecules with the nitro group in the meta position than in the ortho and para positions.

An attempt was made to study $\tau$ as a function of the number of vibrational degrees of freedom for the two groups of similar molecules $n-C_{N+2N+1}^N \text{NO}_2$ and $C(\text{NO}_2)_N$. However, nitropropane $[n-C_3^3\text{H}_7^7\text{NO}_2]$ and tetranitromethane $[C(\text{NO}_2)_4]$ were not found to form long-lived parent negative ions. It was assumed that the smaller molecules in these groups
did not form long-lived parent negative ions (probably because dissociative attachment breaks the system or autoionization occurs in \(\ll 10^{-6}\) sec); therefore, this investigation was carried no further.

II. DISSOCIATIVE ELECTRON ATTACHMENT

Dissociative electron attachment was studied in \(\text{C}_2\text{H}_5\text{Br}\), \(\text{n-C}_3\text{H}_7\text{Br}\), \(\text{n-C}_4\text{H}_9\text{Br}\), \(\text{n-C}_5\text{H}_{11}\text{Br}\), \(\text{n-C}_6\text{H}_{13}\text{Br}\), \(\text{n-C}_7\text{H}_{15}\text{Br}\), \(\text{n-C}_8\text{H}_{17}\text{Br}\), \(\text{n-C}_{10}\text{H}_{21}\text{Br}\), \(\text{CH}_3\text{CHO}\), and \(\text{C}_{10}\text{H}_8\) (azulene). The detailed results for the molecules \(\text{n-C}_N\text{H}_{2N+1}\text{Br}\) are presented in Table III, page 99. The dissociative electron attachment cross sections and the peak cross section energies for all the dissociative electron attachment processes studied are listed in Table VI. The Br resonances in \(\text{n-C}_N\text{H}_{2N+1}\text{Br}\) have been discussed in detail in Chapter VI. After analyzing the data taken on these systems, it can be concluded that the decrease in resonance widths with increased \(\mu\) for the molecules for which \(2 \leq N \leq 6\) can be explained by familiar diatomic-like behavior. Also, an inverse isotope effect is found for the dissociative electron attachment cross section which shows that the effect of autoionization on \(\sigma_{da}\) for these systems is negligible.

Among the physically significant findings of this study are determinations of the types of electron attachment processes which take place in polyatomic molecules upon low energy (\(< 15\) eV) electron impact. Also determinations of \(\sigma_a(\varepsilon)\), \(\sigma_{da}(\varepsilon)\), and \(\tau(\varepsilon)\) for these processes and the EA's of these molecules in both the ground and excited states have been made. Molecular and negative ion schematic potential energy functions have been drawn. These findings are helpful in determining molecular
### TABLE VI

**SUMMARY OF DISSOCIATIVE ELECTRON ATTACHMENT PROCESSES**

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Dissociation Fragment</th>
<th>Peak Cross Section (cm²)</th>
<th>Peak Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₅Br</td>
<td>Br⁻</td>
<td>3.95 x 10⁻¹⁸</td>
<td>0.76</td>
</tr>
<tr>
<td>n-C₃H₇Br</td>
<td>Br⁻</td>
<td>4.14 x 10⁻¹⁸</td>
<td>0.74</td>
</tr>
<tr>
<td>n-C₄H₉Br</td>
<td>Br⁻</td>
<td>5.52 x 10⁻¹⁸</td>
<td>0.72</td>
</tr>
<tr>
<td>n-C₅H₁₁Br</td>
<td>Br⁻</td>
<td>6.14 x 10⁻¹⁸</td>
<td>0.70</td>
</tr>
<tr>
<td>n-C₆H₁₃Br</td>
<td>Br⁻</td>
<td>7.41 x 10⁻¹⁸</td>
<td>0.73</td>
</tr>
<tr>
<td>n-C₇H₁₅Br</td>
<td>Br⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C₈H₁₇Br</td>
<td>Br⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-C₁₀H₂₁Br</td>
<td>Br⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₀H₈</td>
<td>C₁₀H₇⁻</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃CHO</td>
<td>CH₃⁻</td>
<td>6.1, 6.0&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O⁻</td>
<td>9.5, 9.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CH₃CO⁻</td>
<td>6.1, 6.0&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CHCO⁻</td>
<td>9.5, 9.4&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
</tbody>
</table>

structure and in understanding the slowing down of low energy electrons in matter. Many of the molecules included in this study are biologically important, and some of the fundamental molecular processes studied aid in the understanding of electron transport problems in radiation biology, radiation chemistry, and the life sciences.


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