

Ion cyclotron resonance studies of radiative and dissociative electron attachment processes at low pressures^{a)}

R. L. Woodin,^{b)} M. S. Foster,^{c)} and J. L. Beauchamp

Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

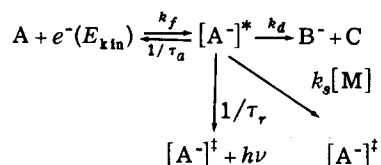
(Received 3 July 1979; accepted 14 August 1979)

Ion cyclotron resonance spectroscopy is used to measure nondissociative electron attachment rate constants for C₆F₆ (perfluorobenzene), C₇F₈ (perfluorotoluene), *c*-C₄F₈ (perfluorocyclobutane), and C₇F₁₄ (perfluoromethylcyclohexane) at low pressure (<10⁻⁶ Torr). Infrared emission is assumed to stabilize excited species leading to long-lived molecular negative ions. Combining the present data with negative ion lifetimes measured at low pressures by time-of-flight methods and electron attachment rates measured at high pressures in swarm experiments allows estimates of radiative lifetimes to be made. These all fall in the range from 0.4 to 1.5 msec, which are typical of infrared radiative lifetimes. Data are also presented for dissociative electron attachment to CCl₄, where the rate limiting step is shown to be thermalization of the electron energy distribution. A number of different buffer gases are examined and the ion cyclotron resonance results extrapolate to yield the attachment rate measured in high pressure swarm experiments.

I. INTRODUCTION

Studies of electron attachment processes using ion cyclotron resonance (ICR) techniques at first glance might appear to have generated more confusion than understanding relating to this important phenomenon.^{1,2} ICR experiments yield negative ion lifetimes¹ which are orders of magnitude longer than those measured using time-of-flight techniques.^{2,3} In addition, rate constants for electron attachment measured at the low pressures typical of ICR experiments (10⁻⁸–10⁻⁵ Torr) are orders of magnitude less than those measured in high pressure (carrier gas pressure usually in excess of 500 Torr) swarm experiments.²⁻⁴ It is well known that lifetimes and attachment rates are sensitive functions of the electron energy distribution.^{3,5,6} However, this alone does not adequately account for the apparent discrepancies among the reported studies of negative ion lifetimes and attachment rates.

The scheme depicted in Eq. (1) can be employed to describe



electron attachment.¹ Reaction of molecule A with an electron of kinetic energy E_{kin} results in formation of the excited negative ion $[A^-]^*$ which contains internal excitation at least equal to the electron affinity of A. The species $[A^-]^*$ may then autodetach an electron (with autodetachment lifetime τ_a), decompose (k_d), radiate (with radiative lifetime τ_r) or be collisionally stabilized ($k_s[M]$). The species $[A^-]^\ddagger$ may still possess internal excitation, but it is insufficient for autodetachment to be

energetically possible. Further radiative or collisional events lead to thermal equilibrium. Processes involving $[A^-]^*$ are expected to be sensitive to the internal energy content of $[A^-]^*$ and hence to the initial electron energy. In general, cross sections for nondissociative electron attachment show sharp maxima for low energy (~0 eV) electrons.^{3,4,6,7}

Earlier we presented an ICR study of SF₆ in which a radiative mechanism for formation of stable SF₆⁻ at low pressure was inferred.¹ In the present study we present results for nondissociative electron attachment to a wide variety of molecules, including C₆F₆ (perfluorobenzene), C₇F₈ (perfluorotoluene), *c*-C₄F₈ (perfluorocyclobutane), and C₇F₁₄ (perfluoromethylcyclohexane). In addition, results for dissociative attachment to CCl₄ are presented. Data are now available from a variety of other experiments such that comparison of high and low pressure data is possible. The combined results are interpreted in terms of the mechanism of Eq. (1).

II. EXPERIMENTAL

Trapped ion ICR techniques have been described in detail in the literature.⁸ An initial electron beam pulse fills the source region of the ICR cell with electrons which may react with neutral species to form negative ions. After a suitable trapping time, mass spectrometric analysis provides relative ion abundances. The instrument used in these studies was built in the Caltech shops and utilizes a 23.4 kG electromagnet, flat ICR cell, and standard marginal oscillator detector. All experiments are carried out at ambient temperature (298 °K).

Pressure measurements is made with a Schultz-Phelps type ionization gauge calibrated against a MKS Baratron Model 90H1-E capacitance manometer. Error in pressure measurement is estimated to be ±20%, and is the major source of inaccuracy in rate constant measurements.

All chemicals used in this study were obtained from commercial sources and used without further purification. Condensable gases were removed by several

^{a)}Contribution No. 5939.

^{b)}Present address: Exxon Research and Engineering Company, Corporate Research Laboratories, Linden, New Jersey 07036.

^{c)}Present address: Chevron Research Company, Richmond, California 94802.

freeze-pump-thaw cycles; impurities were negligible as determined by mass spectrometry.

III. RESULTS AND DISCUSSION

Electron attachment rate constants are measured in the same manner as for SF_6 .¹ It has been shown in previous studies that C_6F_6 , C_7F_8 , $c\text{-C}_4\text{F}_8$, and C_7F_{14} attach low-energy electrons.^{6,7,9} In ICR experiments only electrons scattered from the beam and trapped in the source region of the ICR cell attach to SF_6 ,¹⁰ and the same is assumed for the processes studied here. Consistent with this, negative ion signal intensity increases with increasing electron energy as more inelastically scattered electrons are produced. For C_6F_6 , C_7F_8 , $c\text{-C}_4\text{F}_8$, and C_7F_{14} , nondissociative attachment is observed. In addition, a dissociative attachment process, reaction (2), is observed for C_7F_{14} . The ratio of $\text{C}_7\text{F}_{14}^-$ to $\text{C}_6\text{F}_{11}^-$ is approximately 25 : 1.



Since attachment cross sections peak at very low electron energies (~ 0 eV), observation of reaction (2) implies that $\sim 4\%$ of the C_7F_{14} molecules possess sufficient internal energy prior to electron attachment such that dissociation of $\text{C}_7\text{F}_{14}^-$ is then rapid compared to radiative stabilization.

Figure 1 shows typical trapped-ion data for formation of C_6F_6^- . Similar results obtain for C_7F_8^- , $c\text{-C}_4\text{F}_8^-$, and $\text{C}_7\text{F}_{14}^-$. After the initial 10–20 msec, the curve in Fig. 1 is accurately described by a simple exponential function, Eq. (3), where $[\text{M}^-]_\infty$ is the anion abundance

$$[\text{M}^-] = [\text{M}^-]_\infty \{1 - \exp[-k_{\text{app}}(\text{M})t]\} \quad (3)$$

at long time and k_{app} is the apparent bimolecular rate constant. Figure 2 shows the measured electron attachment rate constant, k_{app} , for C_6F_6 , C_7F_8 , $c\text{-C}_4\text{F}_8$, and C_7F_{14} plotted as a function of pressure of the pure gas. Within experimental error the electron attachment rate constants for these molecules are pressure independent at pressures less than 3×10^{-6} Torr. Measurements of the attachment rate constant for C_7F_{14} was not possible at pressures above 2×10^{-7} Torr because the time scale for formation of $\text{C}_7\text{F}_{14}^-$ becomes comparable to the sampling time of the experiment. Average values of the

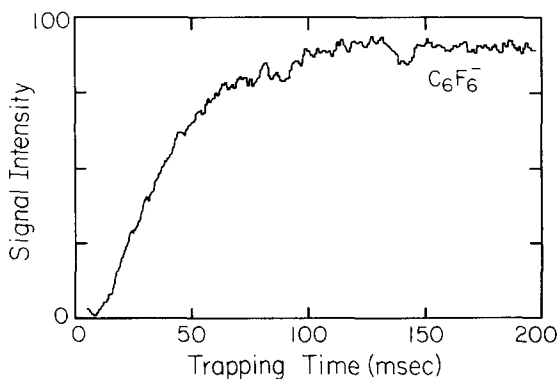


FIG. 1. Typical trapped ion data for electron attachment to C_6F_6 . The trap is filled with electrons by a 10 msec electron beam pulse. C_3F_6 pressure is 2×10^{-7} Torr.

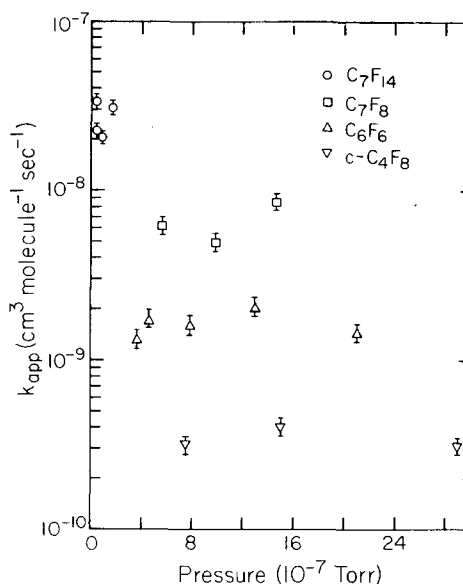


FIG. 2. Electron attachment rate constants as a function of pressure for C_6F_6 (perfluorobenzene), C_7F_8 (perfluorotoluene), $c\text{-C}_4\text{F}_8$ (perfluorocyclobutane) and C_7F_{14} (perfluoromethylcyclohexane).

electron attachment rate constants from Fig. 2 are listed in Table I along with literature values of thermal attachment rate constants determined in swarm experiments. Also included are data for SF_6 at low pressures. Data from swarm experiments are obtained at high buffer gas pressures such that every ion formed is collisionally stabilized.³ In accord with the scheme shown in Eq. (1), we equate the high pressure attachment rate constants with k_f .

As described in our previous ICR study of SF_6 ,¹ scattered electrons in the source region of an ICR cell can have kinetic energy from approximately thermal to 0.9

TABLE I. Attachment rate constants, autodetachment lifetimes and radiative lifetimes for electron attachment to SF_6 , C_6F_6 , C_7F_8 , $c\text{-C}_4\text{F}_8$, and C_7F_{14} . Also included are known electron affinities.

Molecule	k_{app}^a	k_f^b	τ_a^c	τ_r^d	EA ^e
SF_6	1.6 ± 0.2^f	2.72	25	0.4	$> 0.6^g$
C_6F_6	0.16 ± 0.03^h	1.02	12	0.8	$\geq 1.8^g$
C_7F_8	0.66 ± 0.15^h	2.44	12.2	0.5	$\geq 1.7^g$
$c\text{-C}_4\text{F}_8$	0.04 ± 0.01^h	0.11	14.8	0.5	0.4^i
C_7F_{14}	2.7 ± 0.5^h	0.52	793	1.5	NA ^j

^aUnits are 10^{-8} cm^3 molecule⁻¹ sec⁻¹. Errors quoted are for one standard deviation.

^bHigh pressure thermal attachment rate constants, equated with k_f in accordance with Eq. (1). Units are 10^{-7} cm^3 molecule⁻¹ sec⁻¹. Data from Ref. 2.

^cUnits are μsec . Data from Ref. 2.

^dUnits are msec. Calculated according to Eq. (4).

^eUnits are eV.

^fReference 1.

^gReference 2.

^hMeasured in this work.

ⁱReference 13.

^jData not available.

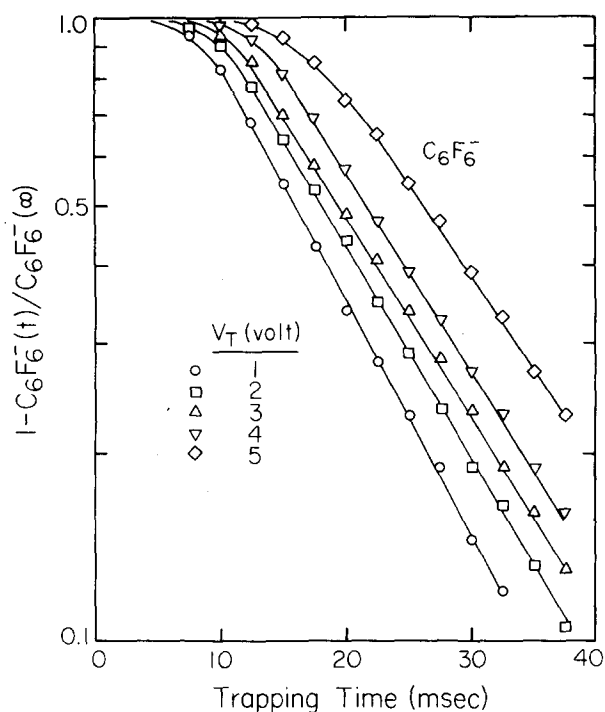


FIG. 3. Effect of trapping voltage on electron attachment to C_6F_6 at 5×10^{-7} Torr. Trapping voltages V_T (in volts) are negative for negative ions. $C_6F_6^-(\infty)$ is the $C_6F_6^-$ ion abundance when all the electrons have been attached, and is equal to the number of free electrons produced during the electron beam pulse.

V_T , where V_T is the trapping voltage. Values of V_T in these experiments range from -1.5 to -2.5 volt, and hence an appreciable fraction of the trapped electrons initially are epithermal. Since k_f , τ_a , and k_d are sensitive functions of the electron kinetic energy, variations of V_T may have a large effect on k_{app} . Measurements of k_{app} as a function of V_T are shown in Fig. 3 for C_6F_6 . For trapping voltages from 1–5 V, an initial period of slower $C_6F_6^-$ formation is followed by rapid electron attachment with limiting slope independent of trapping voltage. This is analogous to results obtained with SF_6 . Since k_{app} is calculated from the limiting slope, Fig. 3, k_{app} is independent of the initial electron distribution. The increased time required for electron thermalization with increasing V_T is a consequence of the electron energy distribution peaking at higher energy with higher trapping voltage. It is evident from Fig. 3 that electron thermalization is rapid compared to attachment. Attachment followed by autoionization is expected to be very efficient at relaxing the electron energy distribution. Results obtained for C_7F_8 , $c-C_4F_8$, and C_7F_{14} indicate behavior similar to that shown in Fig. 3.

Table I includes autodetachment lifetimes, τ_a , as determined from time-of-flight experiments. Comparison of autodetachment lifetimes in Table I ($10 \mu\text{sec}$ – 1 msec) with the time between collisions for data shown in Fig. 2 (10 – 1000 msec) indicates that collisional stabilization of the excited molecular ions is much slower than autodetachment at the pressures used in ICR experiments. As dissociative processes are minor for ions in Table I, radiative stabilization is the most likely mechanism

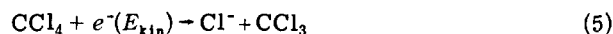
leading to formation of long-lived stable molecular negative ions at low pressure [Eq. (1)]. This conclusion is supported by the bimolecular behavior of the rate constants shown in Fig. 2. Assuming steady-state conditions for $[A^-]^*$ in Eq. (1), Eq. (4) results for k_{app} providing $1/\tau_a \gg 1/\tau_r \gg k_s[M]$.

$$k_{app} = k_f \tau_a / \tau_r \quad (4)$$

The data in Table I in conjunction with Eq. (4) can be used to estimate radiative lifetimes. Calculated values of τ_r are shown in Table I. The calculated radiative lifetimes, 0.4 – 1.5 msec , are not unreasonable for infrared emission.¹¹ Infrared radiative lifetimes (calculated from integrated absorption intensities) for C–F modes in CH_3F , CH_2F_2 , CHF_3 , and CF_4 are 3 , 1.1 , 0.4 , and 0.2 msec , respectively.¹²

It is of interest to examine the data in Table I for $c-C_4F_8$ and C_7F_{14} . Even though C_7F_{14} rapidly attaches electrons at low pressures, the radiative lifetime is somewhat larger than for other species. In contrast with C_7F_{14} , $c-C_4F_8$ is the slowest to attach electrons yet has an autodetachment lifetime and radiative rate comparable to the other ions. In the case of C_7F_{14} the long ($793 \mu\text{sec}$) autodetachment lifetime is responsible for the rapid attachment process. For a large molecule, internal energy is shared by a large number of modes resulting in a slow unimolecular decomposition (autodetachment) rate. For comparable internal energy content, a larger molecule will also have a lower internal temperature since the energy is distributed over more internal modes. The lower internal temperature results in a longer radiative lifetime, and may explain the long radiative lifetime calculated for C_7F_{14} . On the other hand, $c-C_4F_8$ has a short radiative lifetime (Table I). The small attachment rate constant measured at low pressure thus reflects the smaller thermal attachment rate (k_f) measured at high pressure (Table I). While the electron affinity (included in Table I) of C_7F_{14} is not known, it is expected to be comparable to or at most slightly higher than the electron affinity of $c-C_4F_8$.¹³

For electron attachment to the molecules in Table I the rate limiting step at low pressure appears to be stabilization of the excited molecular ion. For molecules which undergo dissociative attachment no stabilization is needed and attachment rates at low pressures should not differ from high pressure results. Carbon tetrachloride undergoes dissociative electron attachment of low energy electrons to give Cl^- and CCl_3 , Eq. (5).¹⁴ In pure CCl_4 , relaxation of the electron energy distribution



is relatively slow and is the rate limiting step at low pressure.¹ This contrasts the behavior observed for the molecules listed in Table I, for which the apparent attachment rates are found to be pressure independent over the accessible range of study (Fig. 2). Addition of a gas efficient at relaxing the electron energy distribution (such as CO_2) should allow low pressure dissociative attachment rates in CCl_4 to approach high pressure attachment rates. Figure 4 shows CCl_4 low pressure dissociative attachment rates plotted as a function of CO_2 pressure added to 5.7×10^{-8} Torr of CCl_4 . The dashed line indi-

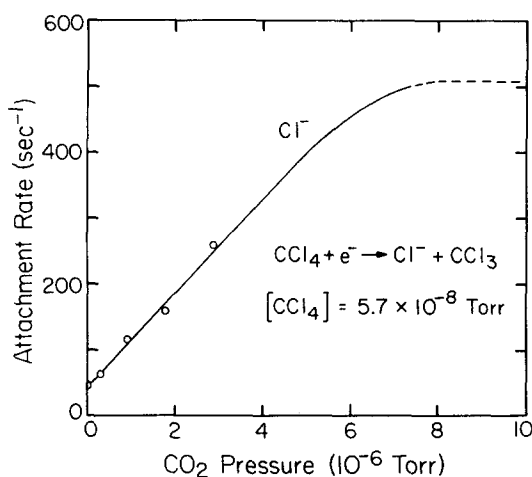


FIG. 4. Low pressure dissociative attachment rates (open circles) for CCl_4 as a function of added CO_2 pressure. CCl_4 pressure is 5.7×10^{-8} Torr. Dashed line indicates attachment rate at 5.7×10^{-8} Torr calculated from high pressure rate constant of $2.7 \times 10^{-7} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.

icates the attachment rate as calculated from the high pressure attachment rate constant of $2.7 \times 10^{-7} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$.¹⁵ Over the range of CO_2 pressures used in the present experiments, attachment rates are proportional to CO_2 concentration. From the slope of the linear portion of the curve in Fig. 4 a rate constant of $2.2 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ is calculated for thermalization of electrons by CO_2 . Higher CO_2 pressures cannot be used because the total rate of Cl^- formation becomes comparable to the experimental sampling time. Compared to CO_2 , CH_4 , and N_2 were found to be inefficient at relaxing the electron energy distribution. Benzene- d_6 thermalizes electrons at a rate only slightly slower than CO_2 . These results are attributed to low-lying temporary electron attachment processes involving CO_2 and C_6D_6 ,^{3,16} not available to CH_4 or N_2 (except at higher energies), which permit energetic electrons to attach and subsequently autodetach with lower energy.

Warman and Sauer¹⁷ have reported related studies of electron thermalization in irradiated gases using CCl_4 as an electron energy probe. They derive a thermalization rate constant of $5.8 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for CO_2 , which is significantly higher than the present result. Phelps¹⁸ has calculated relaxation rates of epithermal electron energy distributions from mobility and diffusion data. In good agreement with the present experiments, his results yield a mean thermalization rate of $2.5 \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ for electrons in CO_2 . The rate is not strongly dependent on electron energy between thermal energies and 1 eV. As reported by Warman and Sauer,¹⁷ the relative thermalization rates for CO_2 , benzene, CH_4 , and N_2 are 1.0, 0.76, 0.15, and 0.004, respectively. Christophorou and co-workers have reported data for electron thermalization times as a function of mean electron energy in a number of gases.^{19,20} Their results indicate that above ~ 0.1 eV, electron thermalization times are relatively constant, and decrease significantly at lower mean electron energies. Using the higher energy limits gives approximate

relative efficiencies of 1.0, 0.053, and 0.0040 for CO_2 , CH_4 , and N_2 , respectively.¹⁹ These results are in agreement with the present work in which CH_4 and N_2 are found to be inefficient compared to CO_2 and benzene.

IV. CONCLUSIONS

With data on electron attachment now becoming available from a variety of experiments under various conditions of pressure, temperature and initial electron energy distribution, the various processes involved [Eq. (1)] are becoming increasingly well characterized. Whereas high pressure experiments yield information on initial attachment rates and autodetachment lifetimes, low pressure ICR techniques are especially well suited for studying processes such as radiative and collisional stabilization. It is seen in this work that formation of stable molecular negative ions at very low pressure is not unique to SF_6 , but is observed for a large variety of molecules where autodetachment and dissociation lifetimes are long enough to allow radiative stabilization. Combination of ICR data with high pressure data allows estimates of radiative lifetimes to be made, with results that are consistent with an infrared emission process. Dissociative electron attachment, such as observed in CCl_4 , occurs at low pressure with nearly the same facility as at high pressure because no stabilization process is required. In low pressure ICR experiments, the rate limiting step in dissociative electron attachment appears to be relaxation of the electron energy distribution.

ACKNOWLEDGMENTS

This work was supported in part by the United States Department of Energy and the President's Fund of the California Institute of Technology.

- ¹M. S. Foster and J. L. Beauchamp, *Chem. Phys. Lett.* **31**, 482 (1975). For more recent data on perfluoromethylcyclohexane, see A. A. Christodoulides and L. G. Christophorou, *Chem. Phys. Lett.* **61**, 533 (1979).
- ²L. G. Christophorou, *Adv. Electron. Electron Phys.* **46**, 55 (1978).
- ³L. G. Christophorou, *Atomic and Molecular Radiation Physics* (Wiley-Interscience, New York, 1971).
- ⁴R. N. Compton, L. G. Christophorou, G. S. Hurst, and P. W. Reinhardt, *J. Chem. Phys.* **45**, 4634 (1966).
- ⁵R. W. Odom, D. L. Smith, and J. H. Futrell, *J. Phys. B* **8**, 1349 (1975), and references contained therein.
- ⁶K. S. Gant and L. G. Christophorou, *J. Chem. Phys.* **65**, 2977 (1976).
- ⁷L. G. Christophorou, D. L. McCorkle, and D. Pittman, *J. Chem. Phys.* **60**, 1183 (1974).
- ⁸J. L. Beauchamp, *Ann. Rev. Phys. Chem.* **22**, 527 (1971); T. A. Lehman and M. M. Bursey, *Ion Cyclotron Resonance Spectroscopy* (Wiley, New York, 1976); T. B. McMahon and J. L. Beauchamp, *Rev. Sci. Instrum.* **43**, 509 (1972).
- ⁹W. T. Naff, C. D. Cooper, and R. N. Compton, *J. Chem. Phys.* **49**, 2784 (1968).
- ¹⁰R. W. Odom, D. L. Smith, and J. H. Futrell, *Chem. Phys. Lett.* **24**, 227 (1974), and references contained therein.
- ¹¹G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, New York, 1945), p. 251.
- ¹²J. H. Newton and W. B. Person, *J. Chem. Phys.* **64**, 3036 (1976); J. H. Newton, R. A. Levine, and W. B. Person, *J. Chem. Phys.* **67**, 3282 (1977).

- ¹³C. Lifshitz, T. O. Tiernan, and B. M. Hughes, *J. Chem. Phys.* **59**, 3182 (1973).
- ¹⁴L. G. Christophorou and J. A. D. Stockdale, *J. Chem. Phys.* **48**, 1956 (1968).
- ¹⁵A. A. Christodoulides and L. G. Christophorou, *J. Chem. Phys.* **54**, 4691 (1971).
- ¹⁶R. N. Compton, L. G. Christophorou, and R. H. Huebner, *Phys. Lett.* **23**, 656 (1966).
- ¹⁷J. M. Warman and M. C. Sauer, *J. Chem. Phys.* **62**, 1971 (1975).
- ¹⁸A. V. Phelps, in *Defense Nuclear Agency Reaction Rate Handbook (DNA 1948H)*, edited by M. H. Bortner and T. Bauer; Chap. 21. See also the discussion of this work in Ref. 17.
- ¹⁹L. G. Christophorou, Proceedings of the XIII International Conference on Phenomena in Ionized Gases (Berlin, G. D. R., Sept. 12–17, 1977), Invited Lectures, Part I, p. 51.
- ²⁰L. G. Christophorou, K. S. Gant, and J. K. Baird, *Chem. Phys. Lett.* **30**, 104 (1975).