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Electron Dissociative Attachment to NF₂ Radicals

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Measurements of discharge current in an electron beam sustained-discharge device have been used to determine the dissociative attachment rate constant of electrons to NF₂ radicals. This was done by measuring the relative rate of electron attachment to NF_2 compared to dilute molecular chlorine in a nitrogen buffer in separate experiments in the same device. A comparison of the steady-state current measured for these two different mixtures at identical total pressures and applied electric fields provides a relative measurement for the rate of disappearance of electrons. Since the attachment rate constant with molecular chlorine is well-known, rate constants for the fluoride radical could be determined. Values near 1.5×10^{-9} cm³/s for average electron energies near 1 eV were obtained.

Introduction

Interest in attachment processes, particularly for the halogen molecules, has been most closely coupled to the interest in the corresponding rare-gas halide lasers, so-called excimer lasers. These lasers typically are operated in an electron beam¹ or a discharge pumped geometry.² Investigations into the fundamental kinetics of these laser systems suggest that one of the routes for forming the upper laser level is via ion-ion combination reactions of positive rare-gas ions with negative halogen ions.³ These halogen anions are formed principally by dissociative attachment of electrons to the halogen fuel present in the laser mix, e.g., F_2 for KrF, NF₃ for XeF, and HCl for XeCl lasers, etc. Knowledge of the rate constants for these processes is fundamental for modeling the kinetics of this important class of lasers.

Beside providing the negative ion source for the upper laser level reaction formation channel, the halogen fuel also helps stabilize the discharge by clamping the electron number density buildup in the gas. This permits more efficient operation of the discharge and reduces the quenching of the upper laser level by electrons, which is a dominant quenching process in typical laser devices.^{4,5}

In electron beam pumped devices, these secondary electrons arise as a result of high-energy electron beam collisions with the high-pressure rare gases present, viz.

$$e_p + Ne \rightarrow Ne^+ + e_p' + e_s$$

where e_p represents the primary electrons, and e_s the secondary electrons. Low-energy electrons are also produced with discharge pumping by source electrons being accelerated in the discharge circuit to energies that eventually produce secondary ionization. Regardless, the secondary electrons thus formed subsequently undergo a variety of energy-transfer collisions and attain average energies near 1 eV under typical laser operating conditions. The values for electron energy were obtained from utilization of a Boltzmann code,⁶ which contains cross sections from swarm data for electron impact processes in N_2 as a function of applied electric field.

These electrons can undergo dissociative attachment reactions with halogen fuels to produce negative ions and radicals, e.g., xenon fluoride lasers operate with neon, xenon, and nitrogen trifluoride mixtures, so for these lasers the dominate process is electron attachment to the nitrogen trifluoride fuel:

$$e_s + NF_3 \rightarrow F^- + NF_2$$

It has also been observed⁷ in XeF lasers that there is a gradual buildup of N_2 as a result of gas-phase reactions initiated with the electron beam firing. For multiple pulses on the same mix, eventually this buildup of nitrogen can prevent the laser from operating.⁸ This arises as a result of absorption processes attributed to the nitrogen that reduce the gain-to-loss ratio in the laser cavity to an unfavorable value.

One proposed reaction sequence⁷ that could produce nitrogen in such mixtures is electron attachment to the nitrogen difluoride radicals:

$$e_s + NF_2 \rightarrow NF + F^-$$

followed by

$$NF + NF \rightarrow N_2 + 2F$$

Ideally, one would like to obtain the elementary, state-selected, rate constants for electron attachment to NF2 radicals in a variety of excited states (vibration, electronic, etc.) and then monitor the fate of the products, but this kind of detailed kinetic information is not available.

Procedure

To obtain some information, we have performed electron dissociative attachment experiments on equilibrium mixtures of dilute tetrafluorohydrazine in nitrogen at total pressures of 1 amagat heated to near 500 K, where thermodynamics indicate that the dominate species (>99%) are NF2 radicals.9

To provide a well characterized source of electrons near the 1-eV energy regime, we used nitrogen as a buffer gas, since the behavior of electrons in nitrogen at total pressures near 1 atm is well-known. With the concentration of halogen small ($\approx 1\%$) and the total pressure constant, the assumption that the electron energy distribution is determined by the nitrogen alone is reasonable.

⁽¹⁾ Searles, S. K.; Hart, C. A. Appl. Phys. Lett. 1975, 27, 243. Brau, C. A.; Ewing, J. J. Appl. Phys. Lett. 1975, 27, 435. Ault, E. R.; Bradford, R. S.; Bhaumik, M. L. Appl. Phys. Lett. 1975, 27, 412.
(2) Mangano, J. A.; Jacob, J. H. Appl. Phys. Lett. 1975, 27, 495. Burnham, R.; Harris, D.; Djeu, N. Appl. Phys. Lett. 1976, 28, 86.
(3) Rokni, M.; Mangano, J. A.; Jacob, J. H.; Hsia, J. C. IEEE J. Quantum Electron. 1978, QE-14, 464.
(4) Trainor, D. W.; Jacob, J. H.; Rokni, M. J. Chem. Phys. 1980, 72, 3646.
(5) Trainor, D. W.; Jacob, J. H.; Appl. Phys. Lett. 1980, 37, 675.
(6) Englehardt, A. G.; Phelps, A. V.; Risk, C. G. Phys. Rev. A 1964, 135, 1566.

^{1566.}

⁽⁷⁾ Slater, R. Appl. Phys. B 1987, 42, 17.

 ⁽⁸⁾ Mandi, A.; Hyman, H. A. Appl. Phys. Lett. 1986, 49, 841.
 (9) Modica, A. P.; Hornig, D. F. J. Chem. Phys. 1968, 49, 629.

The experiment consisted of measuring steady-state discharge currents in mixtures with known amounts of halogen attaching gas present, under controlled conditions for which the value of E/N (E is the applied electric field in kV/cm and N is the neutral-gas density) was varied. Variations in applied field from 2 to 10 kV/(cm atm) in nitrogen provide modest variations in average electron energies near 1 eV.

First, measurements were made with molecular chlorine (10 Torr) present in 1 atm of nitrogen at various values of applied electric field. These experiments were then repeated with the fluoride-containing molecule, but at a much lower halogen density due to the larger observed attachment rate constant. In this manner, the ratio of the discharge currents was obtained for the two different dilute mixtures. Since the value of the attachment rate constant for chlorine is known, the ratios of currents, together with the density of attaching gas, provides a relative measurement for the fluoride compound's attachment rate constant.

Experimental Section

The experimental apparatus used was the same as had been used in prior experiments.^{10,11} The gas mixture is ionized by a beam of electrons having attained energies near 150 keV at currents near 1.2 A/cm². About 40 ns after the electron beam is fired, a precharged capacitor is switched across the anode and cathode of the discharge cell. This discharge chamber contains the reaction mixtures (e.g., 1 Torr of N₂F₄ or 10 Torr of Cl₂, etc., in 1 atm of N₂), which were premixed in Teflon-lined, stainless-steel, 5-L gas cylinders and allowed to mix thoroughly before use in these experiments. The N₂ (New England Oxygen, 99.997%), Cl₂ (Matheson, 99.965%), and N₂F₄ (Air Products, research grade) were used without further purification.

The data consisted of measuring the discharge current, I_s , which can be directly related to the electron number density, and the applied voltage, which relates to the average electron energy. At steady-state

$$dn_e/dt = 0 = S - \alpha n_e n_+ - k_{att} n_e[H]$$

where S is the source term describing the production of electrons by the high-energy electron beam, which is kept constant, α is the electron-ion recombination rate constant, n_e is the electron density, n_+ is the positive ion density (in this case the N₄⁺ ion¹²), $k_{\rm att}$ is the desired attachment rate constant, and [H] is the number density of electron attacher present.

Under our experimental conditions, the attachment process, $k_{\text{att}}n_{\text{e}}[H]$, is much larger than the electron-ion recombination process, $\alpha n_{\text{e}}n_{+}$, and therefore, at steady-state conditions

$$S = k_{\text{att}} n_{\text{e}}[H]$$

Since n_e is proportional to the discharge current, by operating with S equal to a constant (fixed electron beam current, fixed total pressure), and measuring I_s for the chlorine and dinitrogen tetrafluoride mixtures, the ratios for the respective attachment rate constants can be obtained, i.e.

$$\frac{k_{\rm N_2F_4}}{k_{\rm Cl_2}} = \frac{I_{\rm s}({\rm Cl_2})[{\rm Cl_2}]}{I_{\rm s}({\rm N_2F_4})[{\rm N_2F_4}]} \quad (300 \text{ K})$$

Since the dissociative attachment rate constant for chlorine, k_{Cl_2} , is well-known from reported absolute rate constant experiments,^[3] this technique provides a convenient measurement for obtaining the relative attachment rate constant for this much faster process.

Similarly, at 500 K, the steady-state discharge current is related to dissociative attachment to nitrogen difluoride radicals, which are the dominant species (>99%) in equilibrium with the tetra-fluorohydrazine parent.

This same technique has been used to measure the dissociative attachment rate constant for F_2 and NF_3 at 300 and 500 K. These

(11) Trainor, D. W.; Jacob, J. H. Appl. Phys. Lett. 1979, 35, 920.



Figure 1. Discharge currents and voltage for two different mixtures: 10 Torr of Cl_2 in 1 atm of nitrogen at room temperature and 2 Torr of NF_2 at 1 amagat in nitrogen near 500 K.



Figure 2. Attachment rate constants determined in this experiment for nitrogen difluoride and tetrafluorohydrazine as a function of average (mean) electron energy.



Figure 3. XeF (B–X) laser emission observed with 0.2% halogen donor, 0.5% xenon, and the balance neon to total pressures near 3 amagats for NF₃ (room temperature and 475 K) compared to N_2F_4 , and NF₂, respectively.

results have been reported earlier.¹¹

Results

Typical voltage and current traces are shown in Figure 1 for 2 Torr of NF_2 in 1 atm of nitrogen near 500 K (1 Torr of N_2F_4) at 6 kV/(cm atm). Also shown in Figure 1 is the current and voltage traces for 10 Torr of Cl_2 in 1 atm of nitrogen near 300 K also at 6 kV/(cm atm) for comparison. Similar data were taken with 1 Torr of N_2F_4 at room temperature and for all three halogen nitrogen mixtures at applied fields near 2, 4, 8, and 10 kV/(cm atm). These data provide the information needed to obtain values for the attachment rate constants for N_2F_4 at room temperature and average electron energies near 1 eV, as well as for NF_2 radicals at elevated temperatures and near 1-eV electron average energies (see Figure 2).

Discussion

The rate constant values presented here for electron dissociative attachment to N_2F_4 and NF_2 radicals are comparable to the attachment of electrons to other fluorine-containing molecules reported¹¹ (few times 10^{-9} cm³/s). These reported measurements

⁽¹⁰⁾ Rokni, M.; Jacob, J. H.; Mangano, J. A. Appl. Phys. Lett. 1979, 34, 187.

⁽¹²⁾ Douglas-Hamilton, D. H. J. Chem. Phys. 1973, 58, 4820.

⁽¹³⁾ Rokni, M.; Jacob, J. H.; Mangano, J. A. Appl. Phys. Lett. 1979, 34, 187.

of the electron dissociative attachment rate constant for these fluoride compounds should prove useful in the modeling of the xenon fluoride excimer laser using NF₃ as the halogen donor.

In addition, in separate experiments, the nitrogen difluoride radical has also been shown to support XeF laser action when it alone was used as the halogen donor in an electron beam pumped laser device (see Figure 3).

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Electron Attachment to CO₂ Clusters by Collisional Charge Transfer

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Electron transfer from a seeded supersonic beam of alkali-metal atoms to a crossed molecular beam of CO₂ clusters was found to form predominantly $(CO_2)_n^-$ anions, with n = 2-16 under our experimental conditions. The mass spectrum has especially prominent anion peaks at "magic numbers" of n = 4, 7, and 14. Threshold energies for formation of the anion clusters with n = 2-10 were determined by measuring the yield as a function of collision energy. The nominal electron affinities corresponding to these threshold energies are consistent with an impulsive model which postulates that the electron attachment occurs to a subunit within the clusters. This implies that cluster anions larger than the subunit moiety are produced with substantial vibrational excitation. As interpreted with the impulsive model, the threshold data give an approximate value (uncertain by about ± 0.2 eV) for the adiabatic electron affinity of the subunit moiety, but do not unequivocally identify its size. Thus we find EA = 0.8 eV if the electron attachment occurs to a dimer and EA = 0.1 eV if to a trimer.

Introduction

Atomic and molecular cluster anions are prominent in many diverse phenomenona, including solvation and reaction processes in solution, ion-molecule chemistry in the upper atmosphere, and nucleation.¹ The electron affinity (EA) of the corresponding neutral cluster serves as the customary measure of the stability of a cluster anion, equivalent to the ionization potential (IP) of the anion, but as yet EA values have been determined or estimated for only a few cluster species. This prompted molecular beam experiments in our laboratory^{2,3} to produce cluster anions by electron transfer from a fast alkali-metal atom to neutral clusters via $A + X_n \rightarrow A^+ + X_n^-$. In such an endoergic charge-transfer process, the electron attachment occurs isoenergetically at threshold, and thus cluster fragmentation is minimized (in contrast to electron bombardment, which excites and dissociates the target clusters). From the threshold collision energy $E_{\rm T}$, the nominal electron affinity of the neutral cluster can be obtained by

$$EA(X_n) = IP(A) - E_T$$
(1)

where IP(A) is the ionization potential of the alkali-metal atom. Since the collisional time scale is subpicosecond, these nominal EA's do not pertain to adiabatic attachment to the parent cluster and are interpreted in terms of an approximate, impulsive model.² Also, the method yields only modest accuracy, about ± 0.2 eV, because the threshold energies must be evaluated by extrapolating cross sections for ion-pair formation. Despite these limitations, the method offers a useful means to examine the electrophilic character of molecular clusters.

In this paper we report a study of CO_2 clusters. Anions of CO_2 clusters have been produced in several other experiments⁴⁻¹⁰ and theoretical electronic structure calculations^{11,12} have explored the geometry and stability of the $(CO_2)_2^-$ dimer. The $(CO_2)_n$ clusters are able to bind an electron despite the fact that the adiabatic EA for the monomer is quite negative $(-0.6 \pm 0.2 \text{ eV})$.¹³ Recently, Bowen and co-workers¹⁰ have obtained a lower bound (>2.4 eV) to the vertical detachment energy of the $(CO_2)_2^-$ anion, but no other measurements relating to the electron affinity of CO_2 clusters are available. Here we report threshold energies for producing CO₂ cluster anions with n = 2-10 via collisional charge transfer from alkali-metal atoms. These data prove consistent with the impulsive model, which assumes that the electron attachment occurs to a subcluster moiety, while the rest of the cluster is merely a startled spectator during the very brief collision duration. The model relates the observed $E_{\rm T}$ values via a reduced mass factor to the adiabatic EA of the active subcluster. For this we find EA = 0.8 eV if the subcluster is a dimer and EA = 0.1eV is the subcluster is a trimer.

Experimental Results

The crossed-molecular beam apparatus, experimental procedure, and data analysis have been described in detail elsewhere.^{2,3} The cluster anions were produced by crossing a Rb atom beam with neutral CO₂ clusters. The fast Rb atoms were generated from a seeded supersonic jet,¹⁴ and the cluster beam by the expansion of neat CO₂ at a stagnation pressure of 23.5 psig through a 0.08-mm-diameter nozzle at room temperature. The relative kinetic energy E_{rel} was varied by changing the temperature and diluent gas of the seeded Rb atom beam. The product anions were

- (1) See: Märk, T. D.; Castleman, A. W. Jr. Adv. At. Mol. Phys. 1984, 20, 65 and references cited therein.
- (2) Bowen, K. H.; Liesegang, G. W.; Sanders, R. A.; Herschbach, D. R. J. Phys. Chem. 1983, 87, 557
- (3) Quitevis, E. L.; Bowen, K. H.; Liesegang, G. W.; Herschbach, D. R. J. Phys. Chem. 1983, 87, 2076.
 - (4) Klots, C. E.; Compton, R. N. J. Chem. Phys. 1977, 67, 1179.
 (5) Klots, C. E.; Compton, R. N. J. Chem. Phys. 1978, 69, 1636.
- (6) Stamatovic, A.; Leiter, K.; Ritter, W.; Stephan, K.; Märk, T. D. J. Chem. Phys. 1985, 83, 2942.
 - (7) Kondow, T.; Mitsuke, K. J. Chem. Phys. 1985, 83, 2612.
- (8) Knapp, M.; Kreisle, D.; Echt, O.; Sattler, K.; Recknagel, E. Surf. Sci. 1985, 156, 313.
- (9) Alexander, M. L.; Johnson, M. A.; Levinger, N. E.; Lineberger, W.
 C. Phys. Rev. Lett. 1986, 57, 976.
 (10) Coe, J. V.; Snodgrass, J. T.; McHugh, K. M., Freidhoff, C. B.; Bowen,
- K. H. J. Chem. Phys., in press.

- Rossi, A. R.; Jordan, K. D. J. Chem. Phys. 1979, 70, 4422.
 Fleishman, S. H.; Jordan, K. D. J. Phys. Chem. 1987, 91, 1300.
 Compton, R. N.; Reinhardt, P. W.; Cooper, C. D. J. Chem. Phys. 1975, 63, 3821.
- (14) Larsen, R. A.; Neoh, S. K.; Herschbach, D. R. Rev. Sci. Instrum. 1974, 45, 1511.

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