Optically Enhanced Electron Attachment

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The first optically enhanced electron attachment involving electronically excited molecules is reported. The metastable (triplet) states responsible for the photoenhanced electron attachment were produced *indirectly* via internal conversion from higher excited singlet states which are strongly optically allowed and are reached by excimer-laser excitation.

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Slow-electron–excited-molecule interactions have been scarcely studied in spite of their basic and applied significance.[1] Large changes in the cross section for negative-ion formation have been observed when slow electrons collide with molecules excited thermally into vibrational-rotational states of the electronic ground state (see Ref. 1 and references given therein). Enhanced dissociative attachment via electron capture by vibrationally excited molecules produced by laser irradiation has also been reported (e.g., for SF_6 [2] and I_2 [3]). Additionally, enhanced electron attachment to vibrationally excited HCl and HF molecules produced, respectively, by laser photodissociation of the C_2H_3Cl and C_2F_3H molecules has been observed.[4] To our knowledge, the only studies on electron attachment to electronically excited molecules are the experiments[5] on dissociative attachment to $O_2(a\,^1\Delta_g)$ produced in a microwave discharge and the calculation[6] of the dissociative-attachment cross section for $H_2(c\,^3\Pi_u)$; both of these studies indicated larger attachment cross sections for the electronically excited molecule compared with the ground-state molecule. In this paper we report the first observation of optically enhanced electron attachment involving electronically excited molecules.

The principle of the present experiment and the required properties of the electron-attaching molecules, AX, are shown in Fig. 1. The electron-attachment properties of AX—present in minute quantities in a buffer gas (N_2 in the present study)—were first studied without laser excitation with the use of two different electron-swarm methods: the pulse-shape method[7] and a modified pulsed Townsend technique.[8] Subsequently, an excimer laser was used to excite via single-photon absorption a strongly allowed electronic singlet state, S_n, of AX [AX(ground-state singlet, S_0)$+h\nu \rightarrow AX^{**}$(highly allowed second or third excited singlet state, $S_{2/3}$)] which lies below the lowest excited electronic state of N_2. The $AX^{**}(S_{2,3})$ molecule normally undergoes fast ($\sim 10^{-13}$ s) intramolecular relaxation to its first excited singlet state, S_1,

$$AX^{**}(S_{2,3}) \xrightarrow{\sim 10^{13}\,\mathrm{s}} AX^{*}(S_1),$$

except when dissociation into neutral fragments, which depends on the photon wavelength, also occurs. The $AX^{*}(S_1)$ species, then, undergoes rapid (within $\sim 10^{-8}$ to 10^{-11} s, depending on AX) "intersystem crossing" to the lowest triplet state, T_1,

$$AX^{*}(S_1) \xrightarrow{10^{-8}\text{–}10^{-11}\,\mathrm{s}} AX^{*}(T_1).$$

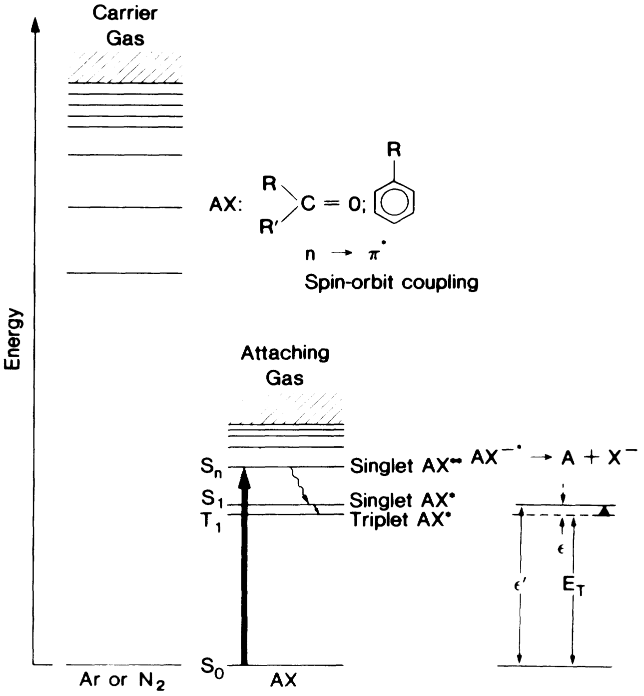

FIG. 1. Schematic energy-level diagram of carrier- and attaching-gas system. A possible electron-attachment mechanism from the triplet state $AX^{*}(T_1)$ (dissociative electron attachment) is shown. While this mechanism may contribute slightly to the observed photoenhanced attachment (and might be the dominant mechanism for other molecules), for the molecules investigated, the observed photoenhanced attachment is attributed predominantly to a nondissociative electron-attachment process involving $AX^{*}(T_1)$ and another ground-state molecule, $AX(S_0)$.

The excited $AX^*(T_1)$ molecule remains in the T_1 state for times $\gtrsim 1$ ms, which allows ample time for collisions with slow electrons. While we expected (see Fig. 1) that electrons would be captured dissociatively into a negative-ion state from T_1, viz.,

$$AX^*(T_1)+e(\varepsilon)\rightarrow AX^{*-}\rightarrow A+X^-, \qquad (1)$$

the present findings (see below) indicate that, for the molecules studied, electron capture is nondissociative and, instead of reaction (1), it involves $AX^*(T_1)$ and another ground-state molecule, $AX(S_0)$, viz.,

$$AX^*(T_1)+AX(S_0)+e\rightarrow \text{anions}. \qquad (2)$$

We have identified two classes of molecules which generally possess the aforementioned characteristics and might thus exhibit optically enhanced electron attachment, namely, certain benzene derivatives[9,10] and certain carbonyl compounds.[9-12] We have selected thiophenol (C_6H_5SH) and thioanisole ($C_6H_5SCH_3$) as representative candidate molecules from the first group. *For both molecules we have observed large optically enhanced electron attachment.* Our initial studies have focused on C_6H_5SH.

The present experiments were performed as follows: The electron-attaching gas was mixed in small amounts (0.0013–0.013 kPa) with N_2 (66.6–266.6 kPa) and was studied *with* and *without* laser irradiation. In the former case the interelectrode space (2 cm in length and ~1 cm^2 cross-sectional area) was irradiated with a laser beam through a gridded anode; this same laser beam, at the end of its path, was absorbed by the cathode and photoelectrically injected a pulse of electrons into the gas which drifted—as an electron swarm—toward the anode, colliding *en route* with $AX^*(T_1)$ produced in the irradiated gas. Since the electron drift times are $\sim 10^{-6}$ s, virtually all $AX^*(T_1)$ molecules remain excited during the entire transit time of the electron swarm. The electron-attachment measurements were made at various laser-pulse energies (0.05–5 mJ) and for the following laser wavelengths: 308 nm (4.03 eV, XeCl); 249 nm (4.98 eV, KrF); 222 nm (5.59 eV, KrCl); and 193 nm (6.42 eV, ArF). Absorption-spectrum measurements of C_6H_5SH in liquid iso-octane[13] indicate that the approximate position of the first excited triplet state T_1 (onset of phosphorescence)[14] is 3.35 eV and that of the first excited singlet state (0-0 transition) is 4.36 eV.[13,14]

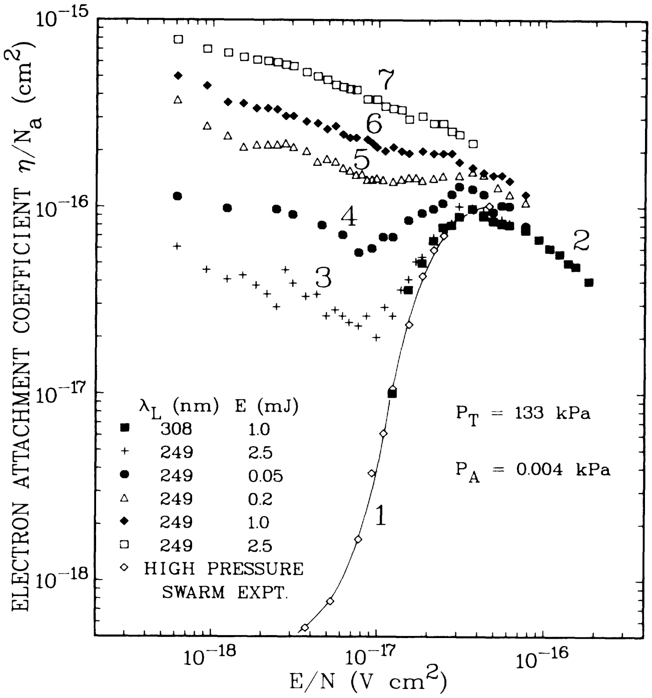

FIG. 2. Electron-attachment coefficient, η/N_a, vs E/N for C_6H_5SH in N_2 for the ground-state (curves 1 and 2) and the electronically excited (curves 3–7; curve 3 is for a single laser pulse, and curves 4–7 are for the double laser pulses C_6H_5SH molecules.

In Fig. 2 are shown the measured electron-attachment coefficients, η, normalized to the ground-state attaching-gas number density, N_a, η/N_a, versus E/N (E is the electric field strength and N the total gas number density) for C_6H_5SH. Curve 1 was obtained without irradiation; curve 2 was obtained with 308-nm laser-light irradiation for a laser-pulse energy of ~1 mJ. Both sets of data are similar; the η/N_a versus E/N functions for both curves 1 and 2 peak at a mean electron energy of ~0.8 eV and are $< 5\times10^{-19}$ cm^2 (the detection threshold of the present technique) at low energies (low E/N). These data are consistent with the results that we obtained from a mass-spectrometric study on *unexcited* C_6H_5SH which indicated that the most abundant negative ion is $C_6H_5S^-$ with an onset energy of 0.7 eV and a peak in the attachment cross section at 1.3 eV. These results are also consistent with electron-transmission studies which indicated[15] that the vertical attachment energy[7] for the lowest π^* negative-ion state of C_6H_5SH lies in the range 0.7 to 1.1 eV. The 308-nm light does not appreciably *monophotonically* excite C_6H_5SH, and unless the laser-pulse energy is high enough for multiphoton absorption to occur, electron attachment involves only ground-state C_6H_5SH molecules. The rest of the data in Fig. 2 were taken with the KrF laser line (249 nm). The curve-3 measurements were taken with a *single* laser pulse of 2.5-mJ energy and show that η/N_a above $E/N\sim 1\times10^{-17}$ V cm^2 is due to electron capture by ground-state molecules and below $E/N\sim 0.5\times10^{-17}$ V cm^2 (corresponding to a mean electron energy of ~0.2 eV) is substantially due to electron capture by electronically excited molecules. Much larger photoenhanced η/N_a values were measured when a second similar (of the same energy) laser pulse followed the first at time intervals between 12.5 and 900 ms. The curves 4 to 7 in Fig. 2 are such measurements for a time delay,

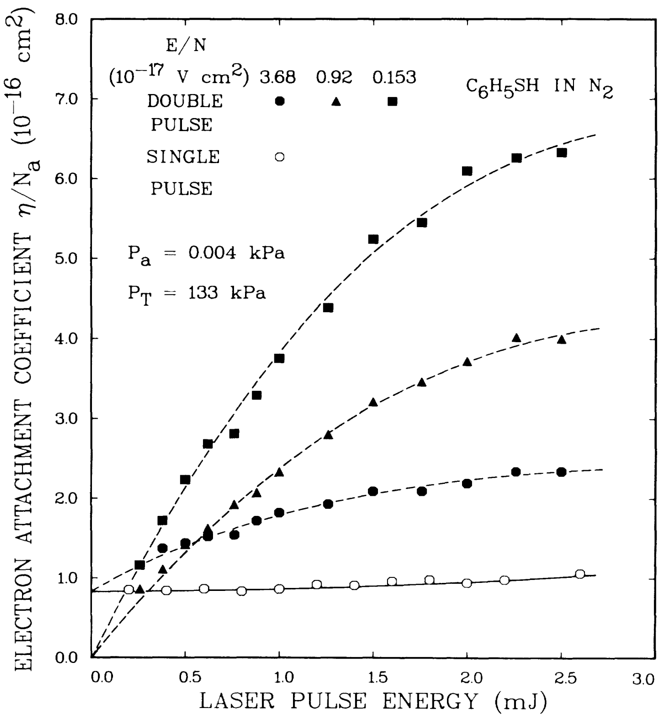

FIG. 3. Electron-attachment coefficient, η/N_a, vs laser-pulse energy at $\lambda=249$ nm for single-pulse and double-pulse ($\tau_d=12.5$ ms) irradiation at three E/N values. At $E/N=0.153\times10^{-17}$ V cm^2, η/N_a is predominantly due to photoenhanced attachment, and at $E/N=3.68\times10^{-17}$ V cm^2, η/N_a is due predominantly to ground-state dissociative attachment (see Fig. 2).

τ_d, between the two similar laser pulses of 12.5 ms and for the pulse energies shown in the figure.

The observed photoenhanced attachment involves $AX^*(T_1)$ and is consistent with a nondissociative-electron-attachment mechanism involving $AX^*(T_1)$ and $AX(S_0)$, as for example,

$$AX^*(T_1)+AX(S_0)\rightarrow \text{triplet excimer}(?),$$
$$\text{triplet excimer}+e\xrightarrow{N_2}\text{anions}, \tag{3}$$

for the following reasons:

(1) The photoenhanced η/N_a is very much larger for the second than for the first laser pulse. This would indicate that the excited species $AX^*(T_1)$ produced by the first laser pulse does not significantly attach the electrons produced by that laser pulse [e.g., via reaction (1)] but rather reacts with an unexcited $AX(S_0)$ molecule to form the electron-attaching species (possibly a triplet-state excimer).[16] For the N_a densities used, this would take times of the order of 10^{-6} s, and thus few species would be formed during the first laser pulse, and many more would be present to attach the electrons produced by the second laser pulse.

(2) The photoenhanced η/N_a decreases with increasing τ_d between the two laser pulses (for $\tau_d\gtrsim 12.5$ ms) indicating diffusion (or decay) of the electron-attaching species outside of the path of the second laser pulse (in this regard studies with shorter τ_d are required; these could not be done with the present system).

(3) At a fixed laser-pulse energy, the photoenhanced η/N_a increases with N_a for low (<5 Pa) partial pressures and, for a fixed N_a, η/N_a increases with increasing N_2 pressure in a manner similar to that of a three-body electron attachment process[1,7] (i.e., the capturing species requires collisional stabilization by N_2).

(4) In the high-(E/N) region ($E/N=3.68\times10^{-17}$ V cm^2 in Fig. 3; see also Fig. 2), where η/N_a is substantially due to ground-state dissociative attachment, η/N_a is only slightly dependent on the N_2 pressure. In this E/N region, η/N_a is almost (Fig. 3) independent of the laser-pulse energy in the case of single pulse; it varies slowly with the pulse energy in the double-pulse experiments. Conversely, in the low-(E/N) range ($E/N=0.153\times10^{-17}$ V cm^2 in Fig. 3; see also Fig. 2), where η/N_a is exclusively due to photoenhanced attachment, η/N_a increases greatly with increasing N_2 pressure [see (3) above] and also with the laser-pulse energy for both the single pulse and, especially, the double pulses.

While the η/N_a data in Figs. 2 and 3 were taken with the 249-nm laser line, other laser wavelengths were also used. Briefly, at the 308-nm laser line whose energy lies at or just below S_1 there is very little laser absorption and, hence, little photoenhanced attachment up to laser-pulse energies of ~1 mJ. For laser light at 222 and 193 nm for which the molecule can photodissociate, the laser absorption coefficients are large, and the photoenhanced attachment is small (one-fifth to one-half in the laser-pulse energy range 0.2–0.6 mJ) compared with that due to the 249-nm line under identical conditions, indicating competition between photodissociation and internal conversion to S_1. This laser-wavelength dependence of the photoenhanced attachment rules out dissociative attachment to vibrationally excited photofragments as the source of the photoenhanced attachment. Laser photoionization is also ruled out as the source of the photoenhanced ion production in view of the observed dependence of the photoenhanced attachment on E/N and the observed greatly enhanced attachment for the second laser pulse. Furthermore, because the experimental arrangement employed for the measurement of η/N_a cannot distinguish between positive and negative ions (both contribution to the observed signal), we devised a new two-field drift technique with which the positive and negative changes can be separately detected. With this arrangement we confirmed that at the laser-pulse energies employed in this study, the contribution of positive ions (due to laser photoionization) to the signal used to determine η/N_a is negligibly small except at very low E/N values where it could cause an increase of $\lesssim10\%$ in η/N_a. The η/N_a values in Fig. 2 have been corrected for this effect.

It should be noted that the photoenhanced η/N_a in Figs. 2 and 3 are actually lower limits to their true values since η was divided by the number density, N_a, of the unexcited C_6H_5SH molecules which is larger than that, N_a^*, of the excited molecules in T_1. For the lowest laser energy (0.05 mJ) used for which no saturation effects are expected (Fig. 3), we estimate that η/N_a^* is about 200 times larger than the values of η/N_a given in Fig. 2 (curve 4).

The present results clearly suggest that laser irradiation can be employed to produce (by strong absorption to an allowed electronic state followed by fast internal conversion to a long-lived state) large numbers of long-lived electronically excited molecules which attach electrons with cross sections 10^5–10^6 times larger than the respectively unexcited species.

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[16] Such triplet excimers have been proposed [e.g., see *Photochemistry,* edited by D. Bryce-Smith (The Chemical Society, London, 1975), Vol. 6, pp. 198,199; T. F. Hunter and M. G. Stock, Chem. Phys. Lett. **22**, 368 (1973), and J. Chem. Soc. Faraday Trans. 2 **70**, 1028 (1974)] to interpret a number of photophysical processes in organic (e.g., benzene) vapors.