A TECHNIQUE FOR THE MEASUREMENT OF ELECTRON ATTACHMENT TO SHORT–LIVED EXCITED SPECIES[1]

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ABSTRACT

A technique is described for the measurement of electron attachment to short-lived ($\lesssim 10^{-9}$ s) excited species. Preliminary results are presented for photoenhanced electron attachment to short–lived electronically–excited states of triethylamine molecules produced by laser two–photon excitation. The attachment cross sections for these excited states are estimated to be $> 10^{-11}$ cm^2 and are $\sim 10^7$ larger compared to those for the unexcited (ground–state) molecules.

INTRODUCTION

The significance of the basic physics of electron–ground state molecule collision processes in understanding the properties of gaseous dielectrics has been amply documented.[1] However, the role of electronically–excited species has not as yet been fully addressed, although it is considered to be important in its effects on the dielectric and "switching" properties of gases.[2-4] The principal reason for this is the lack of knowledge on electron attachment to, electron scattering from, and electron–impact ionization of electronically–excited species, which in turn is due to experimental difficulties encountered in producing sufficient numbers of specific excited species under controlled experimental conditions. Recently, we successfully produced indirectly via laser excitation, sufficient numbers of long–lived electronically–excited molecules under swarm conditions and observed 5 to 6 orders of magnitude increases in the attachment of slow electrons to them compared to the ground electronic states. In Fig. 1a is shown the laser/electrode arrangement used in these studies. The laser pulse which produced the excited species injected at the end of its path a pulse of photoelectrons in the gas from the cathode; these electrons attached to the laser–produced excited species en route to the anode. Figure 1b

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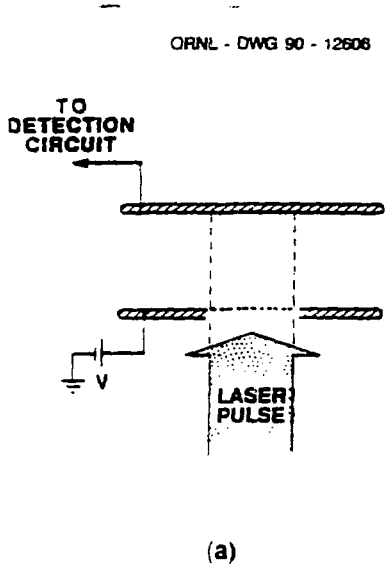
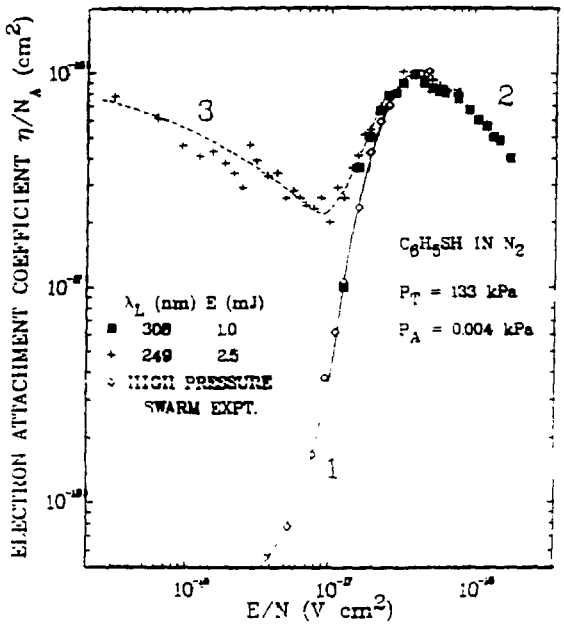
shows the measured electron attachment coefficient for the first excited triplet and the ground singlet state of the thiophenol molecule.[5,6] Besides their intrinsic value these initial observations demonstrated the feasibility of optical switching of the dielectric properties of gases by laser–induced changes in electron attachment involving electronically–excited molecules. In this regard, it is desirable to achieve optically–enhanced electron attachment to short–lived ($\lesssim 10^{-8}$ s) excited electronic states since this would allow optical switching at higher repetition rates.



(a)



(b)

Fig. 1(a). Schematic drawing of the two–electrode configuration employed for measurement of electron attachment to the first–excited triplet state of thiophenol. The detection region is the same as the interaction region and is located between the two electrodes; the same laser pulse irradiates the interaction region (producing excited attaching species) and also produces a pulse of attaching electrons at the cathode via photoelectric emission. At the laser fluences employed, laser photoionization is negligible.

(b) The electron attachment coefficient, η/N_A vs. E/N for thiophenol in N_2 buffer gas. Curve 1 was obtained in a separate high pressure swarm experiment without laser irradiation, and depicts electron attachment to the ground state. Curves 2 and 3 were obtained in the present experiment with XeCl and KrF laser lines respectively. The photon energy of the XeCl line is not sufficient to excite electronically the molecule monophotonically and therefore only the ground state attachment is observed; however, electronic excitation and enhanced electron attachment occurs at the KrF line. Note that η/N_A^* is ~ 100 times larger than η/N_A since the excited molecule number density N_A^* is about one percent of N_A.

In this paper, we describe for the first time a technique for measuring photoenhanced electron attachment to short–lived ($\lesssim 10^{-8}$ s) excited electronic states

of molecules and present preliminary results on low–energy electron attachment to high–lying excited electronic states of the triethylamine molecule.

TECHNIQUE

Description

In Fig. 2a is shown the laser/electrode configuration of the electron swarm apparatus[6] we employed. The gas Ar or N_2 was used as the buffer medium. A single excimer–laser pulse generated (via multiphoton ionization) the attaching electrons volumetrically over the laser–irradiated region (Fig. 2a) and, also, the electronically–excited molecules. Since the excited species and the electrons were produced concomitantly and in close proximity, electron attachment can occur within the short lifetimes of the electronically–excited molecules. The attaching electrons were produced by photoionization of the same gas that produced the electron–attaching excited species, although a suitable gas additive could be added to the binary mixture for this purpose. Since in this technique positive ions are also produced, the negative charges (electrons and anions) must be separated and detected unambiguously. This was accomplished (Fig. 2a) by separating the detection region (located between electrodes 2 and 3) from the interaction region (located between electrodes 1 and 2) via a three–electrode arrangement. Charge transmission between the two regions was through a fine grid. The same electric field was maintained in both regions and—depending on the direction of the field—either negative or positive charges produced in the interaction region were extracted into the detection region.

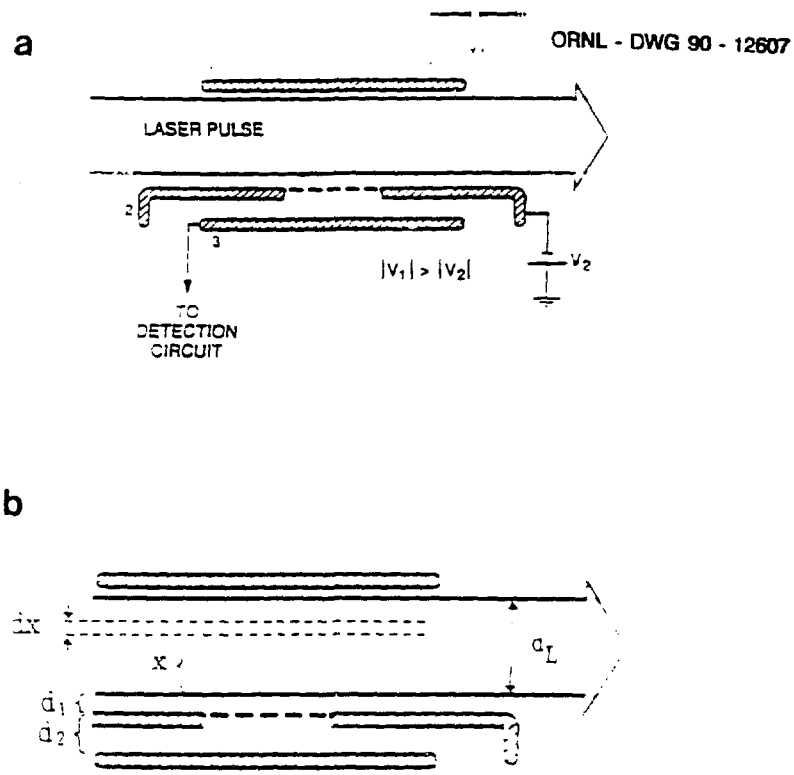


Fig. 2(a). Schematic diagram of the experimental arrangement for the measurement of electron attachment to short–lived excited species.

(b) Subdivision of electrons initially produced via laser photoionization in to "planar swarms" (see text).

Analysis

The data analysis depends on the electron attachment mechanisms involved and the relative values of four time parameters: the life time τ of the excited species; the time τ_{ss} for the photoionization electrons to reach steady state; the time τ_a for an electron to be attached; and the time τ_d for the electrons to drift through the laser irradiated region.

τ: can vary from ms to sub–ns depending on the excited state involved.

τ_{ss}: under our conditions [N_2, Ar pressures in the range 7 to 70 kPa] is in the range 10^{-6} to 10^{-8} s.

τ_a: depends on the electron attachment rate constant k_a and the number density N_a of the electron attaching species; when these are known, τ_a can be estimated from $\tau_a = (k_a N_a)^{-1}$. Since, moreover, electron attachment has to occur before the decay of the excited species,

$$\tau_a < \max\left\{\tau, \tau_L\right\} \tag{1}$$

where τ_L is the duration of the laser pulse.

τ_d: d_L/w, where d_L is the "height" of the laser pulse (Fig. 2a) and w is the electron drift velocity; under our experimental conditions τ_d varies from 10^{-5} to 10^{-6} s.

Two extreme cases can be distinguished:

(i) $\tau > \tau_d$. This is the case of "long–lived" ($\tau \gtrsim 10^{-5}$ s) species for which conventional electron swarm relationships apply in the present experiments. In conventional electron swarm studies $\tau_{ss} << \tau_d \simeq \tau_a < \tau$.

(ii) $\tau < \tau_L$. From Eq. (1), it follows that $\tau_a < \tau_L$ ($\approx 10^{-8}$ s in our experiments). This is the case of "short–lived" species ($\tau < 10^{-8}$ s). In this situation, $\tau_a << \tau_{ss}$ and the electrons are attached before a steady–state condition is reached.

Long–Lived Species ($\tau \gtrsim 10^{-5}$ s)

Molecules in metastable excited states or in their ground electronic state satisfy conditions (i) above. Under such conditions, the photoionization electrons quickly reach a steady–state and drift through the laser–irradiated region toward the anode; electron attachment occurs while the electrons drift. Conventional electron swarm relationships are applicable; for example, the k_a is related to w and the density–normalized electron attachment coefficient η/N_a by

$$k_a = (\eta/N_a)w \tag{2}$$

The present swarm technique differs from the conventional ones however in that instead of a planar electron swarm in the conventional, the electrons are produced over the entire volume irradiated by the laser pulse in the present technique. We can, however, subdivide this volume into an infinite number of "planar swarms" (Fig. 2b) and sum their contributions. If n_0 is the number density of electrons produced via laser photoionization, A the area of the grid in the middle electrode (Fig. 2b), and η the electron attachment coefficient of the attaching species located within the boundaries of the laser pulse, the number of unattached electrons crossing the lower laser boundary (Fig. 2b) is

$$N_E = \int_0^{d_L} n_o A dx\, e^{-\eta x} = \frac{n_o A}{\eta} [1 - e^{-\eta d_L}] \tag{3}$$

If no further electron attachment occurred during the traversal of d_1 and d_2, the measured voltage ratio, R_v, of the total signal, V_T, to the signal component, V_E, due to the unattached electrons would be

$$R_v = \frac{V_T}{V_E} = \frac{N_I + N_E}{N_E} = \frac{n_o A d_L}{N_E} \tag{4}$$

From (3) and (4),

$$R_v = \frac{\eta d_L}{[1 - e^{-\eta d_L}]} \tag{5}$$

and η is, then, determined from the measured R_v by an iterative procedure.

When electron attachment occurs outside the laser–irradiated region, as in the case of electron attachment to ground state molecules, the measured V_E, $(V_E)_m$ would be smaller than one would expect if the attachment occurred only within the laser irradiated region. If η' is the attachment coefficient outside of the irradiated region, the electron component, $(V_E)_{c_1}$, corrected for electron attachment during the drift d_2 (inside the detection region where the applied electric field is the same as that in the interaction region) is

$$\frac{(V_E)_{c_1}}{(V_E)_m} = \frac{\eta' d_2}{1 - e^{-\eta' d_2}} \tag{6}$$

When, in addition, correction is made for electron attachment during the drift d_1, the final corrected value $(V_E)_c$ is

$$(V_E)_c = (V_E)_{c_1} e^{\eta' d_1} = (V_E)_m e^{\eta' d_1} \left\{ \frac{\eta' d_2}{1 - e^{-\eta' d_2}} \right\} \tag{7}$$

In the case of measurement of electron attachment to ground–state molecules, which we have made to only verify the technique, $\eta' = \eta$ and published values of η were used in (7) to obtain $(V_E)_c$, which in turn was used in (5) to determine the electron attachment coefficient within the irradiated volume.

Short–Lived Species ($\tau < 10^{-8}$ s)

Unlike the long–lived species case just discussed, in this case electron attachment does not occur while the electrons drift but rather immediately after they are produced and before they begin to drift. In this case, then, the number density of negative ions formed within the laser irradiated volume is

$$N_I = \int_0^{\tau_L} N_e(t)\, N^*(t)\, k_a\, dt \tag{8}$$

DISCLAIMER

where $N_e(t)$ and $N^*(t)$ are the number densities of electrons and excited species at time t and k_a is now the electron attachment rate constant of the excited species. The number density of electrons initially produced by laser photoionization is

$$N_e(t = \tau_L) = N_T = N_I + N_E \tag{9}$$

where N_I is the number density of negative ions and N_E is the number density of unattached electrons. The expressions for $N_e(t)$ and $N^*(t)$ will depend on the particular case under consideration. Disregarding any possible electron attachment to ground state molecules during the drift to and within the detection region, the measured voltage ratio, R_v, is given by,

$$R_v = \frac{V_I}{V_T} = \frac{N_I}{N_T} \tag{10}$$

The laser fluence F, the partial pressure of the gas which yields the short–lived electron attaching species, and the electron attachment cross section $\sigma_a(\epsilon)$ are among the parameters which determine the value of R_v. Measurements of the R_v vs F, along with assumed or established electron attachment mechanisms can yield[7] the value of—or a quantity related to—$k_a(\epsilon)$ and $\sigma_a(\epsilon)$.

MEASUREMENTS

Electron Attachment to Ground–State SF_6

In order to test the present technique, we first measured electron attachment to ground state SF_6 molecules at room temperature using N_2 as the buffer gas. The attaching electrons were generated by XeF (250 nm; 3.5 eV) laser two–photon ionization of tetrakis–dimethylaminoethylene (TMAE) [adiabatic ionization potential, $I \lesssim 6$ eV] which was added to the SF_6/N_2 mixture. The laser fluence, was $\lesssim 0.3$ mJ cm^{-2} and the only effect of the laser irradiation was to photoionize TMAE. The cross sectional area of the laser pulse was 0.8 x 0.5 cm^2. Correction for electron attachment occurring outside of the laser–irradiated region was carried out (with Eq. (7)) using published values[8] of η' (= η). It can be seen from Fig. 3 that the present measurements of η/N_a (E/N) in the laser–irradiated region are in excellent agreement with the published data[8] obtained on SF_6/N_2 by conventional electron swarm techniques.

Electron Attachment to Short–Lived Electronically–Excited Triethylamine Molecules

We employed the present technique to measure electron attachment to electronically–excited states of triethylamine (TEA) which lie energetically above the first ionization–threshold energy I and are presumably Rydberg in character. Excited states of molecules lying above I are called superexcited states (SES); they normally decay rapidly (lifetimes $< 10^{-9}$ s) by preionization and/or predissociation. These studies were conducted at room temperature in N_2 or Ar buffer–gas mixtures at total pressures of ~ 6 to 60 kPa.

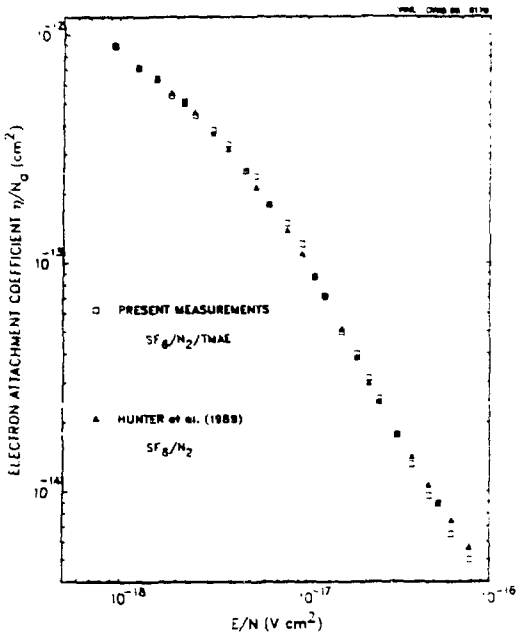


Fig. 3. Comparison of electron attachment measurements for ground state SF_6 obtained using the present technique with published data[8] obtained using a conventional swarm technique.

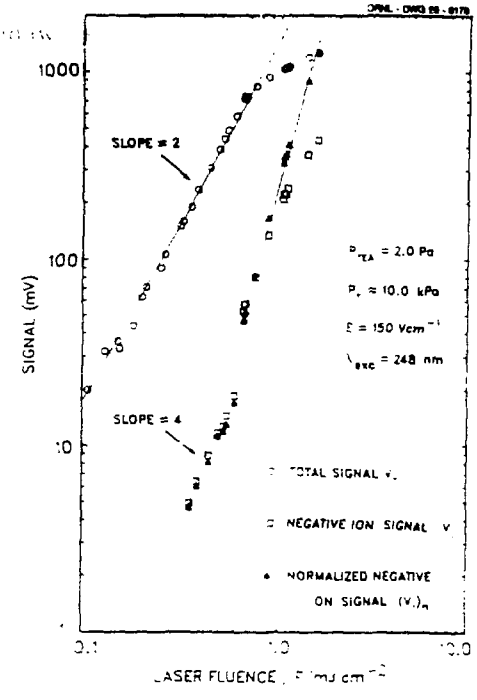


Fig. 4. Laser fluence dependence of the measured total and negative ion signals and the normalized negative ion signal (see text) shown on a log–log plot for the experimental parameters indicated in the figure.

Figure 4 shows the measured total signal (proportional to the number density of electrons initially produced via photoionization; Eq. (8)), $(V_T)_m$, and the measured negative ion signal, $(V_I)_m$, as a function of the laser fluence, F. At low laser fluences, $(V_T)_m$ varies as F^2 indicating two–photon ionization. The deviation from this quadratic dependence at high F (> 0.75 mJ cm^{-2} in this case) is due to space–charge effects. Once corrected for the space–charge effects, the normalized negative ion signal, $(V_I)_n$ varied as F^4 (since four photons are needed to form a negative ion; two photons to produce the SES and two more photons to produce the attaching electron). The $(V_T)_n$ and $(V_I)_n$ were shown to have linear and quadratic dependences, respectively, on the triethylamine pressure. Using these findings and measurements along with the available photophysical studies on triethylamine we concluded[7] that the observed photoenhanced electron attachment is due to the SES of TEA and that their electron attachment cross sections are enormous (> 10^{-11} cm^2). These cross sections are over 10^7 times larger than those for the ground state TEA molecules.

CONCLUSIONS

A technique has been described which allows measurement of electron attachment to short–lived electronically–excited species produced by pulsed–laser light. The technique provided the first results of this nature which indicate that slow electrons attach to short–lived electronically–excited molecules with enormous cross sections. More studies are needed—and are in progress—to establish the photoenhanced electron attachment mechanisms involved, determine accurately the rate constants and cross sections, and assess the potential of these findings for fast optical switching.

REFERENCES

1. L. G. Christophorou and L. A. Pinnaduwage, Basic Physics of Gaseous Dielectrics, IEEE Trans. Electr. Insul. 25:55 (1990).

2. J. M. Meek and J. D. Craggs (eds.), "Electrical Breakdown of Gases," Wiley, New York (1978).

3. L. G. Christophorou and S. R. Hunter, From Basic Research to Application, in: "Electron–Molecule Interactions and Their Applications," (L. G.Christophorou, ed.), Academic Press 2, New York (1990).

4. A. Guenther, M. Kristiansen, and T. Martin (eds.), "Opening Switches," Plenum Press, New York (1987).

5. L. G. Christophorou, S. R. Hunter, L. A. Pinnaduwage, J. G. Carter, A. A. Christodoulides, and S. M. Spyrou, Optically Enhanced Electron Attachment, Phys. Rev. Lett. 58:1316 (1987).

6. L. A. Pinnaduwage, L. G. Christophorou, and S. R. Hunter, Optically Enhanced Electron Attachment to Thiophenol, J. Chem. Phys. 90:6275 (1989).

7. L. A. Pinnaduwage and L. G. Christophorou, Enhanced Electron Attachment to Superexcited Molecular States, submitted to Phys. Rev. Lett. (1990).

8. S. R. Hunter, J. G. Carter, and L. G. Christophorou, Low–Energy Electron Attachment to SF_6 in N_2, Ar, and Xe Buffer Gases, J. Chem. Phys. 90:4879 (1989).