MEASUREMENT AND MECHANISMS OF PHOTOENHANCED ELECTRON ATTACHMENT: IMPLICATIONS FOR AN OPTICALLY-CONTROLLED DIFFUSE DISCHARGE OPENING SWITCH[*]

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Capacitive energy storage has commonly been used in technically-established pulsed power generators. However, the increasing demand for high power pulsed equipment and the fact that inductive energy storage has larger energy storage density, triggered investigations of the possibility of using inductive energy storage in pulsed power applications.[1] The critical component in an inductive energy storage system is a fast, repetitive opening switch for which an optically-controlled diffuse discharge opening switch appears to be a promising possibility.[1,2]

Diffuse discharges are advantageous for switching purposes because of their low inductance, small electrode erosion rates and moderate energy density which allows control by means of e-beams and/or laser beams with reasonable power. However, to obtain fast opening after the external electron source is turned off, electrons in the switch gap must be removed by attachment since diffusion and recombination processes are too slow. To avoid electron losses in the conducting state, electronegative gases can be used which strongly attach electrons only upon optical excitation.[1]

Therefore, the successful operation of an optically-controlled diffuse discharge opening switch requires an understanding of the basic mechanisms of laser-enhanced electron attachment. Appropriate laser irradiation of a gaseous medium can lead to the production of (i) vibrationally-excited states of the ground electronic state, (ii) electronically-excited singlet states, and (iii) electronically-excited triplet states of the parent molecules or of a photofragment and also, (iv) new chemical species produced by the interaction of photoproducts (e.g., photofragments). The species produced in mechanisms (i) through (iv) can have orders of magnitude larger electron attachment cross sections (for thermal and epithermal electrons) compared to the unirradiated parent molecules.

Optically-enhanced electron attachment via mechanism (i) has been observed[3] in several gases and successful operation of diffuse discharge switches using mixtures of these gases with buffer gases has been carried out recently.[3]

We have observed enhanced electron attachment to several molecules (mixed with nitrogen) when irradiated by excimer laser radiation. In the case of thiophenol (C_6H_5SH) and thioanisole ($C_6H_5SCH_3$) the observed[4-6] enhancements in electron attachment have been attributed[4] to mechanisms (iii) and (iv) mentioned above.

Three kinds of experimental configurations have been employed in our studies. These are shown in Fig. 1. The experimental configuration of Fig. 1(a) was used to measure enhanced electron attachment to thiophenol molecules excited to their first electronic triplet state. An excimer laser pulse propagating through the grided anode irradiated the gas in the interaction region and also photoelectrically injected an electron pulse at the end of its path at the cathode. This electron pulse then drifted – as an electron swarm – towards the anode, colliding en route with the molecules in the laser irradiated region. The lifetime of the triplet state molecules produced indirectly[4] via laser-irradiation was ~ 8 ms and therefore virtually all those were available for electron attachment during the drift of the electrons.

The electron attachment coefficient, η/N_A (N_A = ground state attaching gas number density) is shown in Fig. 2 as a function of E/N. When the excimer laser was operated at 308 nm (XeCl) line, there was no enhanced attachment because the photon energy corresponding to that line lay below the first optically-allowed electronic state of thiophenol;[4,5] when the laser was operated at 249 nm (KrF) line a large enhancement in electron attachment was observed (see Fig. 2). This enhanced electron attachment was attributed to the dissociative electron attachment to the first excited triplet state of thiophenol. The enhancement was shown to decrease with (i) increasing buffer gas (N_2) pressure due to the quenching of the precursor of the triplet state (i.e., the singlet state(s) reached by photoabsorption), and (ii) increasing time delay between laser irradiation and subsequent electron attachment to the laser-irradiated molecules. (Electron attachment diminished within a few tens of μs due to the loss of electron attaching triplet states by triplet-triplet quenching).[4]

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Fig. 2: The electron attachment coefficient, η/N_A versus E/N for thiophenol in nitrogen for the ground state (curves 1 and 2) and for the electronically-excited first triplet state (curve 3) molecules.
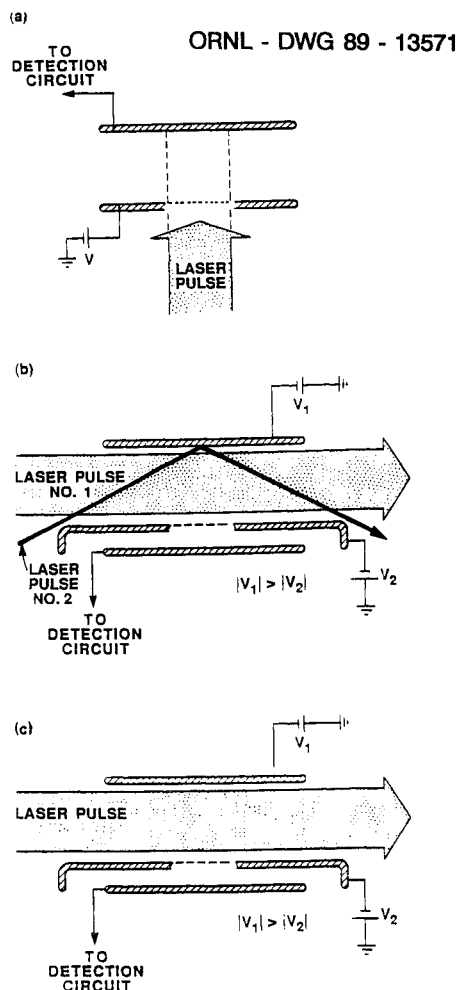

Fig. 1: The three different experimental configurations employed in the present experiments (see the text and Ref. 4).

Electron attachment to laser-irradiated thiophenol molecules at times > 100 μs from laser irradiation was measured by using the "three-electrode" experimental configuration in Fig. 1(b). In this case, laser pulse No. 1 propagating horizontally irradiated the interaction region located between the top two electrodes. Laser pulse No. 2 with a geometrical cross section of ~ 0.1 cm^2 propagating at an angle produced an electron swarm at the top electrode which subsequently drifted through the laser irradiated region. The time delay between laser pulses 1 and 2 could be varied upwards from ~ 100 μs. Only the negative ions and the unattached electrons were extracted into the detection region (located between the bottom two electrodes) through a grid in the middle electrode, and any positive ions produced in the interaction region (for example, via photoionization) were rejected.

In this latter experiment the observed photoenhanced electron attachment increased initially with increasing time delay and then remained constant up to ~ 1 s (see Fig. 3). Clearly this photoenhanced electron attachment is due to the formation of an electron attaching species which is stable. The loss of electron attachment at time delays longer than 1 s is due to the diffusion of the attaching species out

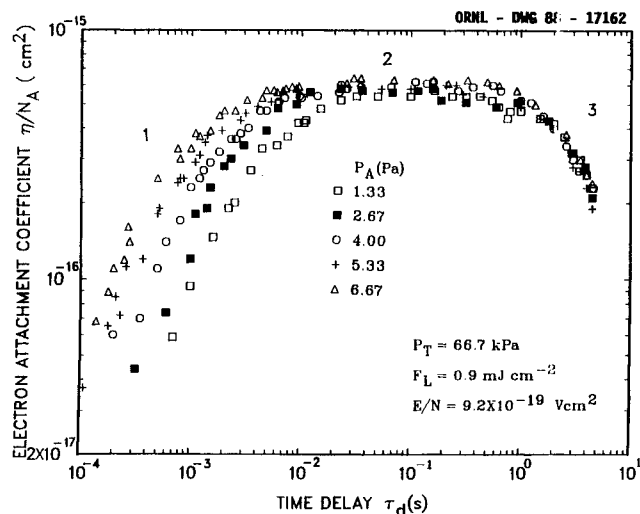Fig. 3: The electron attachment coefficient, η/N_A as a function of time delay, τ_d, between laser irradiation and subsequent electron attachment to capturing species produced by laser irradiation for thiophenol in nitrogen. Data for five thiophenol pressures are shown.

100

of the interaction region before the arrival of the electron swarm. It was also observed[4] that unlike in the previous case involving the first electronically-excited triplet state the electron attachment increased with increasing N_2 pressure. These and other experimental observations[4] are consistent with the formation of diphenyldisulfide (PhSSPh) by the interaction of two thiophenoxy radicals (PhS·) and subsequent N_2-stabilized electron attachment to these new species.[4] The thiophenoxy radicals are formed by the direct photofragmentation of thiophenol molecules.

Now let us consider the implications of these observations for an optically-controlled diffuse discharge opening switch. In the case where the electron attaching species is an electronically-excited triplet state (mechanism (iii)), these species are produced within ~ 10^{-8} s of laser irradiation,[4] and therefore the conductivity of the medium could be switched very rapidly. However, since triplet state lifetimes are normally several ms long, the repetition rate would be < 1 kHz. In the case where the electron attacher is the photoproduced PhSSPh the formation time is ~ 1 ms (see Fig. 3). While the formation time can be shortened by increasing the thiophenol pressure (the data in Fig. 3 were taken at low ($\lesssim$ 6 Pa) thiophenol pressures), mechanism (iv) is not suitable for a repetitive switch because the photoproduced electron attaching species do not decay at all and with repeated operation will interfere with switch conduction.

We have recently developed a new technique (Fig. 1(c)) for measuring photoenhanced electron attachment to very short-lived electronically-excited singlet states (i.e., mechanism (ii)). In this arrangement the same laser pulse which produces the excited species also produces the attaching electrons by photoionization of the same gas or of a suitable additive. Since the positive ions resulting from ionization can be rejected in the three-electrode arrangement, the negative ions resulting from electron attachment can be detected unambiguously along with the unattached electrons. Since, moreover, electrons and electron-attaching excited species are produced in close proximity, the lifetime of the excited attaching species can be as small or smaller than 10^{-9} s. Depending on the attachment cross section and lifetime of the excited species, the concentration of the excited species can be adjusted by varying the gas pressure and/or the laser fluence in order to obtain a measurable negative ion component.

We have used this arrangement (Fig. 1(c)) in our studies of photoenhanced electron attachment to triethylamine (TEA)-N_2 mixtures. While the unirradiated mixture showed no attachment (η/N_A < 10^{-18} cm^2 at E/N < 1 x 10^{-17} V cm^2) preliminary measurements with the 249 nm (KrF) excimer laser line indicated very strong photoenhanced attachment. In Fig. 4 are shown our preliminary measurements of $q\langle\sigma_a\rangle\tau$ versus E/N for a TEA - N_2 mixture. The quantity $q(= N^*/N_L$, where N^* is the number density of the excited attaching species produced and N_L is the corresponding number of laser photons absorbed per unit volume) is the efficiency of production of the excited attaching species; $\langle\sigma_a\rangle$ is the average cross section for electron attachment and τ is the lifetime of the attaching species. An estimate of $\langle\sigma_a\rangle$ with this technique,[6] therefore, requires knowledge of q and τ. The TEA vapor fluorescence lifetime is[7] ~ 3 ns. If, then, the first excited singlet state of TEA—which is presumably responsible for the observed
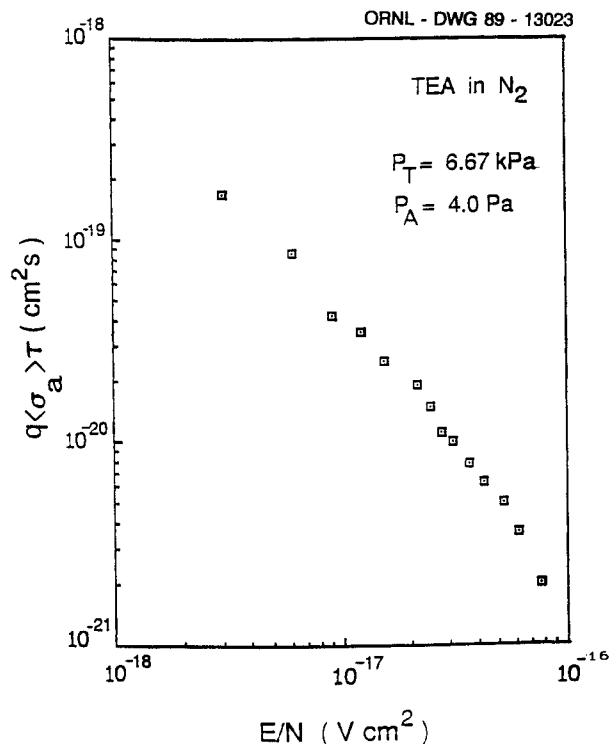
Fig. 4: The quantity $q\langle\sigma_a\rangle\tau$ versus E/N for triethylamine (TEA) in nitrogen. These data were obtained using KrF excimer laser line.

fluorescence of the TEA vapor—is the electron attaching state, then from Fig. 4, $\langle\sigma_a\rangle \geq 6$ x 10^{-11} cm^2 at E/N = 3 x 10^{-18} V cm^2 (mean electron energy ~ 0.13 eV) assuming τ = 3 ns and q $\leq$ 1. This is indeed a very large cross section for a low - lying (fluorescing) valence state reached indirectly by internal conversion from higher-lying states initially produced by photo-excitation. A cross section of this magnitude might indicate electron attachment to the initially produced higher-lying excited (Rydberg?) states prior to their conversion to the fluorescing state. The cross section for slow-electron capture to such states may actually be determined by the long range of the electron-Rydberg dipole interaction, which is larger than the actual size of the Rydberg state and the electron de Broglie wavelength large as these can be. It has been shown that Rydberg states of molecules can have lifetimes in excess of 10^{-9} s[8] and that cross sections for various reactions involving Rydberg states can be > 10^{-10} cm^2.[9] While we have not been able to determine the lifetime of the electron attaching excited species in these experiments, we were able to obtain an upper limit of 10^{-6} s for their lifetime by carrying out a two-laser experiment similar to that of Fig. 1(b).

The buffer gas (N_2) pressure dependence of the observed photoenhanced electron attachment to TEA is shown in Fig. 5. The enhanced attachment decreased with increasing nitrogen pressure even though the fluorescence emission from TEA-N_2 mixtures increased with N_2 pressure (compared to a pure TEA sample, fluorescence from a TEA-N_2 mixture with the same TEA pressure and a N_2 pressure of 133 kPa was twice as strong).[7] This can be considered as another indication that the attacher is not the first excited singlet state (i.e., the fluorescing state), but one of another (Rydberg?) character. Rydberg states can

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TEA in N_2

$E/N = 9.2 \times 10^{-18}$ V cm^2

$P_A = 4.0$ Pa

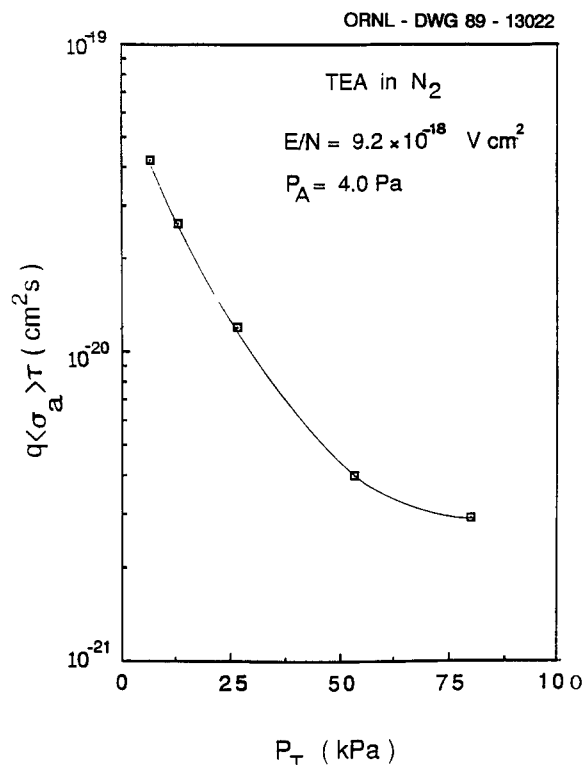$q\langle\sigma_a\rangle\tau$ (cm^{2}s)

P_T (kPa)

Fig. 5: The quantity $q\langle\sigma_a\rangle\tau$ versus buffer gas (nitrogen) pressure for the experimental parameters indicated in the figure.

be easily quenched[8,9] and internally convert[10] to the low-lying fluorescing state by collisions. Further studies on TEA-N_2 and other gas mixtures are in progress.

Large photoenhanced electron attachment whether it is to the first excited singlet state (for which the lifetime is $\gtrsim 10^{-9}$ s) or to Rydberg states (where the effective lifetime can be greatly manipulated by varying the attaching and/or the buffer gas pressures) can be exploited in a diffuse discharge opening switch, and due to the short lifetimes involved can be most appropriate for high repetition switches.

Acknowledgement

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