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Abstract

In this paper the limited but significant knowledge to date on electron scattering from vibrationally/rotationally excited molecules and electron scattering from and electron impact ionization of electronically excited molecules is briefly summarized and discussed. The profound effects of the internal energy content of a molecule on its electron attachment properties are highlighted focusing in particular on electron attachment to vibrationally/rotationally and to electronically excited molecules. The limited knowledge to date on electron-excited molecule interactions clearly shows that the cross sections for certain electron-molecule collision processes can be very different from those involving ground state molecules. For example, optically enhanced electron attachment studies have shown that electron attachment to electronically excited molecules can occur with cross sections 10^6 to 10^7 times larger compared to ground state molecules. The study of electron-excited molecule interactions offers many experimental and theoretical challenges and opportunities and is both of fundamental and technological significance.

1 Introduction

The interactions of slow ($\sim 0 - 20$ eV) electrons with molecules in their lowest states of excitation (vibrational/rotational, electronic) have been studied for almost a century [e.g., 1-4]; they aided the unraveling of the mysteries of the microcosmos and led to stimulating advances both in basic and applied science and in technology [e.g., 1-5]. In contrast, our knowledge on the interactions of slow electrons with excited (energy rich) molecules—especially electronically excited molecules—is very limited in spite of its fundamental (e.g., theory of collision processes and the structure of matter; energy loss mechanisms and cross sections; plasma, electron, ion and laser physics and chemistry; radiation and life sciences) and applied/technological (e.g., plasmas, lasers, gas discharges, pulsed power switches, optogalvanic effects) significance.

The limited knowledge on electron-excited molecule interactions to date, clearly shows that the cross sections for certain electron-excited molecule collision processes can be very different from those involving ground-state molecules. Thus, studies [6-8] on optically-enhanced electron attachment have shown that (dissociative) electron attachment to electronically-excited molecules often occurs with cross sections 10^6 to 10^7 times larger compared to ground-state (unexcited) molecules. Moreover, the optical modification of electron attachment processes allows optical control of the impedance characteristics of gaseous matter on the millisecond to the subnanosecond time scale (depending on the laser pulse duration and the lifetime of the electron attaching electronically-excited molecule).

Many technologies (e.g., pulse power) which rely on the conversion of free electrons to anions (or vice-versa) will benefit from such basic studies [e.g., 9-11].

Especially for electron-electronically excited molecule interactions, the availability of lasers now allows the production—directly or indirectly (via cascading from upper states)—of sufficient numbers of excited species to make the study of electron-electronically excited molecule interactions feasible under controlled experimental conditions. This was extremely difficult in the past when electronically-excited species (mostly metastable atoms) could only be produced in small concentrations employing gas discharges, charge exchange or electron beam techniques. The much higher densities of excited species that can be produced by lasers opens up a new and exciting field namely, that of electron-electronically excited molecule interactions.

In this paper, I shall first discuss (i) electron scattering from vibrationally/rotationally-excited molecules, (ii) electron scattering from electronically-excited molecules, and (iii) electron impact ionization of electronically-excited molecules. Following that I shall focus on (iv) electron attachment to vibrationally/rotationally-excited molecules, and (v) electron attachment to electronically-excited molecules.

2 Scattering of Slow Electrons by "Hot" (Vibrationally/Rotationaly Excited) Molecules

Little is known about the scattering (elastic, inelastic, superelastic) of slow electrons from vibrationally/rotationally-excited molecules in spite of its effect on electron transport and significance in many applied fields (e.g., lasers, plasmas, switches). The few scattered studies to date indicate that vibrational excitation enhances electron scattering.

In Figure 1 is plotted the density-normalized thermal electron mobility $(\mu N)_{th}$ as a function of the temperature T for CH_4 and C_2F_6 [12]. The momentum transfer cross sections $\sigma_m(\epsilon)$ of both molecules possess a Ramsauer-Townsend (R-T) minimum; at an energy $\epsilon \approx 0.3$ eV [13] for CH_4 and at $\epsilon \approx 0.08$ eV [14] for C_2F_6 . In view of this, $(\mu N)_{th}$ would be expected to increase with increasing T as indeed it does for CH_4 . However, for C_2F_6 which has very low vibrational thresholds (six of its twelve fundamental vibrational frequencies lie below 0.077 eV and all twelve lie below 0.155 eV [15]), the opposite behavior is observed due at least in part to the enhanced electron scattering from vibrationally excited C_2F_6 molecules as T is increased.

Another example is the low-energy total electron scattering cross section measurements for unexcited and for vibrationally excited (principally in the low-lying (~ 0.083 eV) 010 bending mode) CO_2 molecules shown in Figure 2a [16]. At energies ≤ 2 eV, the excited-state cross section is

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considerably larger than that for electron scattering from the ground-state CO_2 molecule. The CO_2 bending vibration has an associated electric dipole moment and it was suggested [16, 18] that the observed increase in the cross section from "hot" CO_2 principally comes from enhanced scattering due to the electric dipole moment associated with this, the lowest bending vibration (010) of CO_2 . Earlier calculations [19] indicated that sizable inelastic electron-molecule scattering cross sections can arise from electron scattering by the electric dipole moments associated with molecular bending and stretching vibrations. The cross sections for scattering of slow electrons by polar molecules have long been known [1] to be very large.

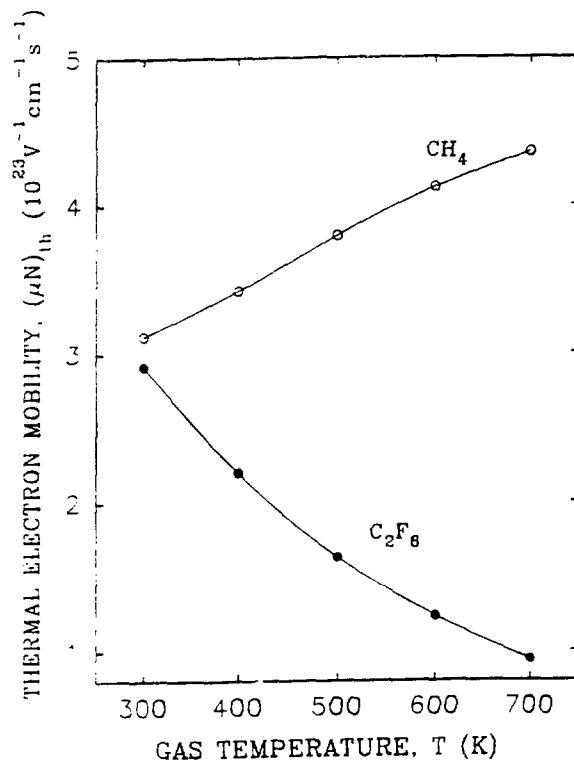


Figure 1: Density-normalized thermal electron mobility, $(\mu N)_{th}$ as a function of gas temperature, T, for CH_4 and C_2F_6 (see the text) [12].

A more recent study of CO_2 at 250 and 520 K using a time-of-flight electron spectrometer [20] confirmed the earlier work [16] below ~ 2 eV but, in contrast, observed a significant increase in the total electron scattering cross section beyond 2 eV, especially between 3 and 5 eV where the $^2\Pi_u$ negative ion state of CO_2^- is located (see Figure 2b). The enhancement in the scattering cross section in this energy range was attributed principally to the indirect population of the bending mode of CO_2 via the decay of the $^2\Pi_u$ resonance of CO_2^- . The position of the cross section peak is shifted (Figure 2b) to lower energy by ~ 0.3 eV as is expected from calculations of the potential energy surface of CO_2^* ($^2\Pi_u$) (see [2]; Vol. 1, Chapt. 6).

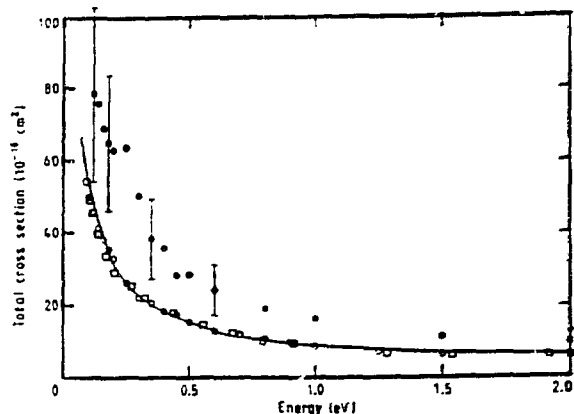


Figure 2a: Total cross sections for electron scattering from CO_2 in the energy range 0 - 2 eV: vibrationally excited CO_2 (\bullet , [16]); ground-state CO_2 (\circ , [16]; \square , [17a]; — , [17b]), From [16].

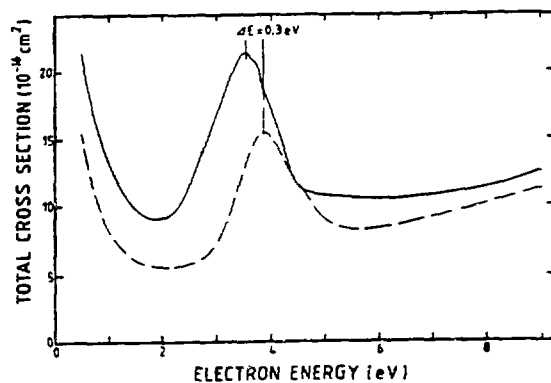
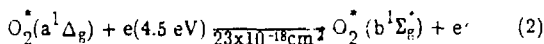
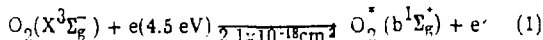


Figure 2b: Total cross sections for electron scattering from CO_2 molecules in the vibrational ground state (dashed curve), and from molecules in excited states of bending vibration (solid curve) [20].

3 Scattering of Slow Electrons by Electronically-Excited Molecules

As in the case of vibrationally-excited molecules, our knowledge on the scattering of slow electrons by electronically-excited molecules is very limited. Virtually the only molecule that has been studied to date is singlet oxygen, i.e., O_2 in the metastable state $a^1\Delta_g$. This state lies 0.98 eV above the ground state ($X^3\Sigma_g^-$) of O_2 ; it has a long lifetime ($\sim 2.7 \times 10^3$ s [21]) and it is relatively easy to produce in reasonable quantities in microwave discharges. The cross section for the excitation of the $b^1\Sigma_g^+$ state (located 1.63 eV above the ground state) of O_2 from the $a^1\Delta_g$ state of O_2 has been shown experimentally [22] to be more than one order of magnitude larger than that from the ground state $X^3\Sigma_g^-$ of O_2 , viz.,



Moreover, the energy loss spectrum of $\text{O}_2^*(a^1\Delta_g)$ (see Figure 3) shows [23] superelastic electron scattering—the electron-collision-induced decay of the $a^1\Delta_g$ state to the ground state at -0.98 eV . The energy-loss region in Figure 3 also shows direct excitation from the $a^1\Delta_g$ to the $b^1\Sigma_g^+$, and direct excitation from the $X^3\Sigma_g^-(v=0)$ to the $X^3\Sigma_g^-(v=2)$ and the $a^1\Delta_g(v=0.1)$ states.

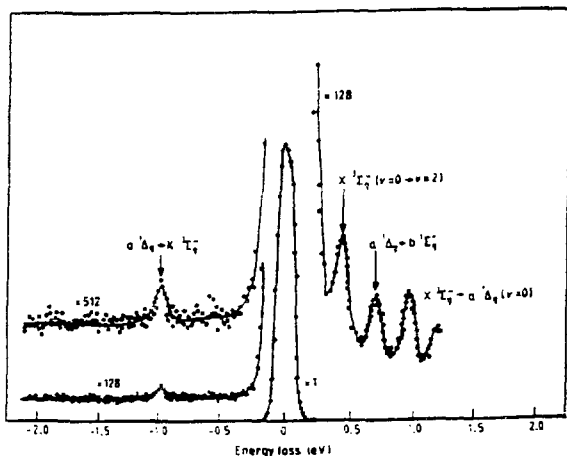


Figure 3: Electron-impact energy-loss spectrum showing the electron energy gain due to the de-excitation of $\text{O}_2^*(a^1\Delta_g; v=0)$ molecules to the ground state by electron impact. Also shown are other excitation processes. The incident electrons had 30 eV energy and the scattering angle was 20° [23].

The aforementioned results for singlet oxygen are consistent with the limited data which have been reported on the scattering of slow electrons from excited atoms. In Figure 4 are presented the total cross sections for electrons scattered by excited $\text{Na}^*(3^2P_{3/2})$ and unexcited $\text{Na}(3^2S_{1/2})$ sodium atoms measured [24–26] in a crossed-beam apparatus: many electron scattering processes contribute to the total cross section in the 6–25 eV energy range: elastic ($3P \rightarrow 3P$) superelastic ($3P \rightarrow 3S$), as well as excitation and ionization. Among the few other studies on excited atoms are the experimental measurements of the cross sections for electron impact excitation from the metastable 2^3S level of He to various triplet states [27], and the superelastic scattering of slow electrons from $\text{Hg}(^3P_1)$ atoms [28].

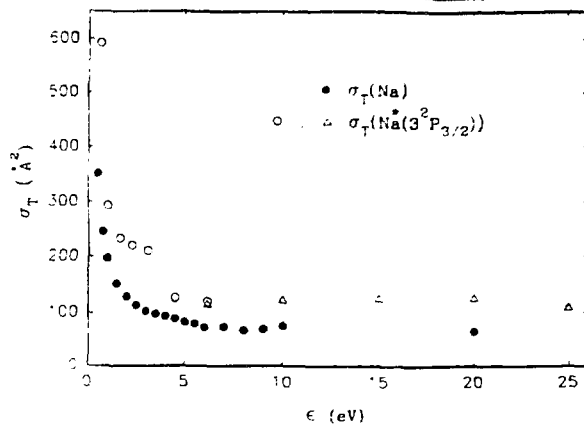
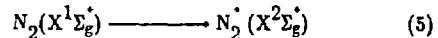
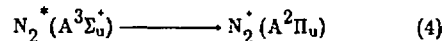
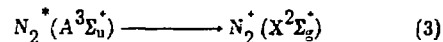


Figure 4: Total electron scattering cross section σ_T as a function of the electron energy ϵ for excited $\text{Na}^*(3^2P_{3/2})$ (o [25]; Δ [24]) and unexcited $\text{Na}(3^2S_{1/2})$ (• [26]) sodium atoms.

4 Electron-Impact Ionization of Electronically-Excited Molecules

In contrast to the many experimental and theoretical studies on electron impact ionization of ground-state molecules, there is only very limited information on electron-impact ionization of electronically-excited molecules. The few studies in this area include the calculations on electron-impact ionization of metastable rare gas excimers [29] and $\text{N}_2^*(A^3\Sigma_u^+)$, $\text{N}_2^*(a^1\Sigma_u^-)$ and $\text{CO}^*(a^3\Pi)$ [30], and the experimental measurements [31] on $\text{N}_2^*(A^3\Sigma_u^+)$. In Figure 5 are compared [31] the experimental and calculated cross sections for the nondissociative ionization of $\text{N}_2^*(A^3\Sigma_u^+)$ with that from the ground state $\text{N}_2(X^1\Sigma_g^+)$, viz.,



The threshold energies for reactions (3) – (5) are, respectively, 9.35, 10.47, and 15.58 eV. While the variation with electron energy, ϵ , of the cross section $\sigma_i(\epsilon)$ is similar for processes (3) and (5), the peak value for (3) is surprisingly lower than that for (5). It was suggested [31] that this may be partly due to the fact that the A state $^1\pi_g$ orbital is occupied by one electron while the X state $3\sigma_g$ orbital is occupied by two electrons.

Electron impact ionization cross sections have been reported for a number of metastable rare gas atoms [30–32].

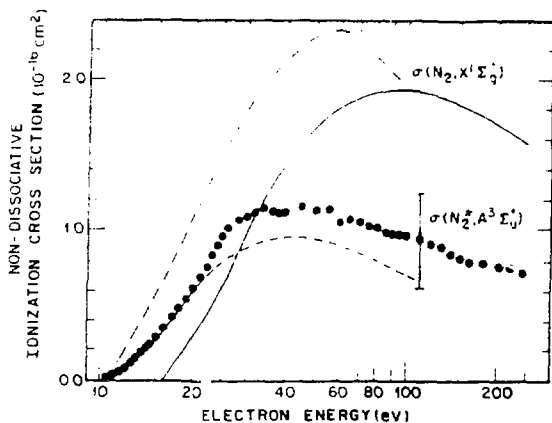
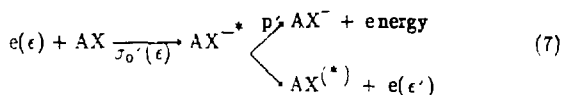
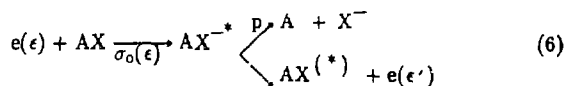


Figure 5: Experimental nondissociative electron impact ionization cross section [31] for: $N_2(X^1\Sigma_g^+)$ (—) and $N_2^*(A^3\Sigma_u^+)$ ($A^3\Sigma_u^+$) (\bullet); calculated cross sections for $N_2^*(A^3\Sigma_u^+)$ \longrightarrow $N_2^*(A^2\Pi_u)$ ionization: (— · —, [30]); (--- (see [31]). From [31].

5 Electron Attachment to Vibrationally/Rotationally Excited Molecules

Electron attachment reactions depend strongly on both the kinetic energy, ϵ , of the attached electron and the internal energy, E_{int} , of the electron attaching molecule [1-4]. As E_{int} is increased, delicate and often profound changes occur in the electron attaching properties of the molecule which crucially depend on the molecule itself and the mode (dissociative or nondissociative) of electron attachment [2,33]. Thus, dissociative attachment to molecules has been shown to increase and nondissociative attachment has been found to decrease (often dramatically) with increasing E_{int} . Within the resonance scattering theory of electron attachment, the electron, e , of energy, ϵ , is initially captured by the molecule AX —with a cross section $\sigma_0(\epsilon)$ —forming a transient anion AX^{-*} which, then, decays by attachment ($A + X^-$ or AX^-) or autodetachment ($AX^{(*)} + e$), viz.,



The cross sections for dissociative attachment, σ_{da} , and for nondissociative attachment, σ_{nda} , can be written, respectively, as σ_{0p} and $\sigma_0'p'$, where p and p' are the probabilities, respectively, for AX^{-*} to decay producing $A + X^-$, or AX^- . The reported [e.g., 2,33] increases in σ_{da} and decreases in σ_{nda} with increasing E_{int} of AX can largely be attributed to the increase of p and to the decrease of p' with E_{int} . Changes in σ_0 or σ_0' may also occur. For example, σ_0 may increase with increasing E_{int} due to the capture of lower energy electrons by molecules in higher vibrational levels; also, σ_0' will be affected if increases in E_{int} introduce geometrical changes in either AX or AX^{-*} .

The easiest way to increase the E_{int} of a molecule is by nonselective vibrational/rotational excitation, i.e., by heating. Selective excitation can be—and has been—achieved by the use of appropriate lasers [34,35].

A. Dissociative Electron Attachment to "Hot" Molecules

The rate constant (cross section) for dissociative electron attachment generally increases with increasing E_{int} of the molecule, i.e., with increasing T . This has been shown for both diatomic (e.g., [2], [33a], [36-38]) and polyatomic (e.g., [2], [33]) molecules. In Figure 6 is shown an example of the latter.

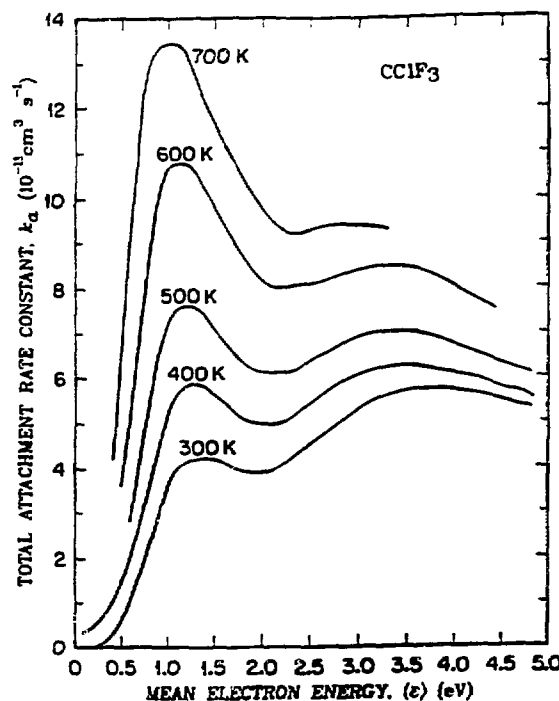


Figure 6: Total electron attachment rate constant, k_a , versus mean electron energy $\langle \epsilon \rangle$ for $CClF_3$ at various T [33e].

The profound effect of the increase in E_{int} (vibrational/rotational) of a molecule on the magnitude of its σ_{da} can be seen from the data in Figure 7. Here the ratio $\sigma_{da}(v > 0)/\sigma_{da}(v = 0)$ for the production of H^-/D^- from H_2/D_2 and for Cl^- from HCl/DCl —determined at energies very close to the thermodynamic onset—is plotted as a function of the E_{int} of the molecule. The effect of rotational excitation can be seen from the data in Figure 7b. For H_2/D_2 the theoretical calculations using resonance scattering theory [37a,b] agree well with the experimental measurements [36a]. For Cl^- from HCl/DCl , calculations based on resonance scattering theory [37c] predict a large variation of σ_{da} with increasing E_{int} . The results of calculations using effective range theory [38] shown in Figure 7b reproduce nicely the experimental data [36a]. In the effective-range theory calculations the collision equation was solved [38] for the associative detachment process—which is known to populate the highest vibrational level that is energetically accessible (i.e., the detachment process preferentially yields low-energy electrons)—and the dissociative attachment process was obtained through the

detailed balance principle. Non-adiabatic effects were considered responsible for the dissociative attachment process rather than an intermediate resonance state; this mechanism was considered appropriate for molecules such as HCl where "the almost s-wave symmetry of the incoming electron precludes an easy definition of a resonance state." This formalism may explain the profound increases in k_a with T reported recently for CH_3Cl [33g] and $\text{C}_2\text{H}_5\text{Cl}$ [33h] and shown in Figure 8 for CH_3Cl .

The profound effects of temperature on electron attachment have been shown (e.g., [39]) to have rather interesting practical implications, e.g., in gaseous dielectrics and pulsed power switches.

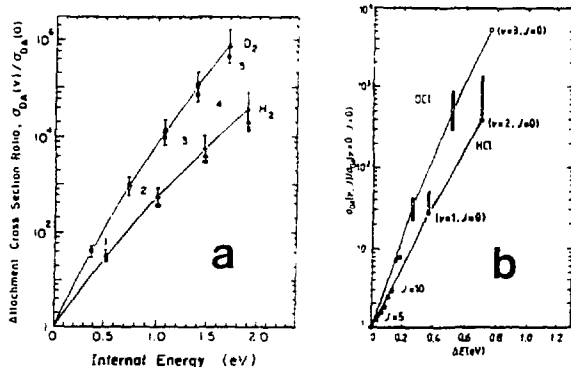


Figure 7: (a) $\sigma_{\text{DA}}(v)/\sigma_{\text{DA}}(0)$ versus internal energy for H_2/D_2 via the $2\Sigma^+$ resonance close to the thermodynamic threshold: \circ (experiment [36a]); \square (theory [37a]); Δ (theory [37b]) (From [37b]).

(b) $\sigma_{\text{DA}}(v, J)/\sigma_{\text{DA}}(v=0, j=0)$ versus internal energy for HCl/DCl: error bars (experiment [36b]); \bullet (HCl, $v, j=0$); \circ (DCl, $v, j=0$); \blacksquare ($v=0, J$) (calculation by [38] 25 meV above the respective thermodynamic threshold).

B. Dissociative Electron Attachment to Laser-Produced Vibrationally-Excited Molecules and Photofragments

Direct or indirect laser-induced selective vibrational excitation of parent or fragment species leading to enhanced electron attachment has been reported in a number of cases [34,35,40-42] and may be useful in gas switching schemes [42,43] and isotope-separation processes [34,35]. Photon-enhanced dissociative attachment to vibrationally-excited molecules produced directly via CO_2 -laser excitation has been reported for SF_6 [34,35]. The observed strong dependence of $\sigma_{\text{da}}(\epsilon)$ on the vibrational level of the

target molecule led to the suggestion [34,35] that isotope separation might be possible by optically exciting the vibrational mode(s) of one isotopic species followed by preferential attachment of slow electrons to the vibrationally-excited species.

Dissociative attachment studies have been reported, also, for optically-pumped lithium molecules ($\{\text{Li}_2^*(X^1\Sigma_g^+)$, [41]) and I_2^* (produced indirectly via the decay of an upper electronic state reached by laser excitation [40]).

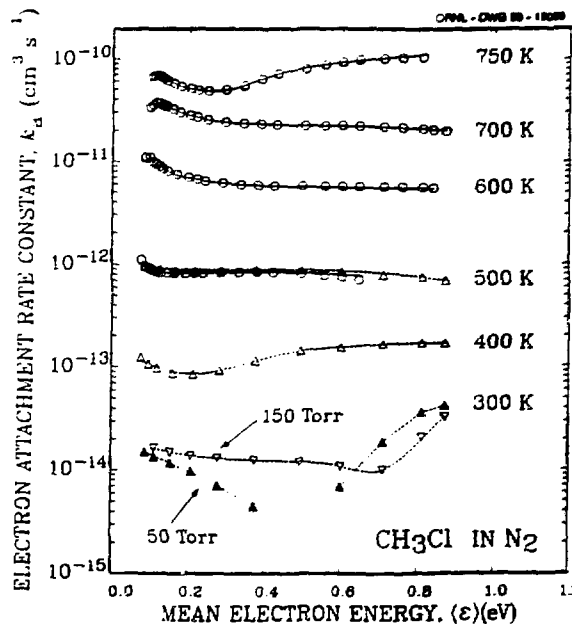


Figure 8: Total electron attachment rate constant $k_a(\langle\epsilon\rangle, T)$ versus $\langle\epsilon\rangle$ for CH_3Cl [33g].

Additionally, enhanced electron attachment to vibrationally-excited HCl* and HF* molecules produced, respectively, by laser photodissociation of the $\text{C}_2\text{H}_3\text{Cl}$ and $\text{C}_2\text{F}_3\text{Cl}$ molecules has been reported ([42a]; Figure 9) and has been considered for optical switching purposes [42].

C. Nondissociative Electron Attachment to "Hot" Molecules

The rate constant (cross section) for nondissociative electron attachment has been found to decrease with increasing E_{int} , i.e., with increasing T for many molecules [2,33a,b,d,f,44]. An example of this type of behavior is shown in Figure 10 for $\text{C-C}_4\text{F}_8$ [44]. The decrease in $k_a(\langle\epsilon\rangle, T)$ with increasing T is mostly due the increase in p' (see Eq. (7)) as T increases. No direct laser selective excitation studies of this process have been performed.

When dissociative and nondissociative electron attachment processes occur concomitantly over a common energy range, then $k_a(\langle\epsilon\rangle, T)$ and $\sigma_a(\epsilon, T)$ can increase or decrease with increasing T depending on the relative significance of the two processes (see Figure 11 and [33b]).

6 Electron Attachment to Electronically-Excited Molecules

We shall separate these studies into three groups: those involving (i) metastable, long-lived (lifetimes, $\tau > 10^{-5}$ s) electronic states, those involving (ii) short-lived ($\tau < 10^{-6}$ s) or very short-lived (superexcited, $\tau < 10^{-9}$ s) electronic states, and (iii) those involving electronically-excited photofragments. We shall discuss only (i) and (ii) since, to our knowledge, no reports on (iii) have appeared to date. Electron attachment to electronically-excited molecules normally leads to dissociative attachment.

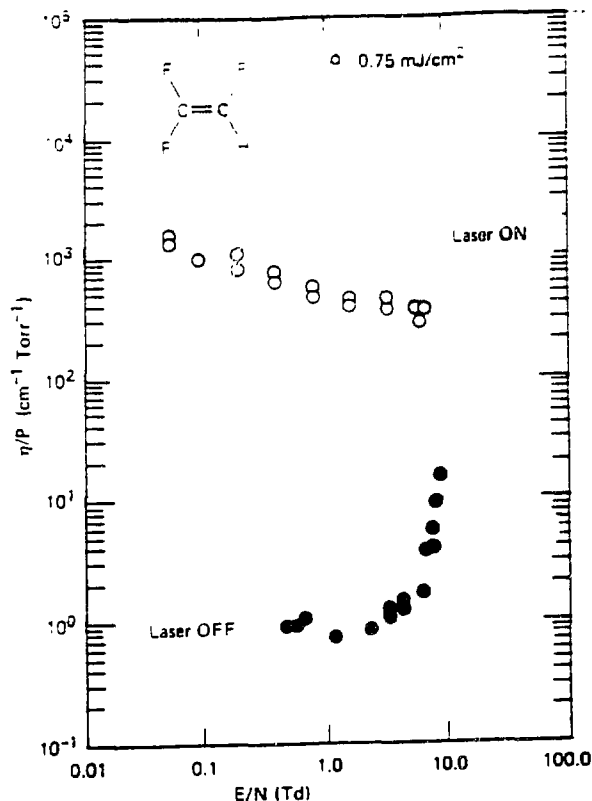


Figure 9: Enhanced dissociative electron attachment to vibrationally excited HF molecules produced by laser photodissociation of C_2F_3H . Attachment coefficient η/P (expressed in terms of the unexcited C_2F_3H pressure) versus E/N . If η/P were expressed in terms of the excited molecule number density it would be ~ 100 times larger than shown (From [42a]).

Prior to discussing recent findings in this area it should be pointed out that electron capture in the field of an excited molecular electronic state for very short times ($\leq 10^{-14}$ s) has long been known to occur as resonances in electron scattering and in dissociative electron attachment reactions [1,2]; this mode of electron capture is known as "electron-excited Feshbach resonance." Very interestingly, also, it has been reported [45] that long-lived (mean autodetachment lifetime $\tau_a > 10^{-5}$ s) anions of the *p*-benzoquinone ($p-C_6H_4O_2$) molecule can be formed in collisions with slow ($\sim 2-3$ eV) electrons whereby the initial kinetic energy of the colliding electron is almost entirely expended in exciting the molecule to its lowest excited (triplet) state with the resultant thermal electron being concomitantly captured by the so-produced electronically-excited molecule. The process was described as:

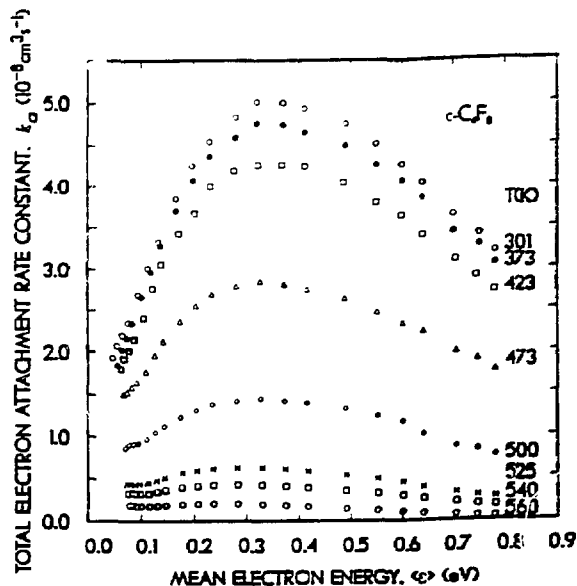
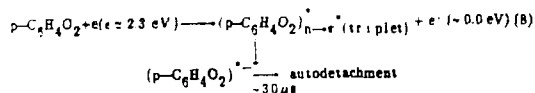


Figure 10: Total electron attachment rate constant as a function of the mean electron energy and the gas temperature, $k_a(\langle \epsilon \rangle, T)$ for $c-C_4F_8$ [44].

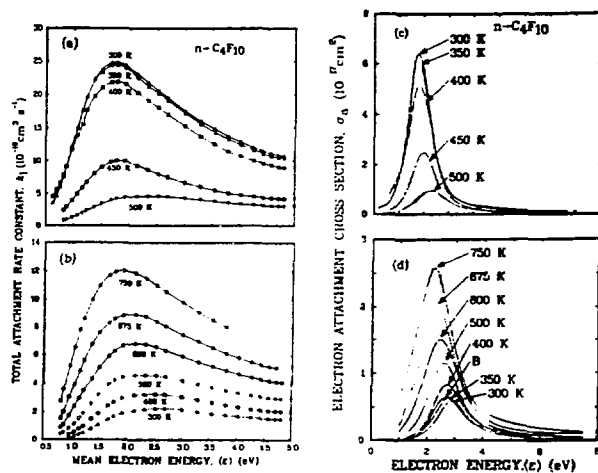


Figure 11: (a) Total electron attachment rate constant versus mean electron energy for $n-C_4F_{10}$ measured [33b] in a buffer gas of Ar at $T \leq 500$ K (the plotted rate constant values are for $N_{Ar} \rightarrow \infty$, see Ref. [33b]).

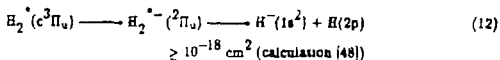
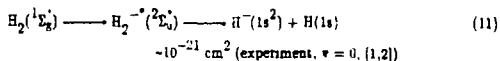
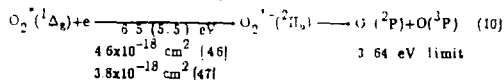
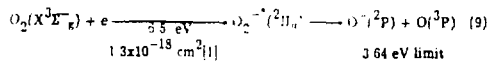
(b) As for (a) except that the data plotted for 300, 400, and 500 K are only the dissociative attachment component of the total rate constant at these temperatures.

(c) Total electron attachment cross sections unfolded from the data in Figure 11(a).

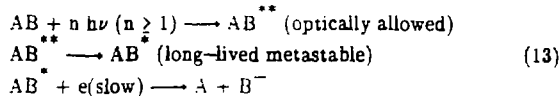
(d) Dissociative attachment cross sections unfolded from the data in Figure 11(b).

A. Dissociative Electron Attachment to Metastable Electronic States of Molecules

The first example of dissociative electron attachment to pre-prepared electronically-excited molecules is that for metastable (singlet) oxygen $O_2^*(^1\Delta_g)$ produced in a microwave discharge [46,47], and the calculation [48] of the cross section for dissociative attachment to $H_2^*(c^3\Pi_u)$. Both of these studies indicated that $\sigma_{Aa}(e)$ is larger for the electronically-excited molecule than for the ground-state molecule, viz.,



Recently several mechanisms of photoenhanced electron attachment to electronically-excited molecules have been demonstrated in spite of the fact that excited electronic states are normally—but not always—short-lived and their production can be in competition with photoionization and/or photodissociation; dissociative electron attachment to laser-produced short-lived molecular electronic states can have several orders of magnitude larger cross sections compared to ground electronic states so that electron attachment can occur in a very short time. Thus in 1987 the first observation of optically-enhanced electron attachment to excited electronic states of molecules was reported [6] for the thiophenol (C_6H_5SH) molecules which were excited indirectly to their long-lived (lifetime $\tau \approx 6$ ms) first-excited triplet state (located at ~ 4 eV). The thiophenol molecules in their ground state (1S_0) were first excited efficiently to their high-lying π -singlet states ($^1S_n, n \geq 1$) via single-photon absorption of 249 nm excimer laser light. Following this initial step these high-lying excited states quickly (within $\leq 10^{-12}$ s) internally convert to the lowest excited singlet state (1S_1) of the molecule which, in turn, undergoes rapid (within $10^{-8} - 10^{-9}$ s) "intersystem crossing" to the long-lived lowest triplet state T_1 . Attachment of low-energy electrons to the so-produced $C_6H_5SH^*(T_1)$ excited molecules has been studied in swarm experiments using N_2 as the buffer gas; it was found to be orders of magnitude larger compared to that for the ground state (unexcited) molecules. The aforementioned sequential processes can be generalized as:



The observed large enhancements in the electron attachment coefficient η/N_a for thiophenol effected by UV excimer laser irradiation is shown in Figure 12. Curves 1 and 2 are the η/N_a for dissociative attachment to thiophenol molecules excited to their lowest triplet state populated indirectly as described above. The values of the photoenhanced electron attachment are at least 100 times larger than shown since the number density N^* of excited $C_6H_5SH^*(T_1)$ molecules is $< 1\%$ of that, N_a , in the ground state [6,7]. Moreover, since ground state C_6H_5SH molecules

attach electrons very weakly (electron attachment rate constant $< 10^{-14} \text{ cm}^3 \text{ s}^{-1}$) below ~ 0.5 eV, an enhancement in electron attachment by a factor of 10^5 to 10^6 at thermal energies is seen when the C_6H_5SH/N_2 mixture is irradiated by 249 nm laser radiation.

At the 308 nm laser line, which lies below the first excited electronic state which is optically allowed, there is no photoenhanced attachment up to laser pulse energies of ~ 1 mJ. For laser lines at 222 nm and 193 nm for which the molecules can photodissociate, the photoenhanced attachment is small compared with that for the 249 nm line.

In Figure 12 curves 4–7 show the measured η/N_a for a double laser pulse experiment where the gas was excited by a laser pulse and electron attachment was measured 12 ms later when the attaching electrons were produced by a second similar laser pulse. This "delayed" photoenhanced electron attachment process occurred at times $> 100 \mu\text{s}$ after the first laser pulse and is much stronger than that for a single pulse [6,7]. The single pulse attachment is due to dissociative electron attachment to thiophenol molecules in their lowest triplet state and occurs within a few μs of laser irradiation, while the "delayed" photoenhanced attachment is believed [7] to be due to electron attachment to diphenyl disulfide ($C_6H_5SSC_6H_5$) produced by the interaction of

thiophenoxy radicals ($C_6H_5S^*$) formed directly or indirectly via laser irradiation.

The results in Figure 12 were obtained using a modified Townsend technique [6,7,49] with the electrode-laser arrangements (a) and (b) in Figure 13. In Figure 13a a single laser pulse is used; it enters the interelectrode space through a gridded anode, en route to the cathode produces

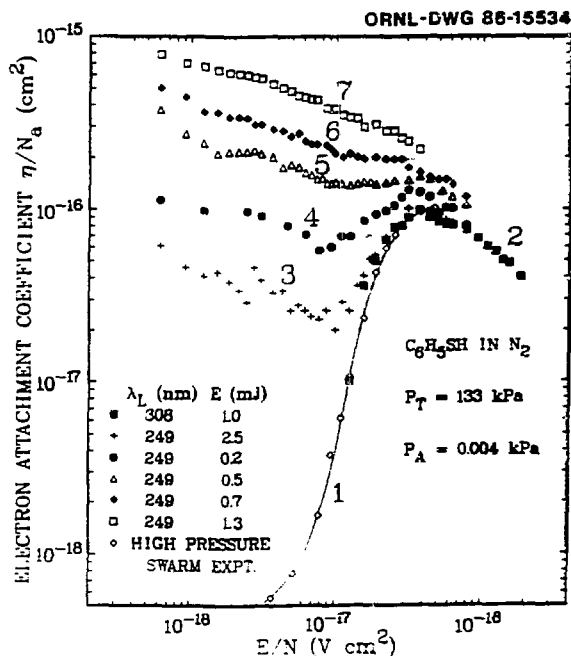


Figure 12: Electron attachment coefficient η/N_a versus E/N for C_6H_5SH in N_2 for the ground-state (curves 1 and 2) and the first-excited triplet state (curve 3) molecules. Curves 3–7 are photoenhanced attachment due to stable photoproducts formed in a double laser-pulse experiment [see the text and [6, 7]].

the excited species (as described above) and at the end of its path (at the cathode) photoinjects a pulse of electrons which drift in the opposite direction; these electrons are attached to the excited species during their drift. In Figure 13b two laser pulses are employed, one (#1) to produce the excited species and the other (#2) the electron pulse. The time delay between the two could be varied down to $\sim 100 \mu\text{s}$.

Quite similar to the case of thiophenol, 5 to 7 orders of magnitude enhancement in electron attachment has been reported recently [50] due to the first excited triplet states of *p*-benzoquinone and its methylated derivatives.

Additionally, electron attachment to the $A^2\Sigma^+$ state of NO (located at $\sim 5.5 \text{ eV}$ with a lifetime $\sim 0.2 \mu\text{s}$) was shown to have about an order of magnitude enhancement [51].

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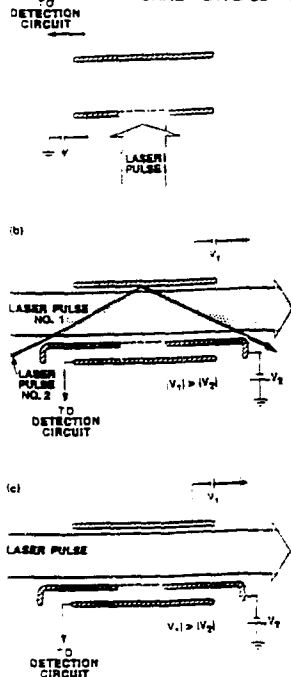


Figure 13: Schematic electrode-laser pulse(s) arrangements used in studies of photoenhanced electron attachment to electronically-excited molecules [6-8; see the text].

B. Dissociative Electron Attachment to Short-Lived Excited Electronic States of Molecules

1. A New Technique

Recently a new technique has been developed [8,52] for the study of electron attachment to short-lived ($\tau \lesssim 10^{-8} \text{ s}$) laser-excited electronic states. In this technique the gas under study is mixed in small amounts with a suitable abundant buffer gas (Ar or N_2 in the study of [8, 52]) at pressures of $\lesssim 1 \text{ atm}$. The excited electronic states are produced volumetrically via (excimer) laser irradiation and the attaching electrons are also generated volumetrically and concomitantly with the excited molecules by the same laser pulse via multiphoton ionization of the gas under study or an additive gas. Negative ion production would occur when

$$[k_a N^*]^{-1} < \tau \quad (14)$$

where N^* is the excited state number density; relation (14) can be satisfied even when τ is very short since the electrons and the excited molecules are produced in close proximity and since k_a can be very large. The positive and negative ions produced are detected separately via a three-electrode configuration arrangement (Figure 13c).

The data analysis depends on the electron attachment mechanism(s) involved and the relative values of four time parameters: the lifetime 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. Since electron attachment has to occur before the decay of the excited species,

$$\tau_a < \max \{ \tau, \tau_L \}$$

where τ_L is the duration of the laser pulse. Normal electron swarm conditions would prevail when $\tau_a \gg \tau_{ss}$ (see [8,52] for further details).

2. Photoenhanced Electron Attachment to Electronically-Excited Tertiary Amines

I shall restrict the discussion on this topic to only the triethylamine (TEA) molecule although photoenhanced electron attachment has also been observed [8] for trimethylamine (TMA) and tripropylamine (TPA). The lowest electronic transitions in TEA (and in other amines) are associated with the excitation of the lone-pair electrons of the N atom to Rydberg orbitals. The lowest two optically-allowed transitions, $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$, have been identified as the $n_N \rightarrow 3s$ and $n_N \rightarrow 3p$ Rydberg transitions. Their zero vibrational levels are located at $\sim 4.8 \text{ eV}$ and $\sim 5.2 \text{ eV}$ and the adiabatic ionization threshold, I_a , of TEA is $\sim 7.5 \text{ eV}$ [53].

The unexcited TEA molecules do not attach slow ($< 1 \text{ eV}$) electrons ($k_a < 10^{-12} \text{ cm}^3 \text{ s}^{-1}$). When, however, a mixture of TEA and N_2 was irradiated by laser light (248, 222, or 193 nm excimer lines) in an arrangement such as in Fig. 13c, a very large negative ion signal was observed [8]. A single excimer laser pulse excited the TEA molecules and also produced—by photoionization of TEA—the electrons which attached to these excited TEA molecules. The attached and unattached electrons produced by each laser pulse drifted to the anode and generated a voltage waveform in the anode circuit consisting of a component $V_I(t)$ due to the negative ions and a component $V_E(t)$ due to the unattached electrons. The saturation (maximum) values V_I and V_E of $V_I(t)$ and $V_E(t)$ are related to the attachment rate constant via the ratio $R_v = V_I / (V_I + V_E)$ (see reference 8 for further discussion).

Figure 14 shows the variation of the total signal $V_T (\equiv V_I + V_E)$; V_T is proportional to the total number of electrons produced via photoionization and the negative ion signal V_I on the laser fluence F . With the exception of high F values ($> 0.6 \text{ mJ cm}^{-2}$ for the data in Figure 14) where space charge affects the dependence of V_T and V_I on F , V_T

increased as F^2 and V_I increased as F^4 for all three laser lines employed in the study of reference 8; the former indicates that two photons are required to produce an "attaching" electron and the latter indicates that four photons are required to produce one negative ion. Additionally, V_T increased linearly and V_I increased quadratically with TEA pressure, P_{TEA} , indicating that one TEA molecule is required to produce an "attaching" electron and two TEA molecules are required to produce a negative ion. The V_I depended on the applied electric field E but not on the nature of the buffer gas (Ar or N_2).

The data in Figure 14 are for the 248 nm line. Similar results were obtained for the 222 and 193 nm lines except that for these lines V_T and V_I were expected—on the basis of the photophysical properties of TEA (see below, Figure 15 and references 8 and 54)—to depend on the buffer gas pressure, as was indeed found to be the case. For the 308 nm line for which the TEA molecule cannot be monophotonically excited to the S_1 state, $V_T = V_I = 0$ for the fluence values ($\lesssim 9 \text{ mJ cm}^{-2}$) employed in reference 8.

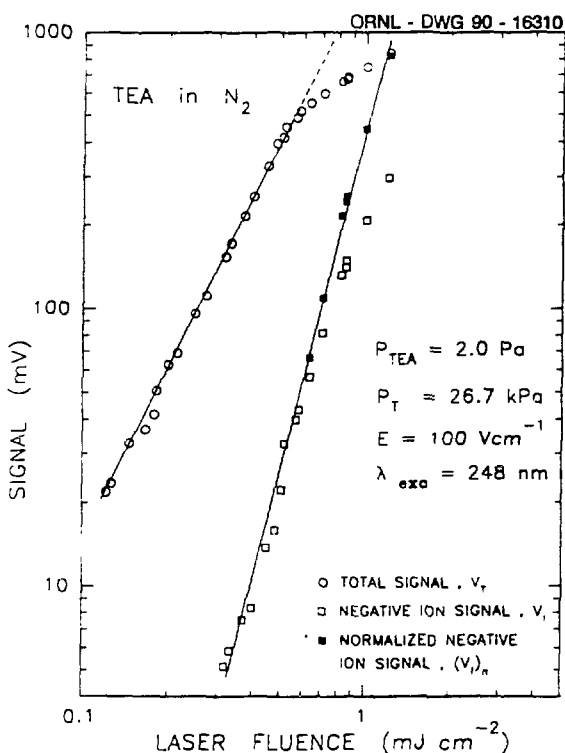


Figure 14: Dependence of the measured total, V_T , and negative ion, V_I , signals on the laser fluence F for a mixture of TEA and N_2 for the experimental parameters indicated in the figure. Corrections for the space charge effects on V_T and V_I were carried out [8] by forcing the total signal $(V_T)_n$ to follow the quadratic dependence, and then calculating the "normalized" ion signal $(V_I)_n$ via..

$$\frac{(V_I)_n}{(V_T)_n} = \frac{(V_I)_m}{(V_T)_m}$$

where, $(V_I)_m$, $(V_T)_m$, are the measured values. (From Ref. [8]).

In Figure 15 are shown the basic processes and some of the parameters used to interpret the observed photoenhanced electron attachment to TEA. A superexcited state (SES, i.e., an excited electronic state which lies above I_a) of TEA is produced by the laser pulse in a two-step excitation process via the low vibrational states $S_{1,\ell}$ of S_1 (Figure 15).

These intermediate states $S_{1,\ell}$ are populated either directly (at the KrF line) or indirectly (at the KrCl and ArF lines) via vibrational relaxation from higher vibrational levels of S_1 or internal conversion from S_2 ; they are stable against non-radiative decay and have a radiative lifetime of $\sim 60 \text{ ns}$ [53, 54]. The photoabsorption at the S_1 state is very strong allowing the absorption of a second photon from S_1 into the continuum within the duration ($\sim 10 \text{ ns}$) of the same laser pulse which produces the $S_{1,\ell}$ states. This second excitation

step into the continuum produces the SES (AB^{**} in Figure 15) and concomitantly free electrons by direct photoionization or via preionization of the SES. It is these highly excited SES of TEA that are assumed to capture electrons with exceedingly large cross sections forming short-lived parent anions which subsequently to their formation quickly decay by dissociative attachment (Figure 15) producing the observed anions.

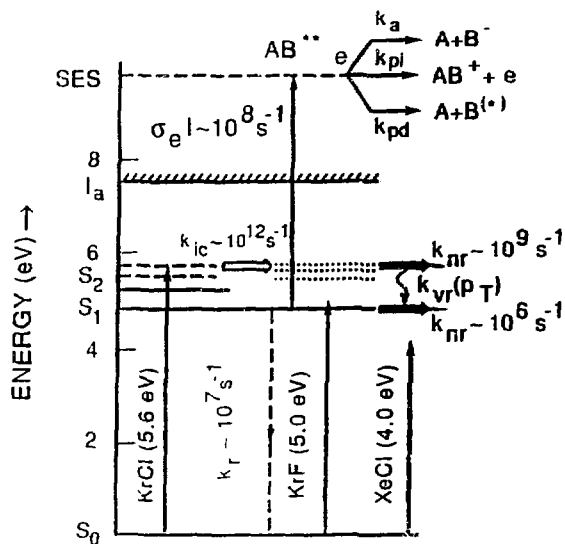


Figure 15: Schematic energy-level diagram for triethylamine (TEA \equiv AB) together with the relative photon energies of the three of the four laser lines employed. Approximate values of rates for relevant processes are also indicated. Photon absorption by Ar and N_2 buffer gases is negligible. Note that the second photon absorption occurs from the low vibrational levels of the S_1 manifold which are produced directly at the KrF line and indirectly at the KrCl and ArF (not shown in the figure) lines. [From Ref. 8].

Rate equations involving the excitation of and subsequent electron attachment to the SES of TEA consistent with the experimental observations were devised and led to the following expression for R_v [8]:

$$R_v = V_I/V_T = (1/4) N_0 \sigma_1 \sigma_e \eta \tau_s k_a F^2 \quad (15)$$

In Eq. (15) N_0 , σ_1 , σ_e , η , τ_s , and k_a are, respectively, the number density of TEA, the photoabsorption cross section from S_0 , the photoabsorption cross section from S_1 , the fraction of the molecules in S_1 which survive dissociation, the lifetime of the SES of TEA and the attachment rate constant (Fig. 15).

From plots of R_v vs F^2 for the KrF line and knowledge of N_0 and σ_1 ($= 2.5 \times 10^{-19} \text{ cm}^2$ for the KrF line) Pinnaduwa et al. estimated that $\sigma_e \tau_s k_a \approx 5 \times 10^{-27} \text{ cm}^5$. They, moreover, argued that $\sigma_e \approx 10^{-15} \text{ cm}^2$ and, thus, obtained $\tau_s k_a \approx 5 \times 10^{-12} \text{ cm}^3$. Since the lifetime τ_s of the SES is likely to be $< 10^{-9} \text{ s}$, one finds that $k_a > 5 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$ which for an electron of, say, 0.5 eV energy corresponds to a $\sigma_a > 10^{-10} \text{ cm}^2$. This cross section is enormous. It may indicate that the magnitude of the capture cross section for slow electrons by high-lying excited (SES Rydberg?) states is determined by the long-range of the electron-Rydberg dipole interaction; electron-dipole and electron-molecular positive ion recombination cross sections are known to be very large [2].

Finally, since the k_a for the unexcited TEA molecule is $< 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and the k_a for the electronically-excited TEA** molecule is $> 5 \times 10^{-3} \text{ cm}^3 \text{ s}^{-1}$, a photoenhancement in the electron attachment process of $> 10^9$ is apparent. Even though the dissociative electron attachment to molecules has been known to increase dramatically with increasing internal energy of the molecule, the $> 10^{-10} \text{ cm}^2$ cross sections reported for the highly-excited electronic states of saturated tertiary amines are by far the largest electron attachment cross sections known to date.

7 Concluding Remark

The study of electron-excited molecule interactions is just beginning and it is full of challenge, surprises and opportunity. Apart from their fundamental significance, studies of electron-excited molecule interactions can be expected to have important applications in various fields ranging from life and atmospheric sciences to plasma and engineering physics.

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References

- [1] L.G. Christophorou. 1971, *Atomic and Molecular Radiation Physics*, Wiley-Interscience, New York.
- [2] L.G. Christophorou (Ed.), 1984, *Electron-Molecule Interactions and Their Applications*. Volumes 1 and 2, Academic Press, New York.
- [3] H.S.W. Massey, 1969, *Electronic and Ionic Impact Phenomena*, Volumes 1-2, (Oxford, London).
- [4] H.S.W. Massey, 1976, *Negative Ions*, Cambridge University Press, London; B.M. Smirnov, 1982, *Negative Ions*, McGraw-Hill, New York.
- [5] H.S.W. Massey, E.W. McDaniel, and B. Bederson (Eds.), 1982-4, *Applied Atomic Collision Physics*, Vols. 1-5, Academic Press, New York.
- [6] L.G. Christophorou, S.R. Hunter, L.A. Pinnaduwa, J.G. Carter, A.A. Christodoulides, and S.M. Spyrou, 1987, *Phys. Rev. Lett.*, **58**, 1316-1319.
- [7] L.A. Pinnaduwa, L.G. Christophorou, and S.R. Hunter, 1989, *J. Chem. Phys.*, **90**, 6275-6289.
- [8] L.A. Pinnaduwa, L.G. Christophorou, and A. Bitouni, *J. Chem. Phys.* (in press).
- [9] A. Guenther, M. Kristiansen, and T. Martin (Eds.), 1987, *Opening Switches*, Plenum, New York.
- [10] G. Schaefer and K.H. Shoenbach, 1986, *IEEE Trans. Plasma Sci.*, **14**, 561-574.
- [11] L.G. Christophorou, 1990, in *Nonequilibrium Processes in Partially Ionized Gases*, M. Capitelli and J.N. Bardsley (Eds.), Plenum, New York, 291-309.
- [12] J.G. Carter, L.G. Christophorou, and S.R. Hunter (unpublished results).
- [13] M. Hayashi, 1987, in *Swarm Studies and Inelastic Electron-Molecule Collisions*, L.C. Pitchford, B.V. McKoy, A. Chutjian, and S. Trajmar (Eds.), Springer-Verlag, New York, 167-187.
- [14] M. Hayashi and A. Niwa, 1987, in *Gaseous Dielectrics V*, L.G. Christophorou and D.W. Bouldin (Eds.), Pergamon, New York, 27-33.
- [15] T. Shimanouchi, 1972, NSRDS-NBS 39, 95.
- [16] S.J. Buckman, M.T. Elford, D.S. Newman, 1987, *J. Phys. B*, **20**, 5175-5182.
- [17] (a) J. Ferch, C. Masche, and W. Raith, 1981, *J. Phys. B.*, **14**, L97-L100; (b) M.A. Morrison, N.F. Lane, and L.A. Collins, 1977, *Phys. Rev. A*, **15**, 2186-2201.
- [18] G.N. Haddad and M.T. Elford, 1979, *J. Phys. B*, **12**, L743-L746.
- [19] H.T. Davis and L.D. Schmidt, 1972, *Chem. Phys. Lett.*, **15**, 260-264.
- [20] J. Ferch, C. Masche, W. Raith, and L. Wiemann, 1989, *Phys. Rev. A*, **40**, 5407-5410.
- [21] R.M. Badger, A.C. Wright, and R.F. Whitlock, 1965, *J. Chem. Phys.*, **43**, 4345-4350.
- [22] R.I. Hall and S. Trajmar, 1975, *J. Phys. B*, **8**, L293-L296.
- [23] M.A. Khakoo, W.R. Newell, and A.C.H. Smith, 1983, *J. Phys. B*, **16**, L317-L322.
- [24] B. Jaduszliwer, G.F. Shen, J.-L. Cai, and B. Bederson, 1985, *Phys. Rev. A*, **31**, 1157-1159.
- [25] B. Jaduszliwer, P. Weiss, A. Tino, and B. Bederson, 1984, *Phys. Rev. A*, **30**, 1255-1268.
- [26] A. Kasdan, T.M. Miller, and B. Bederson, 1973, *Phys. Rev. A*, **8**, 1562-1569.
- [27] D.L.A. Rall, F.A. Sharpton, M.B. Schulman, L.W. Anderson, J.E. Lawler, and C.C. Lin, 1989, *Phys. Rev. Lett.*, **62**, 2253-2256.
- [28] P.D. Burrow, 1967, *Phys. Rev.*, **158**, 65-69.
- [29] K.J. McCann, M.R. Flannery, and A. Hazi, 1979, *Appl. Phys. Lett.*, **34**, 543-545.
- [30] D. Ton-That and M.R. Flannery, 1977, *Phys. Rev. A*, **15**, 517-526.

- [31] P.B. Armentrout, S.M. Tarr, A. Dori, and R.S. Freund, 1981, *J. Chem. Phys.*, 75, 2786-2794.
- [32] D.R. Long and R. Geballe, 1970, *Phys. Rev. A*, 1, 260-265.
- [33] (a) L.G. Christophorou, 1987, *Plasma Physics*, 27, 237-281; (b) P.G. Datskos and L.G. Christophorou, 1987, *J. Chem. Phys.*, 86, 1982-1990; (c) 1989, 90, 2626-2630; (d) S.M. Spyrou and L.G. Christophorou, 1985, *J. Chem. Phys.*, 82, 1048-1049; (e) 1985, *J. Chem. Phys.*, 82, 2620-2629; (f) 1985, *J. Chem. Phys.*, 83, 2829-2835; (g) P.G. Datskos, L.G. Christophorou, and J.G. Carter, 1990, *Chem. Phys. Lett.*, 168, 324-329; (h) in *Gaseous Dielectrics VI*, L.G. Christophorou and I. Sauers (Eds.), Plenum, New York, 1991, 35-42; (i) P.J. Chantry and C.L. Chen, 1989, *J. Chem. Phys.*, 90, 2585-2592.
- [34] C.L. Chen and P.J. Chantry, 1979, *J. Chem. Phys.*, 71, 3897-3907.
- [35] I.M. Beterov, V.P. Chebotaev, N.V. Fateev, and D.V. Yakovin, 1978, *Sov. J. Quantum Electron.*, 8, 533-534.
- [36] M. Allan and S.F. Wong, (a) 1978, *Phys. Rev. Lett.*, 41, 1791-1794; (b) 1981, *J. Chem. Phys.*, 74, 1687-1691.
- [37] (a) J.M. Wadehra and J.N. Bardsley, 1978, *Phys. Rev. Lett.*, 41, 1795-1798; (b) J.N. Bardsley and J.M. Wadehra, 1979, *Phys. Rev. A*, 20, 1398-1405; (c) 1983, *J. Chem. Phys.*, 78, 7227-7234.
- [38] D. Teillet-Billy and J.P. Gauyacq, 1984, *J. Phys. B*, 17, 4041-4058.
- [39] L.G. Christophorou, R.A. Mathis, S.R. Hunter, and J.G. Carter, 1988, *J. Appl. Phys.*, 63, 52-59; Ref. 11.
- [40] I.M. Beterov and N.V. Fateyev, 1982, *Optics Communications*, 40, 425-429.
- [41] M.W. McGeoch and R.E. Schlier, 1986, *Phys. Rev. A*, 33, 1708-1717.
- [42] (a) M.J. Rossi, H. Helm, and D.C. Lorentz, 1985, *Appl. Phys. Lett.*, 47, 576-578; (b) M. Saporoschenko, M.J. Rossi, and H. Helm, 1988, *J. Appl. Phys.*, 63, 4849-4853; (c) O. Kobayashi, T. Sasagawa and M. Obara, 1987, *Appl. Phys. Lett.*, 51, 2103-2105.
- [43] G. Schaefer, M. Giesselmann, B. Pashaie, and M. Kristiansen, 1988, *J. Appl. Phys.*, 64, 6123-6127.
- [44] A.A. Christodoulides, L.G. Christophorou, and D.L. McCorkle, 1987, *Chem. Phys. Lett.*, 139, 350-356.
- [45] L.G. Christophorou, J.G. Carter, and A.A. Christodoulides, 1969, *Chem. Phys. Lett.*, 3, 237-240; 1970, 4, 646-650; Ref. [1], 511 and 523.
- [46] P.D. Burrow, 1973, *J. Chem. Phys.*, 59, 4922-4931.
- [47] D.S. Belic and R.I. Hall, 1981, *J. Phys. B*, 14, 365-373.
- [48] C. Rottcher and B.D. Buckley, 1979, *J. Phys. B*, 12, L497-L500.
- [49] S.R. Hunter, J.G. Carter, and L.G. Christophorou, 1986, *J. Appl. Phys.*, 60, 24-35.
- [50] R.S. Mock and E.P. Grimsrud, 1990, *J. Phys. Chem.*, 94, 3550-3553.
- [51] C.T. Kuo, Y. Ono, J.L. Hardwich and J.T. Moseley, 1988, *J. Phys. Chem.*, 92, 5072-5074.
- [52] L.G. Christophorou, L.A. Pinnaduwege, and A.P. Bitoumi, 1991, in *Gaseous Dielectrics VI*, L.G. Christophorou and I. Sauers (Eds.), Plenum Press, New York, 9-17.
- [53] See discussion and initial sources of data in Ref. 8.
- [54] Y. Matsumi and K. Obi, 1980, *Chem. Phys.*, 49, 87-93; K. Obi and Y. Matsumi, 1980, *Chem. Phys.*, 49, 95-106; C.G. Cureton, K. Hara, D.V. O'Connor, and D. Phillips, 1981, *Chem. Phys.*, 63, 31-49.

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ELECTRON-EXCITED MOLECULE INTERACTIONS¹

JUN 05 1991

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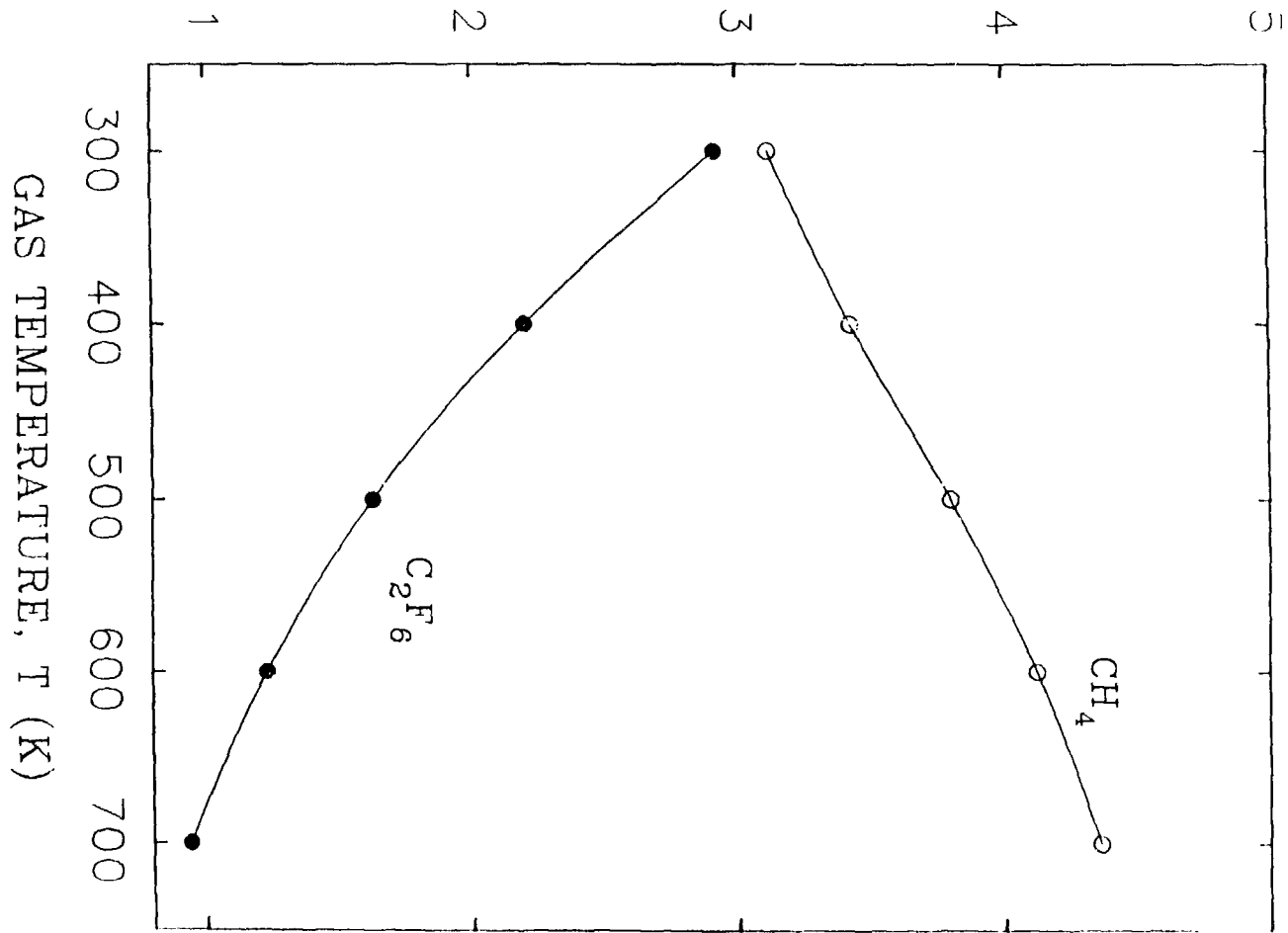
ELECTRON-EXCITED MOLECULE INTERACTIONS

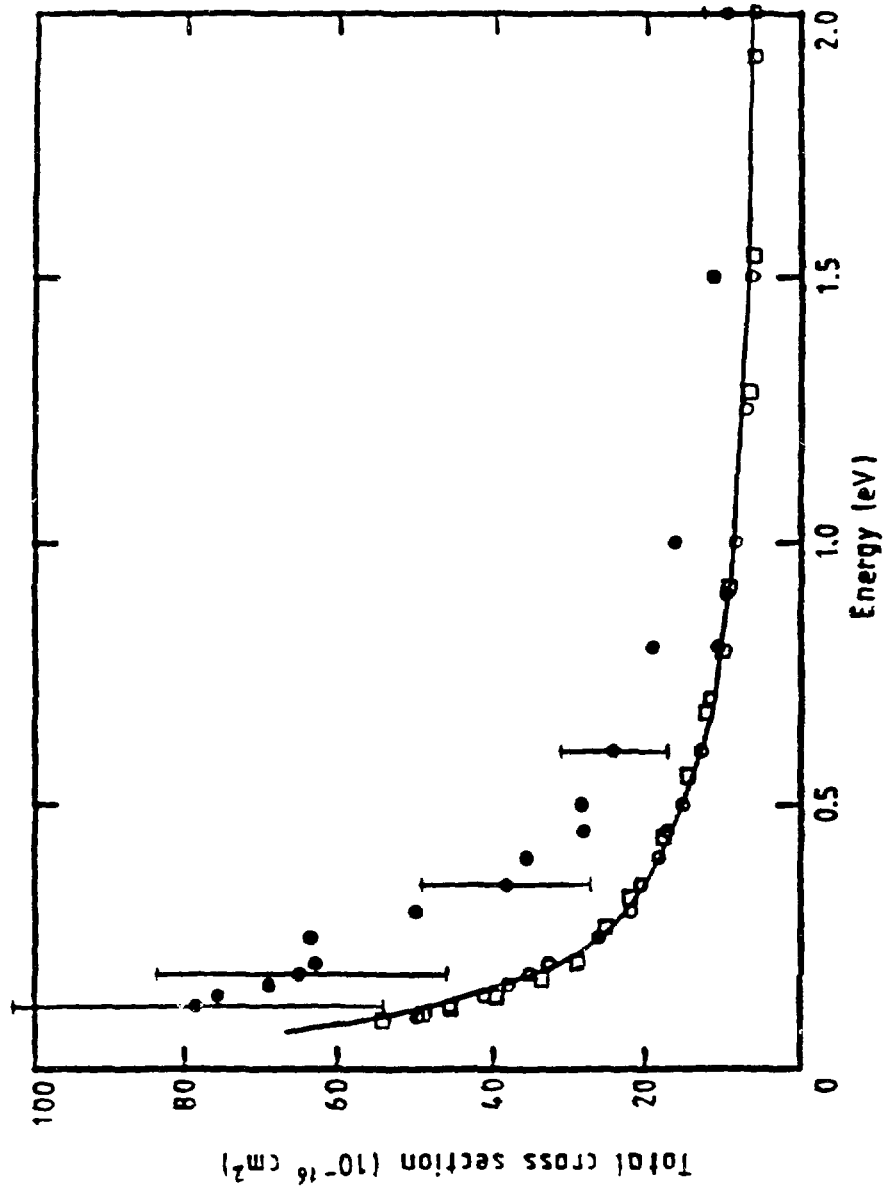
- Limited but significant knowledge
- Cross sections may differ greatly from those of ground-state molecules
- New experimental and theoretical challenges and technological opportunities
- Lecture outline:
 - Electron scattering from vibrationally/rotationally-excited molecules
 - Electron scattering from electronically-excited molecules
 - Electron-impact ionization of electronically-excited molecules
 - Electron attachment to vibrationally/rotationally-excited molecules
 - Electron attachment to electronically-excited molecules

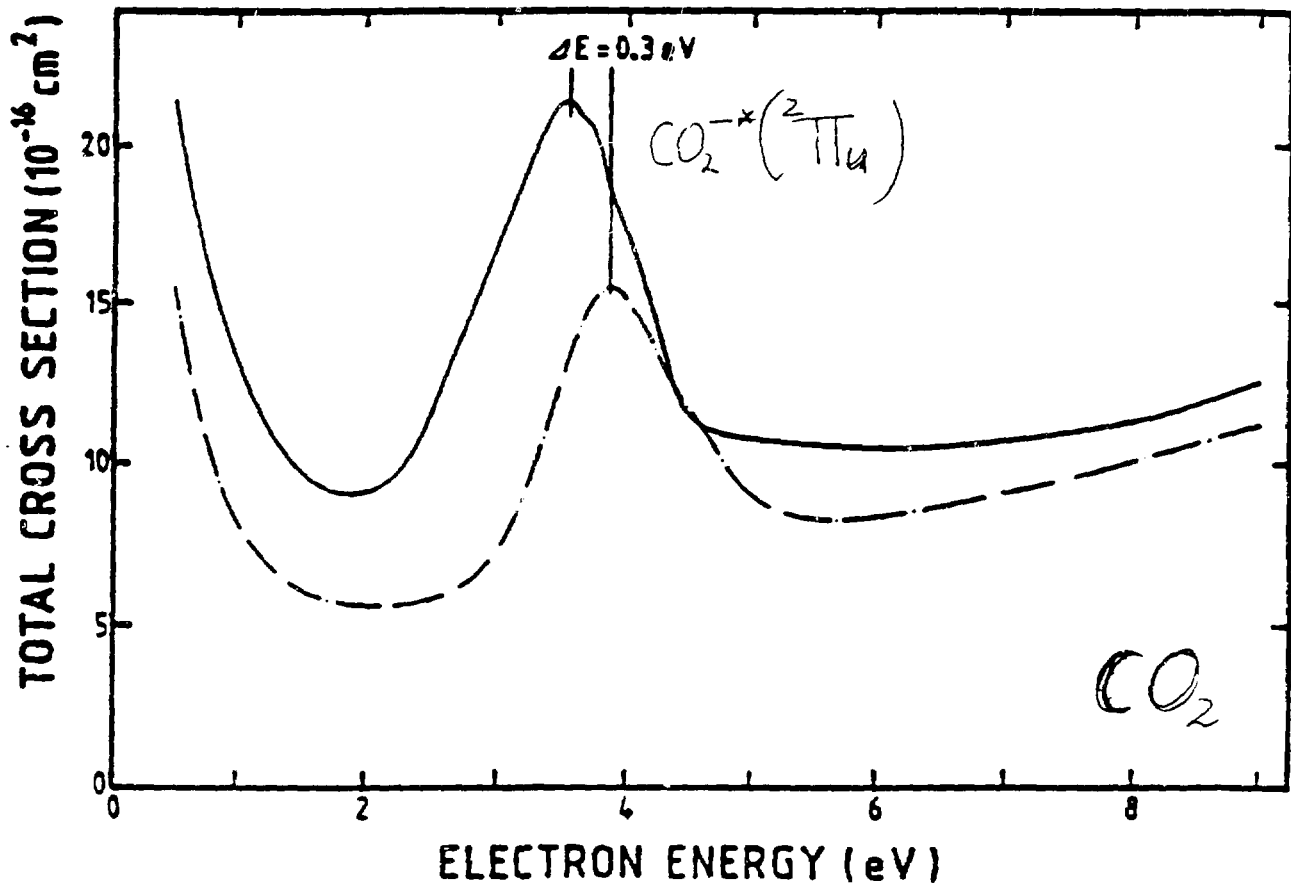
SCATTERING OF SLOW ELECTRONS BY "HOT"
(VIBRATIONALLY/ROTATIONALLY-EXCITED) MOLECULES

- Little known
- Limited studies indicate vibrational excitation enhances electron scattering
- Effect on electron transport (CH_4 vs C_2F_6)
- Electron-vibrational dipole scattering (CO_2)

THERMAL ELECTRON MOBILITY, $(\mu N)_{th}$ ($10^{23} \text{V}^{-1} \text{cm}^{-1} \text{s}^{-1}$)



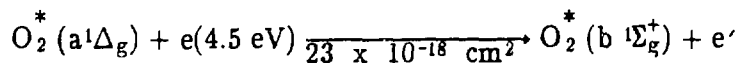
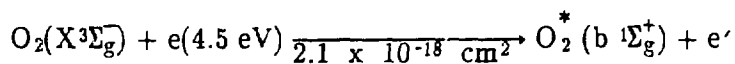




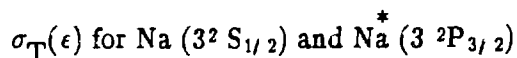
SCATTERING OF SLOW ELECTRONS BY
ELECTRONICALLY-EXCITED MOLECULES

- Little known (O_2^* ($a^1\Delta_g$))
- Cross sections expected to be larger than for ground-state species

– O_2 :

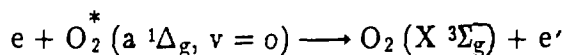


– Atoms:

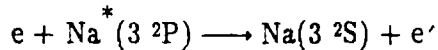
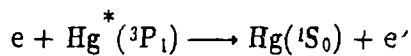


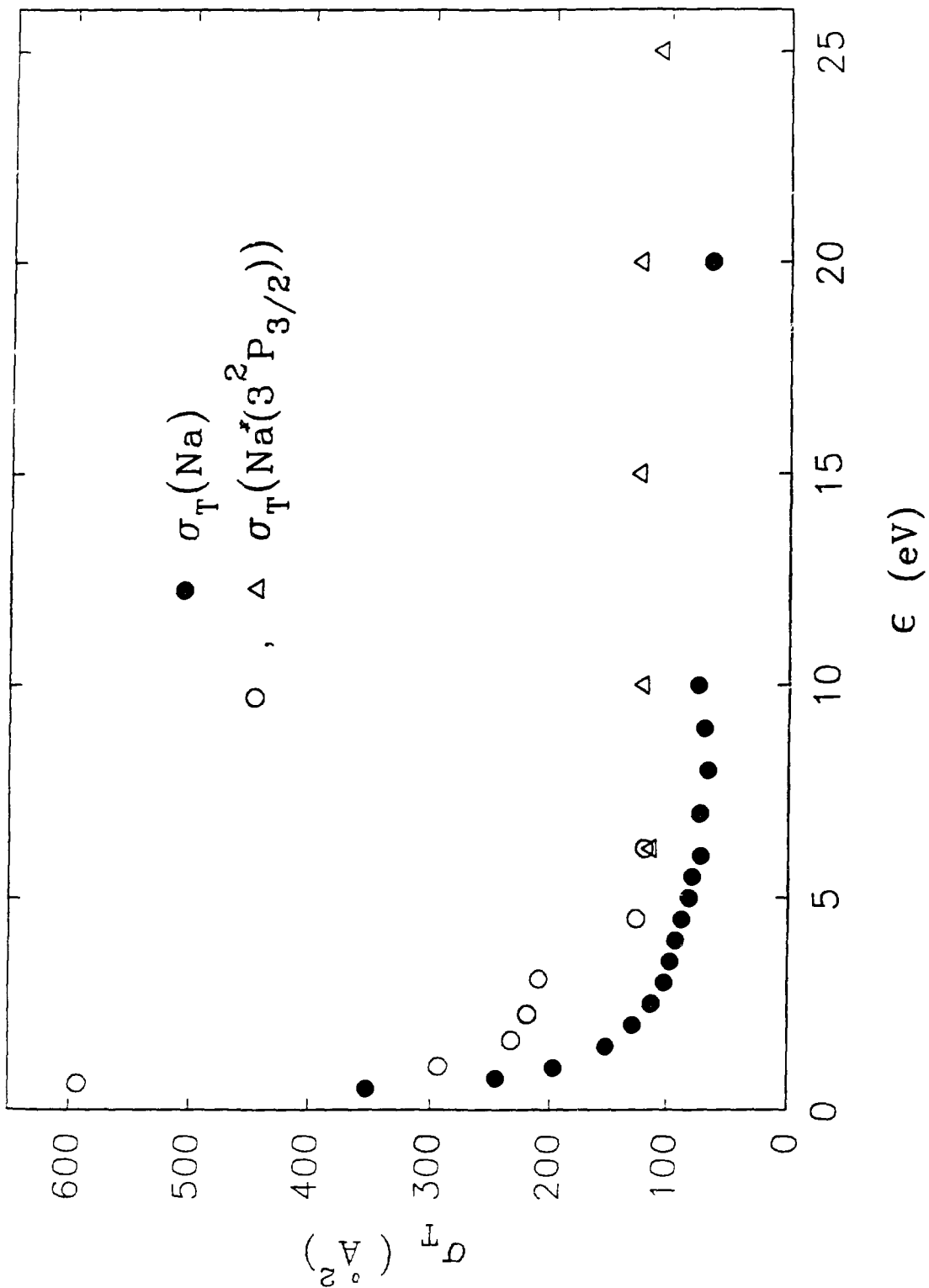
- Energy gain by slow electrons scattered off metastable species

– Molecules:



– Atoms:



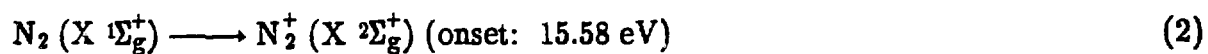
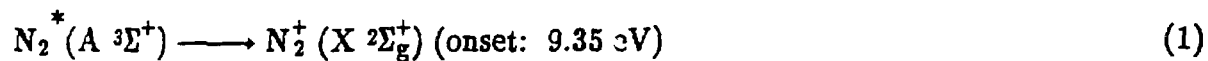


ELECTRON IMPACT IONIZATION OF ELECTRONICALLY-EXCITED MOLECULES

- Limited Knowledge

- Calculations (rare gas excimer, N₂, and CO metastables)

- Experiment



$\sigma_1(1) < \sigma_1(2)$; A state $1\pi_g$ orbital occupied by 1 and X state $3\sigma_g$ orbital occupied by 2 electrons.

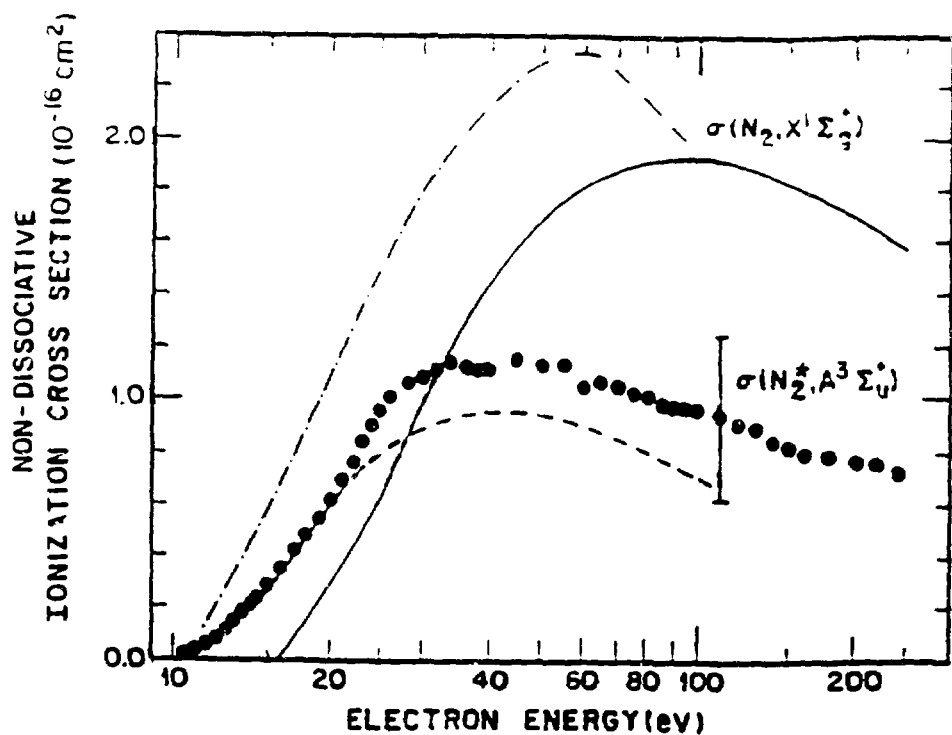
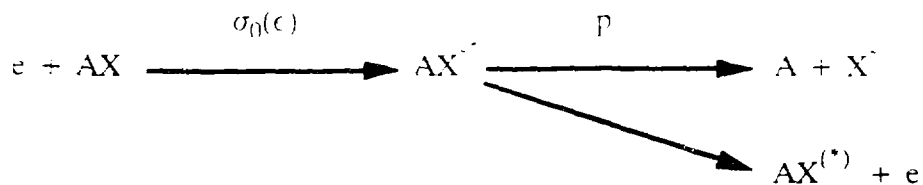


Figure 5: Experimental nondissociative electron impact ionization cross section [31] for: $N_2(X^1\Sigma_g^+)$ (—) and $N_2^*(A^3\Sigma_u^+)$ (\bullet); calculated cross sections for $N_2^*(A^3\Sigma_u^+)$ ——— $N_2^*(A^2\Pi_u)$ ionization: (— — —, [30]); (--- (see [31]). From [31].

EFFECT OF MOLECULAR INTERNAL ENERGY ON ELECTRON ATTACHMENT

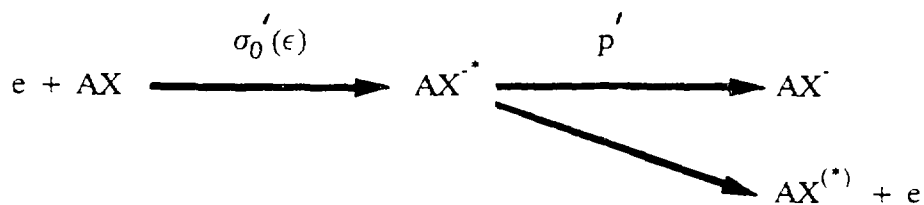
1. DISSOCIATIVE



$$\sigma_{da} = \sigma_0 p$$

σ_{da} increases with increasing temperature, T. i.e., with increasing molecular internal energy E_{internal}

2. NONDISSOCIATIVE



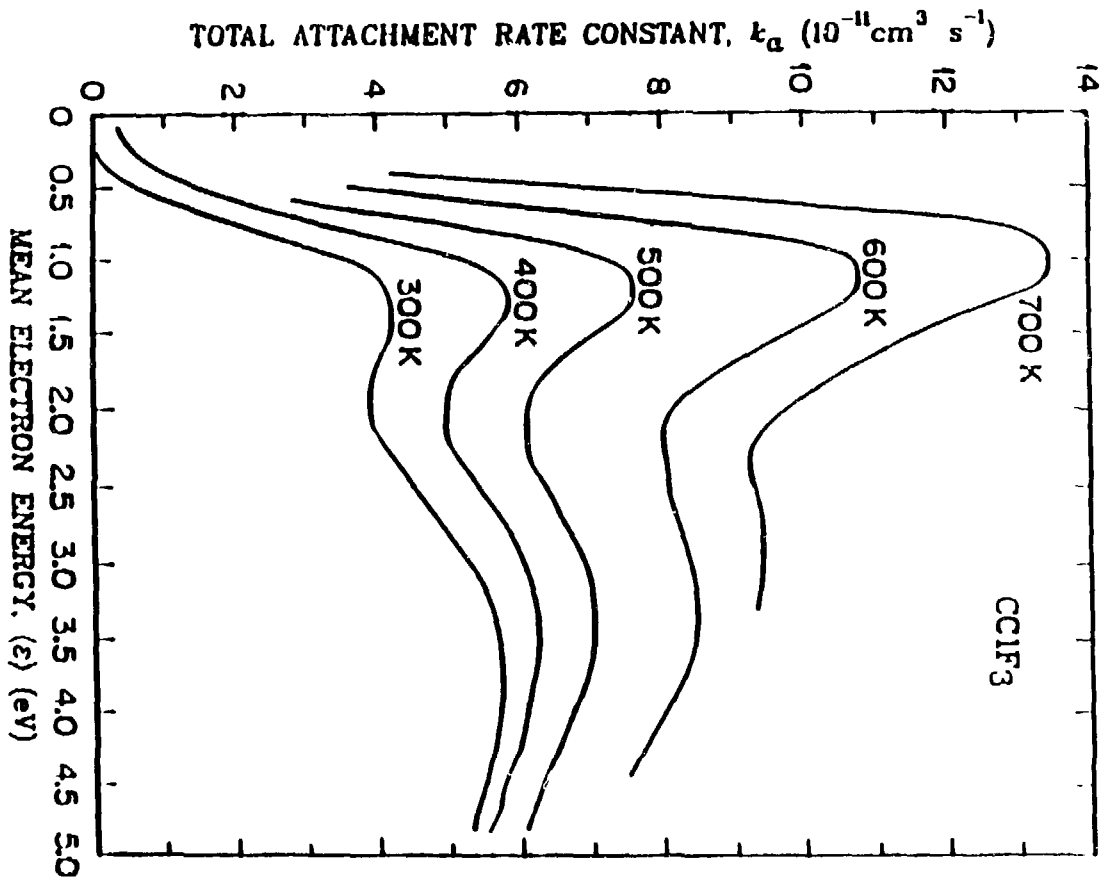
$$\sigma_{nd} = \sigma'_0 p'$$

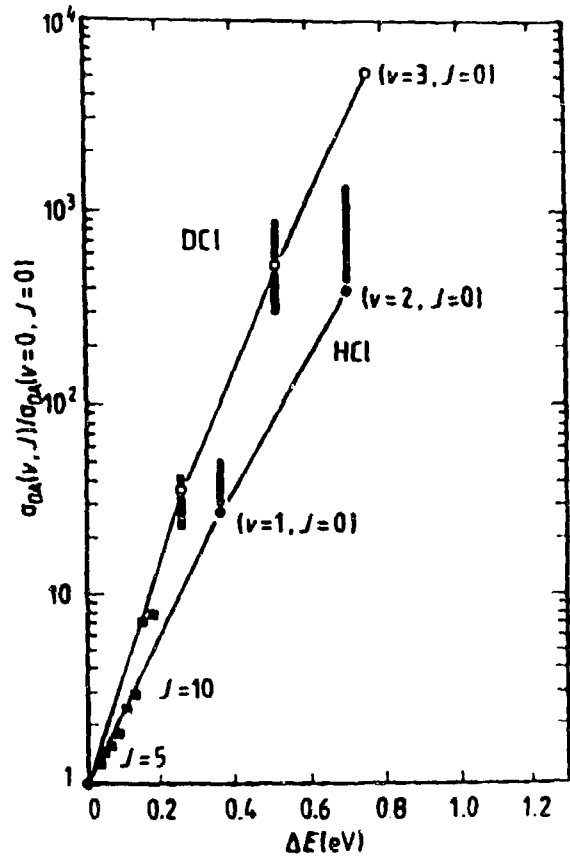
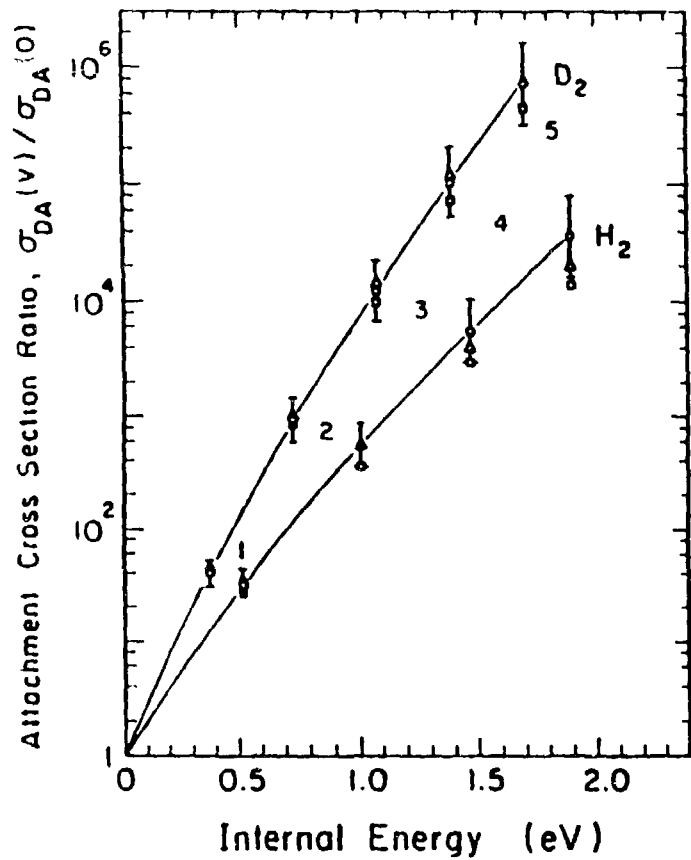
σ_{nd} decreases with increasing, T. i.e., E_{internal}

3. DISSOCIATIVE + NONDISSOCIATIVE

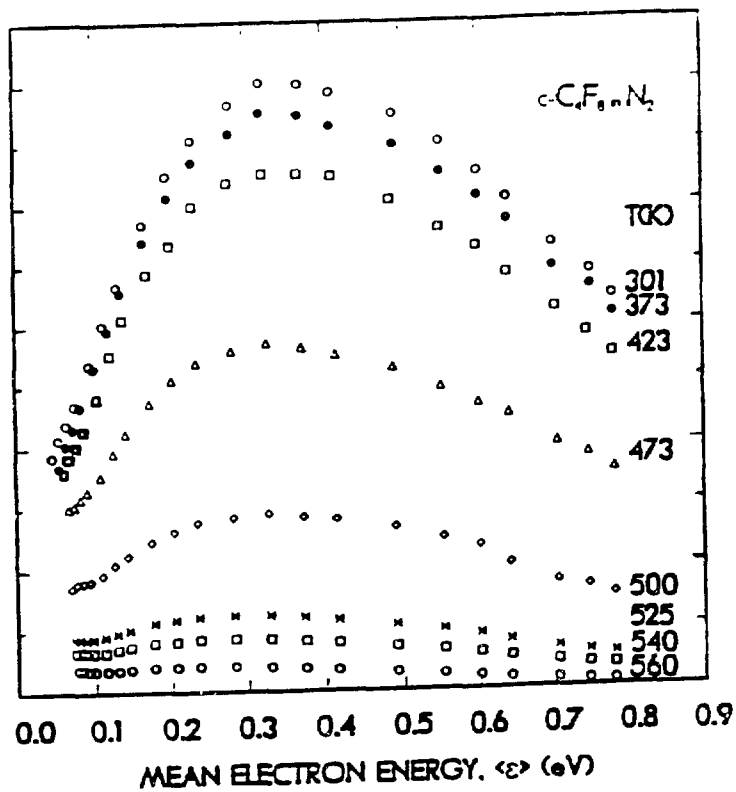
σ_{total} decreases or increases with increasing T. i.e., E_{internal}

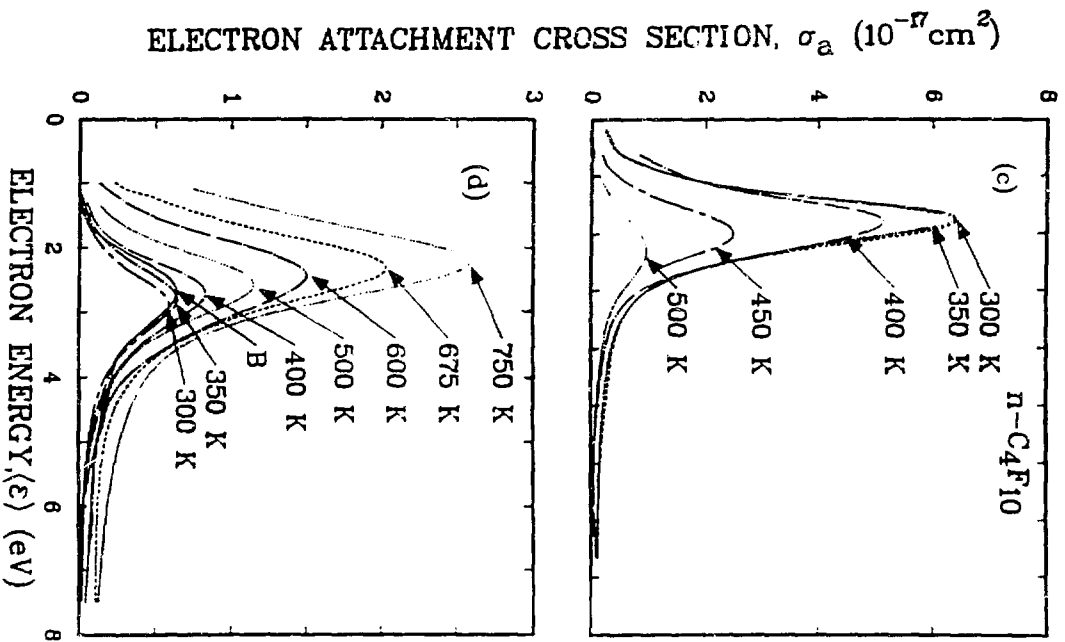
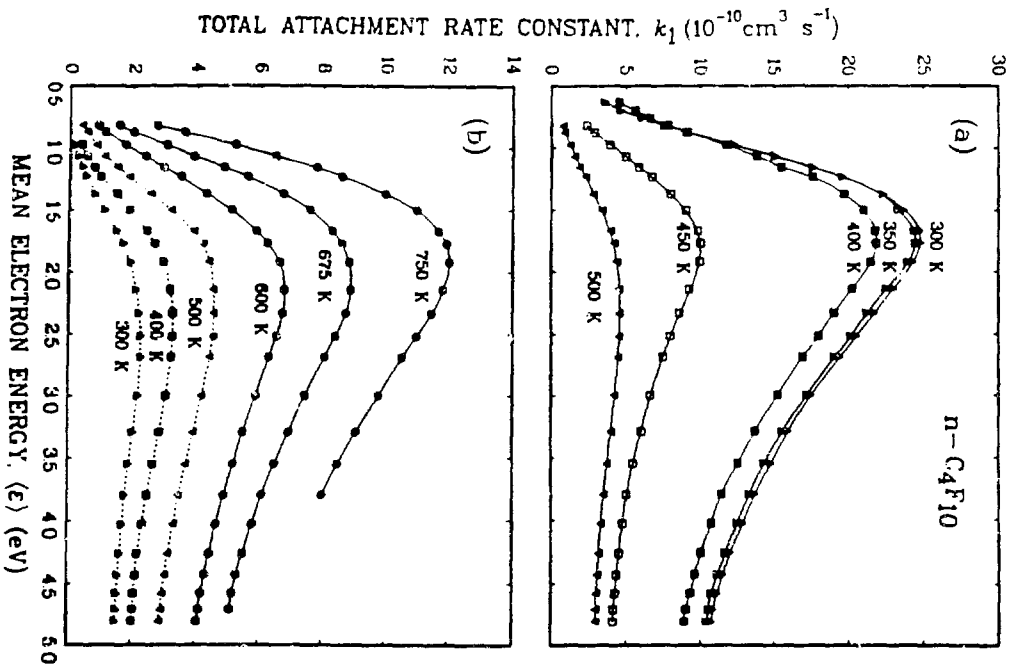
depending on which process is dominant





TOTAL ELECTRON ATTACHMENT RATE CONSTANT, k_0 ($10^{-8} \text{ cm}^3 \text{ s}^{-1}$)





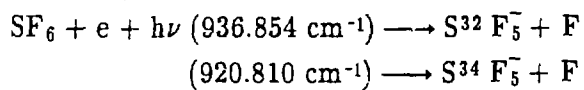
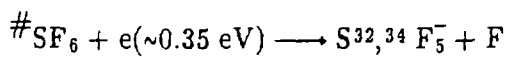
DISSOCIATIVE ELECTRON ATTACHMENT TO LASER-PRODUCED
VIBRATIONALLY-EXCITED MOLECULES AND PHOTOFRAGMENTS

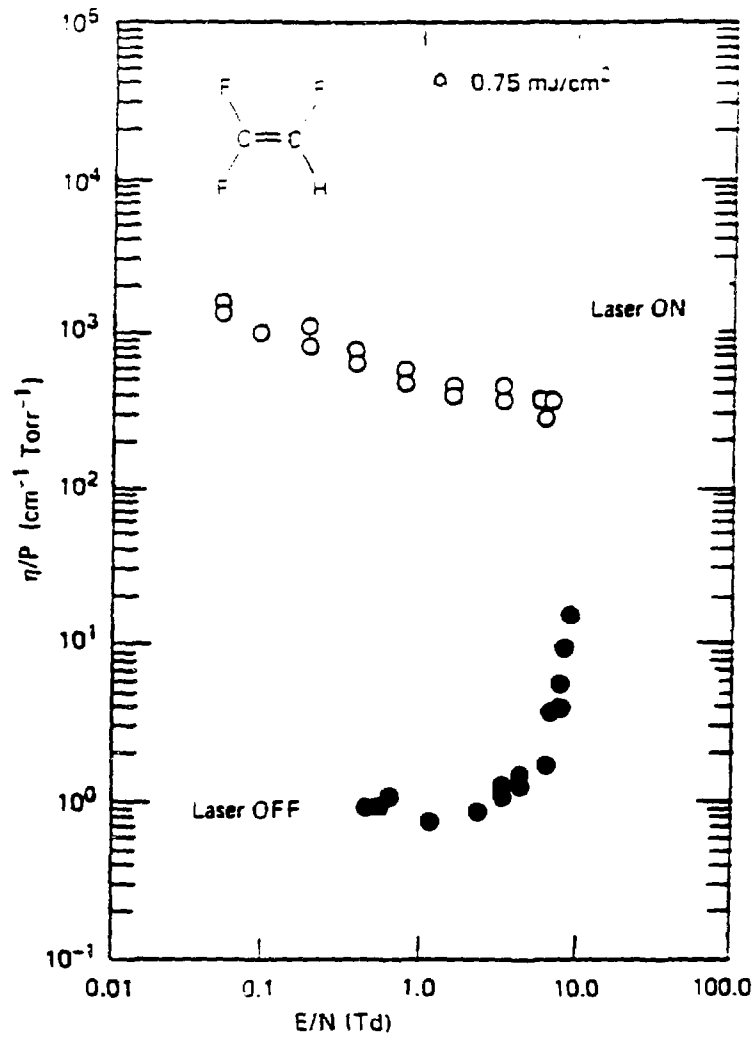
Molecules:

- SF₆, I₂, Li₂
(Isotope Separation)[#]

Photofragments:

- HCl^{*}/C₂H₃Cl, HF^{*}/C₂F₃H
(Switches)

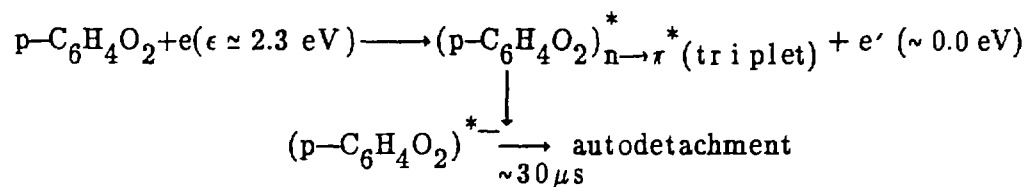




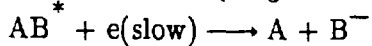
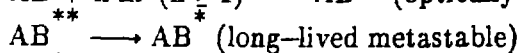
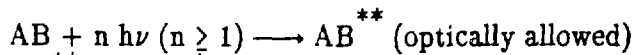
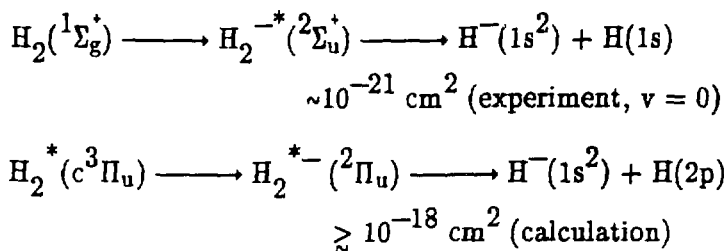
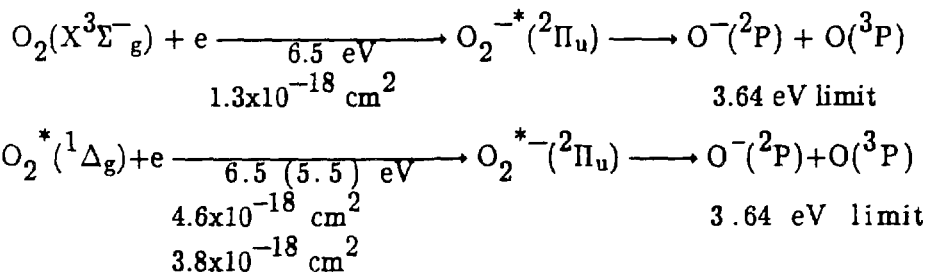
ELECTRON ATTACHMENT TO ELECTRONICALLY-EXCITED MOLECULES

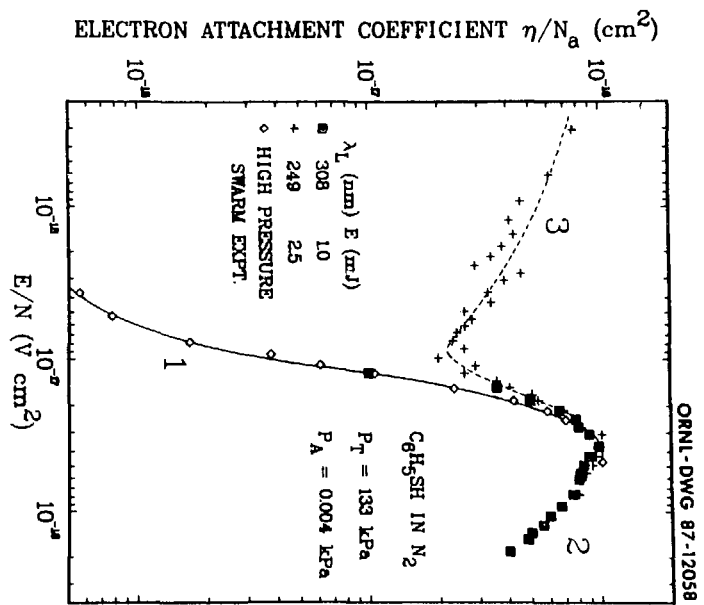
- Metastable ($\gtrsim 10^{-5}$ s), long-lived excited molecules
 - Short-lived ($\lesssim 10^{-8}$ s) excited molecules
-

- Electron-excited Feshbach resonance

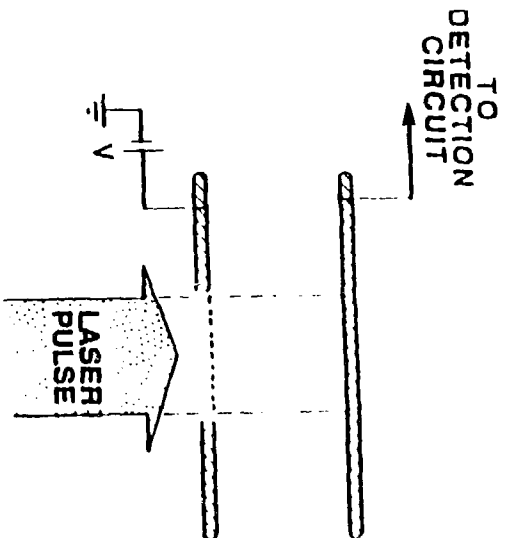


Dissociative Electron Attachment to Metastable Electronic States of Molecules

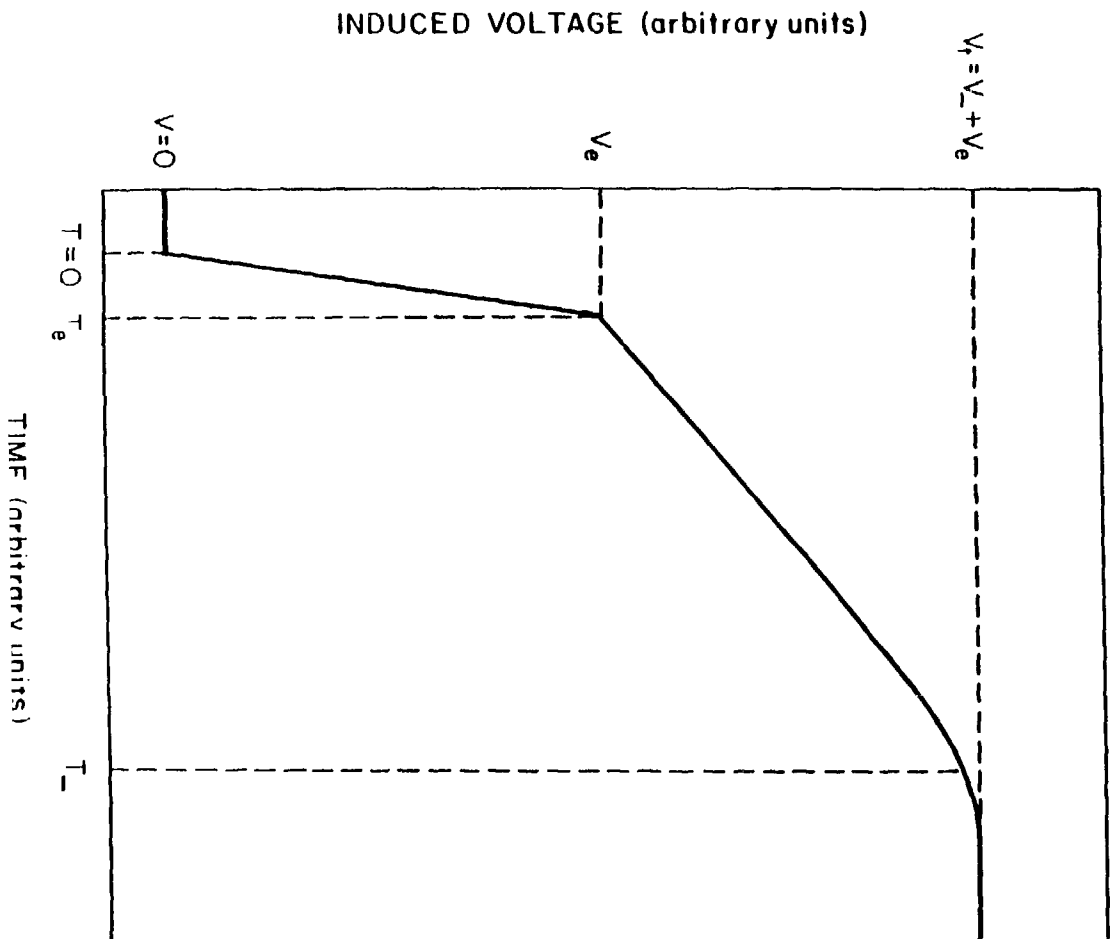


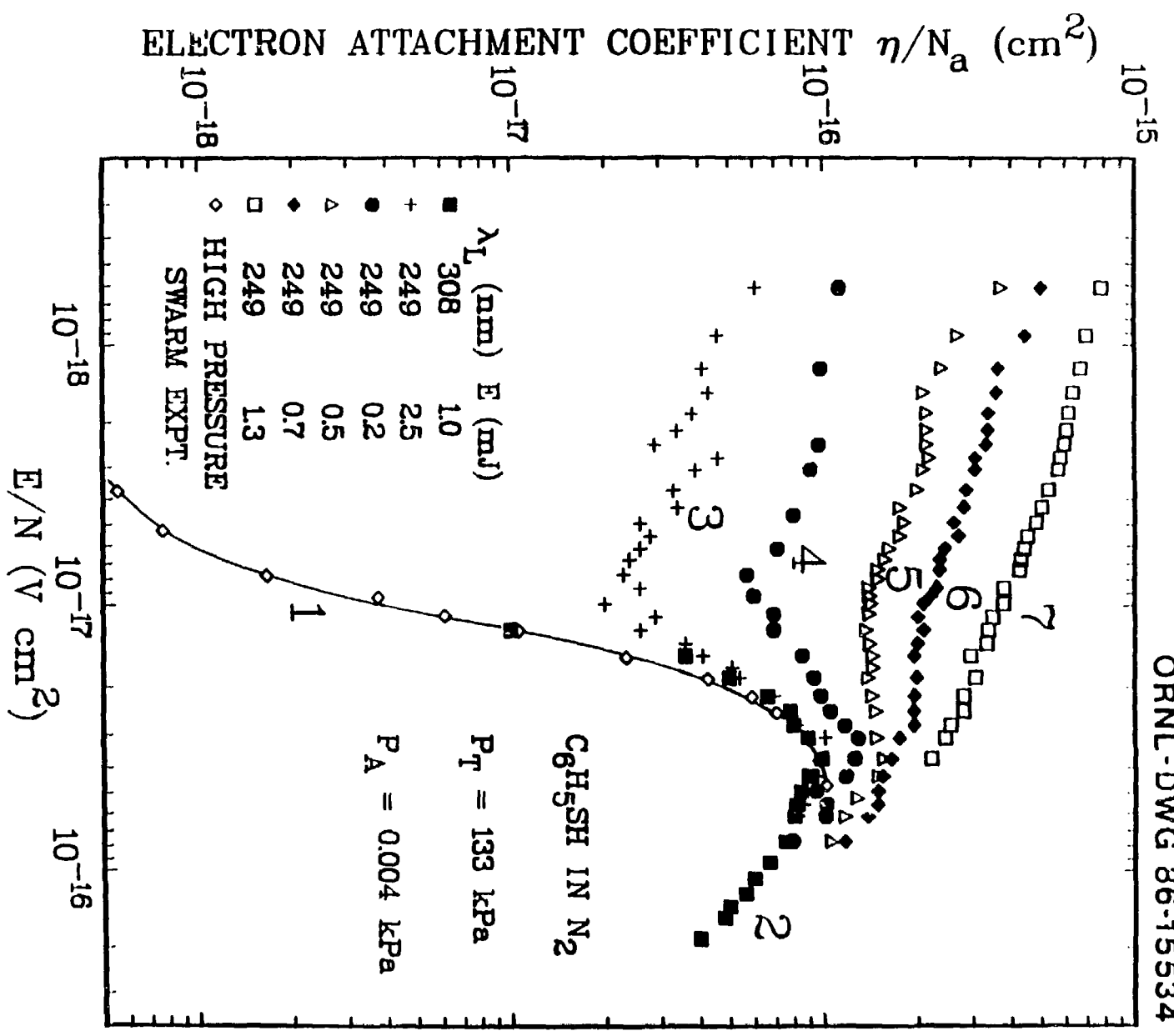


(a)



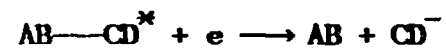
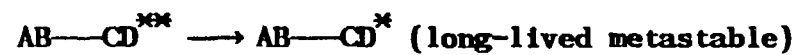
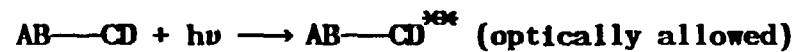
(b)





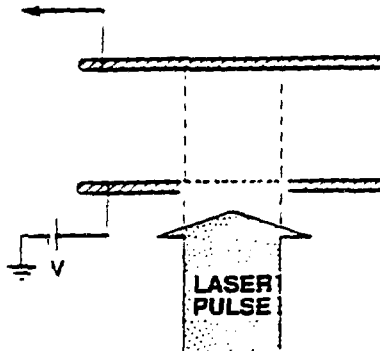
OPTICALLY-ENHANCED ELECTRON ATTACHMENT TO
ELECTRONICALLY-EXCITED MOLECULES

- Indirect Electronic Photoexcitation of Long-Lived Molecules (C_6H_5SH)

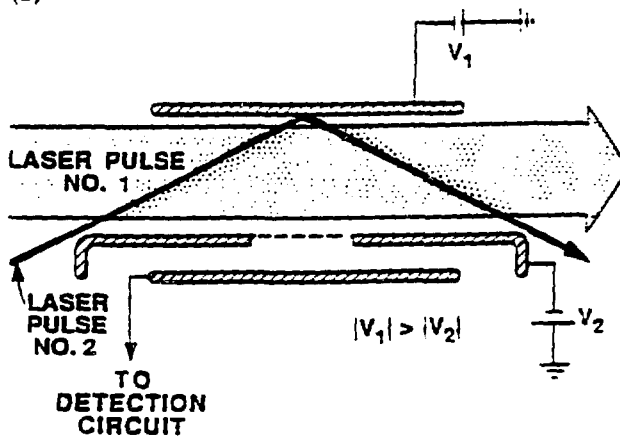


(a)

TO
DETECTION
CIRCUIT



(b)



(c)

