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# APPLICATIONS OF CROSS SECTIONS FOR ELECTRON-MOLECULE COLLISION PROCESSES

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Electron-impact proccesses with atoms and molecules play a central role in a wide variety of naturally occurring and laboratory-produced phenomena and, as a result, have been the subject of considerable research, particularly in the last ten years. The importance of electron-impact excitation processes involving ground-state molecules, and molecules in metastable excited states, has been recognized for many years in the study of ionospheric [1] and auroral [2] processes in planetary atmospheres. The discovery of high-power (electron-beam and discharge-pumped) gas lasers has resulted in an increased interest in electron collision processes because of the important role they play in creating the population inversion [3]. This renewed interest in electron scattering has resulted in the measurement of many of the electron-impact excitation cross sections of importance during the past ten years. The need for cross section information involving targets that are presently difficult to study experimentally (eg, molecular free radicals, etc), and recent results from electron-photon coincidence measurements [4] which probe the details of the scattering process, have further stimulated theoretical studies. In spite of this renewed activity, however, much of the electron-impact excitation cross section information needed to model a variety of plasma and planetary processes is still not known and the absence of these basic cross section data hinders progress toward a more thorough understanding of various phenomena.

## The Earth's Ionosphere and Aurora

Electron impact processes play a major role in two naturally occurring atmospheric phenomena. In the earth's ionosphere, processes associated with production and loss of free electrons (and the related ion-chemistry) determine the characteristics of the secondary electron distribution and the ionospheric emissions. Auroral emissions are produced as a result of energy deposition by charged particles, primarily electrons, entering the earth's polar atmospheres along magnetic field lines. These two atmospheric phenomena involve electrons of somewhat different energies, but require essentially the same cross-section information.

Free electrons in the ionosphere are produced by photoionization of atmospheric constituents and the subsequent cascade-ionizations of these "primary" electrons as they move through the atmosphere. These electrons lose their energy by ionization, electronic, vibrational and rotational excitation of the atmospheric constituents, and collisions with other electrons, until they thermalize and ultimately recombine with the positive ions.

The full range of electron impact processes, elastic scattering through ionization, is possible because the flux of electrons ranges from 0 to greater than 100 eV. Molecular nitrogen, however, is the only atmospheric constituent for which extensive results have been reported for the differential and integral cross sections for electronic excitation and, even for $N_2$, there remain a number of atmospherically important issues for which the available data are in major disagreement. Two of the leading issues involving electronic excitation in $N_2$ has to do with the magnitudes and shapes of the integral cross sections from threshold to about 25 eV and with the absolute cross sections for dissociation of $N_2$ into $N(^4S)$, $N(^2D)$, and $N(^2P)$ fragments. As illustrated in Figure 1, Zipf and McLaughlin [5] have reported integral "apparent" cross sections for excitation of the dipole-allowed states that are a factor of two larger than those determined [6] from electron energy-loss spectra and the origin of this difference has not yet been explained. This difference needs to be resolved because nitrogen atoms, in their ground and excited states, play key roles in the formation of NO and similar constituents in the ionosphere and dissociation of $N_2$ by electron impact appears to be the major mechanism for producing N atoms.

The data situation for $O_2$, also a major molecular constituent in the ionosphere, is currently worse than for $N_2$ because there are relatively few absolute differential and integral cross sections for excitation of specific states in $O_2$. One of the major reasons for this deficiency is because the very strong perturbations present in the excited

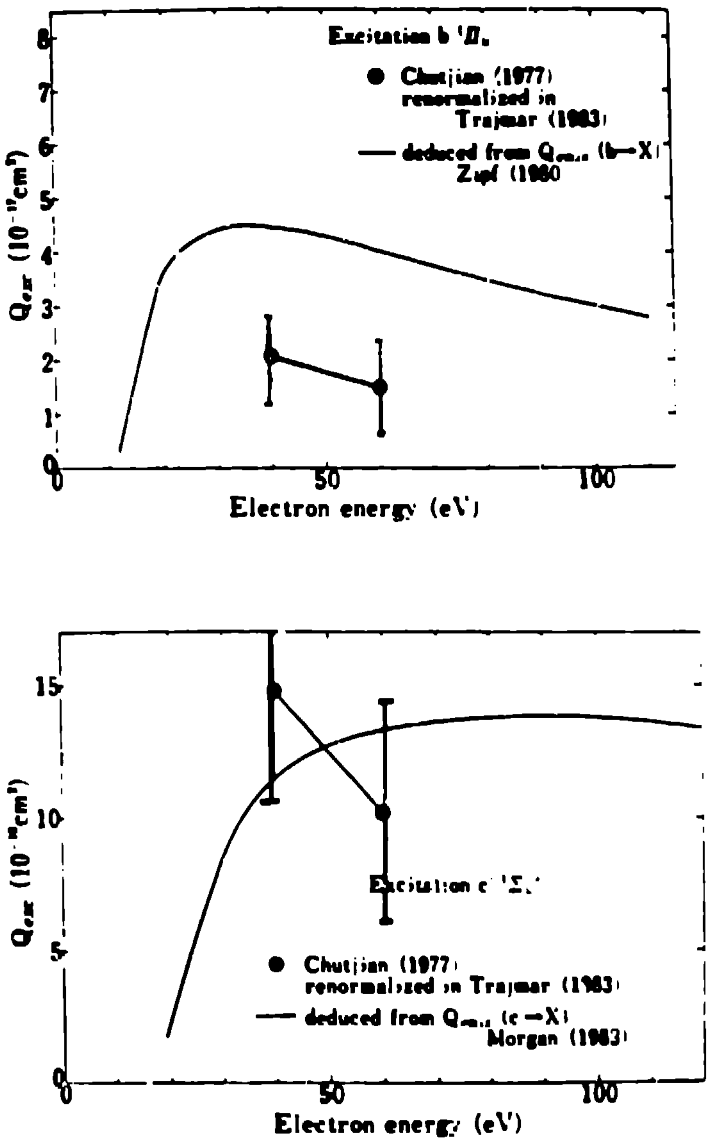


**Figure 1.** Comparison of recent measurements of the integral cross sections for excitation of the b $^1\pi_u$ state (upper panel) and c' $^1\Sigma_u^+$ state (lower panel) of $N_2$. The solid curves are from Zipf and Gorman [11] and from Morgan and Mentall [12]. The data points are from Chutjian and Cartwright [6]. (Composite figures from Itikawa et al 1985 [13]).

states of $O_2$ so complicate the electron energy-loss spectra in $O_2$ that a straightforward analysis of the data is not possible. In the atmospheric sciences, the primary interest in electron impact excitation of $O_2$ is as a source of excited-state O-atoms because electron-impact excitation of essentially every electronic state above the b $^1\Sigma_g^+$ state (at 1.6 eV) results in dissociation into O-atom fragments. Progress has been made recently in understanding the photodissociation of $O_2$ via the atmospherically important Schumann-Runge continuum [7] and the magnitudes of the electron impact cross sections for excitation of composite (ie, more than one electronic state in the energy-loss spectra [8]. However, differential and integral cross sections for excitation of individual electronic states, and the correlation to excited state fragments, is still not available. Providing this information will require a particularly close collaboration between theorists and experimentalists because the very strong perturbations in the electronic state of $O_2$ preclude application of existing theoretical techniques on the one hand, and make straightforward interpretation of the energy-loss data impossible on the other.

As a final comment on molecules for which electron impact excitation data are useful in the atmospheric sciences, we mention the molecule NO. This molecule, although not a dominant neutral species in the earth's atmosphere, is of particular interest because of the key role it plays in the ion chemistry in the ionosphere and the aurora [2]. The excited electronic states of this molecule are also strongly perturbed and, again, very little data are currently available on the direct electronic excitation and/or the excited state and kinetic energy distribution of the dissociation atomic fragments. As in the case of $O_2$, determination of the cross sections for electronic excitation of NO is a fertile area for collaborative theoretical and experimental efforts because of strong perturbations in the excited state spectrum.

Gas discharges/excimer lasers. There is considerable renewed interest in the general properties of gas discharges, primarily because they serve as efficient means to drive gas lasers. Gas breakdown and the transport of moderate-energy electrons through gas media are not yet very well understood and remain the subject of considerable research. The origin of the current difficulties with modeling these phenomena can be traced to be a combination of (1) the mathematical and computational problems in dealing with a non-LTE plasma, and (2) the general absence of the cross section data necessary to model the charged-particle interactions in the medium.

Excimers are the class of exciplex molecules formed from identical atoms or atomic groups (eg, rare-gas excimers).

Exciplex molecules are defined as those which are bound in their excited electronic states but dissociate readily in their ground electronic state. The general characteristics of, and detailed processes occurring in, exciplex lasers have been discussed in a number of excellent review articles [9]. Because of the importance in a wide variety of applictions, the rare-gas KrF excimer system will be used as the example to illustrate the relevant mechanisms. Figure 2 illustrates the potential-energy curves for KrF. The upper lasing level is the B state and is dipole connected to the weekly bound X ground electronic state.

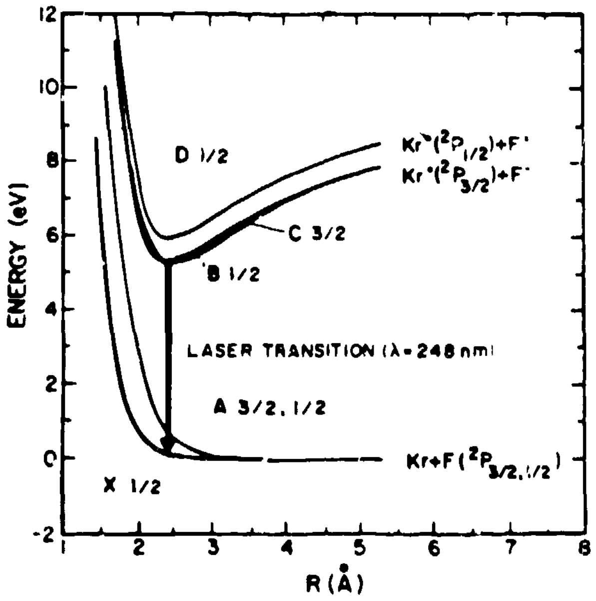


Figure 2. Electronic structure characteristics of the lasing KrF monohalide molecule. The lowest electronic state is repulsive, or only slightly bound, and therefore the ground-state (X) molecule is thermally unstable against dissociation into atomic fragments. The upper laser level (B) is an ionic electronic state that dissociates into the indicated ionic fragments.

The KrF excimer laser is usually produced from an atmospheric-pressure mixture of Ar-Kr-$F_2$ having various percentage proportions of the component gases. Usually, the constituents that form the lasing molecule are diluents in a carrier gas.

The production and loss of the active exciplex media involve a large number of electron and heavy-particle collision processes. A thorough analysis of the basic collision processes that take place in an electron-beam stabilized electrical discharge in atmospheric Ar-Kr-$F_2$ mixtures has been provided by Nighan [10], and Figure 3 is an adaptation

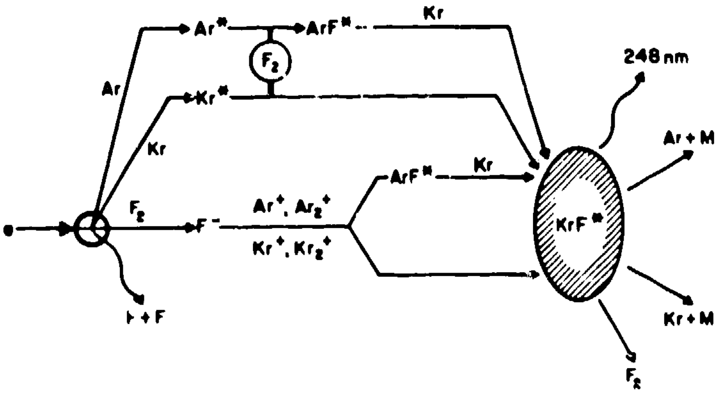


Figure 3. Schematic diagram of the primary reactions for formation of KrF by electron-impact excitation of atmospheric-pressure mixtures of Ar-Kr-$F_2$ (Adapted from Nighan [10]).

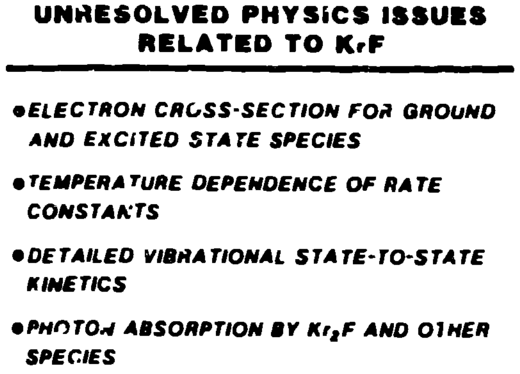
of his schematic summary of the primary collision processes contributing to KrF molecule which, as shown in Figure 3, occurs via either ion-molecule reactions or reactions involving metastable rare-gas atoms. Although no single mechanism completely dominates the production of KrF, Nighan's analysis shows that two- and three-body positive and negative ion recombination is most important for electron-beam excitation (lowest path in Figure 3), while reactions between $F_2$ and metastable rare-gas atoms are most important in the case of gas-discharge pumping (upper two paths in Figure 3).

A key factor in achieving high efficiency for these lasers is the efficient production of rare-gas atoms in metastable states. Analysis shows [10] that there is a substantial electron energy loss to electron-impact dissociation of $F_2$. Vibrational excitation of $F_2$ is not an important energy loss mechanism (because the energy lost per collision is relatively small) but is very important in the formation of KrF because of its possible effect on dissociative attachment. Accurate assessments of these loss mechanisms are, unfortunately, not yet possible because there are currently very few data available on the electronic and vibrational excitation of $F_2$, and these deficiencies hamper the assessment of the role of electron-$F_2$ processes in the KrF laser.

As shown schematically in Figure 3, $F^-$ plays a central role in the formation of KrF but the role of excitation to electronic states of $F_2$ that dissociate into $F^+ + F^-$ could not be determined because the relevant cross section data are not available. Theoretical work suggests that ionic-character states that dissociate into $F^+ + F^-$ are abundant in $F_2$ and, consequently, the electron-impact excitation of these states should be studied to determine if this source of $F^-$ is important in the KrF laser. In the short term, theoretical techniques may be the best way to obtain this information.

Table 1 is a summary of the key physics issues that need to be addressed in order to better understand the KrF laser. One of the most important is the determination of electron impact cross sections involving molecules in excited electronic states.

Table 1.

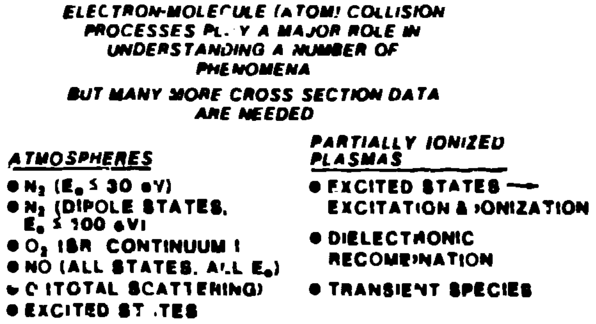


**UNRESOLVED PHYSICS ISSUES RELATED TO KrF**

- *ELECTRON CROSS-SECTION FOR GROUND AND EXCITED STATE SPECIES*
- *TEMPERATURE DEPENDENCE OF RATE CONSTANTS*
- *DETAILED VIBRATIONAL STATE-TO-STATE KINETICS*
- *PHOTON ABSORPTION BY $Kr_2F$ AND OTHER SPECIES*

Table 2 is a summary of the kinds of electron-impact cross section data that are needed to better understand certain aspects of atmospheric and discharge processes.

Table 2.



*ELECTRON-MOLECULE (ATOM) COLLISION PROCESSES PLAY A MAJOR ROLE IN UNDERSTANDING A NUMBER OF PHENOMENA*

*BUT MANY MORE CROSS SECTION DATA ARE NEEDED*

*ATMOSPHERES*

- $N_2$ ($E_0 \leq 30$ eV)
- $N_2$ (DIPOLE STATES, $E_0 \leq 100$ eV)
- $O_2$ (SR CONTINUUM)
- NO (ALL STATES, ALL $E_0$)
- O (TOTAL SCATTERING)
- EXCITED STATES

*PARTIALLY IONIZED PLASMAS*

- EXCITED STATES → EXCITATION & IONIZATION
- DIELECTRONIC RECOMBINATION
- TRANSIENT SPECIES

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