

Total electron-scattering cross sections for CHF₃, C₂F₆, C₃F₈, and c-C₄F₈

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The total electron-scattering cross section has been measured for 0–20 eV electrons incident upon CHF₃, C₂F₆, C₃F₈, and cyclo-C₄F₈. The cross sections all have a broad maximum for electron energies near 9 eV, with more or less sharper peaks attributed to temporary-negative ion resonances at lower energies. For the linear molecules a resonance in the 3–6 eV range is associated with electron capture into the lowest unoccupied orbital. The shape of the cross section for the cyclic compound implies a stable ground-state negative ion. © 1998 American Institute of Physics. [S0021-9606(98)03702-7]

Owing to the threat to the atmosphere posed by CF₄, one of the most common gases used in the plasma processing of semiconductor devices, the industry is considering a change to another fluorocarbon. At present, the primary candidates are CHF₃, C₂F₆, C₃F₈, and cyclo-C₄F₈. Modeling the function of various gases in low-pressure, cold plasmas will require cross sections for scattering (both elastic and inelastic), fragmentation, dissociative attachment, and ionization by electrons in the 0–20 eV range, as well as similar cross sections for electron interactions with the fragmented molecules. As a first step, we have measured the total electron-scattering cross sections for these four candidate gases over the 0–20 eV range. As expected, we see peaks in the cross sections due to resonant electron–molecule interactions for particular incident electron energies. These resonances are attributable to the formation of transient negative ions with lifetimes considerably in excess of the electron transit time in nonresonant electron–molecule collisions. The extended lifetime of the electron–molecule complex during resonant interactions allows the complex to enter channels leading to excitation and fragmentation that produce the active species in the processing plasma.

Measurements are carried out in a simple transmission experiment employing a low-current electron gun followed by a trochoidal electron monochromator, a target gas cell, and a retarding potential preceding an electron collector. The transmission, $T = I/I_0 = e^{-n\sigma l}$, gives the cross section, σ , with a measurement of the target gas density, n , the target cell length, l , and the incident and transmitted currents, I_0 and I , respectively. The details of the apparatus and the uncertainties in the result have been published previously.^{1,2} In the present measurements the energy resolution is about 40 meV. The position of prominent peaks was determined by a Gaussian fitting routine. The data are shown in Fig. 1.

The scattering cross section for CHF₃ rises sharply as the electron energy approaches 0 eV. This is typical of the scattering from fairly symmetrical methanes. The phenomenon is characterized as “s-wave scattering.”^{1,3–5} In addition broad weak enhancements of the cross section appear at about 6.5 and 9.3 eV. These are consistent with weak features at 6.3 and 9.3 eV in the derivative electron transmission spectrum reported by Modelli *et al.*⁶ On the basis of MS-X α calculations, these authors infer that the higher energy feature re-

sults from electron capture into the lowest energy σ^* orbitals of the molecule while the lower feature is an artifact due perhaps to an impurity in the sample. Our observation of an enhancement in the absolute cross section at 6.6 eV would tend to rule out this interpretation. A strong sharp resonance in a trace impurity may be observable in the derivative transmission spectrum, however, it would not contribute to the total scattering cross section.

The total electron-scattering cross section of C₂F₆ exhibits its resonant enhancement at 4.7 and 8.5 eV. The cross section observed here agrees in both shape and magnitude with a recently reported cross section measured by a time-of-flight technique.⁷ Analogous features appear in the derivative electron-transmission spectrum,⁸ the dissociative-attachment cross section,^{9,10} the electron-attachment cross section,^{11,12} and vibrational-excitation differential cross sections.¹³ In general, the enhancement of secondary processes requiring nuclear motion appears at slightly lower energy since these depend on the lifetime of the temporary negative ion that increases with decreasing energy. Ishii *et al.*⁸ performed simple Hartree–Fock calculations employing the STO-3G basis set and assign the lower energy resonance to electron capture into the σ^*e_u LUMO. On the other hand, Weik and Illenberger,⁹ quoting unspecified MO calculations, attribute the lower energy resonance to $3a_{2u}(\sigma^*_{CC})$ and $2e_u(\sigma^*_{CF})$ virtual orbitals and, indeed, both Weik and Illenberger, and Harlan and Franklin¹⁴ have presented evidence of two separate F[–] kinetic energy distributions arising from dissociative attachment of electrons in the 4 to 5 eV range suggesting the possibility of two, closely spaced, negative-ion states. The strongest argument for assigning the 5.0 eV resonance comes from the work of Takagi *et al.*¹³ They have measured the differential cross section for elastic and vibrationally inelastic excitation and observe a prominent resonance at about 4.3 eV. A symmetry analysis in which they account for the vibrational modes excited leads to an assignment of $a_{2u}(\sigma^*_{CC})$ for the orbital associated with the resonance and an assignment of e_u for the higher energy feature near 9 eV.

In C₃F₈ there are resonances at 3.6 and 6.1 eV along with the broad peak near 9 eV that appears to be a ubiquitous, but, to date, unassigned, feature not only of all the compounds investigated here but of the saturated hydrocarbons in general. The two lower-energy peaks correspond to

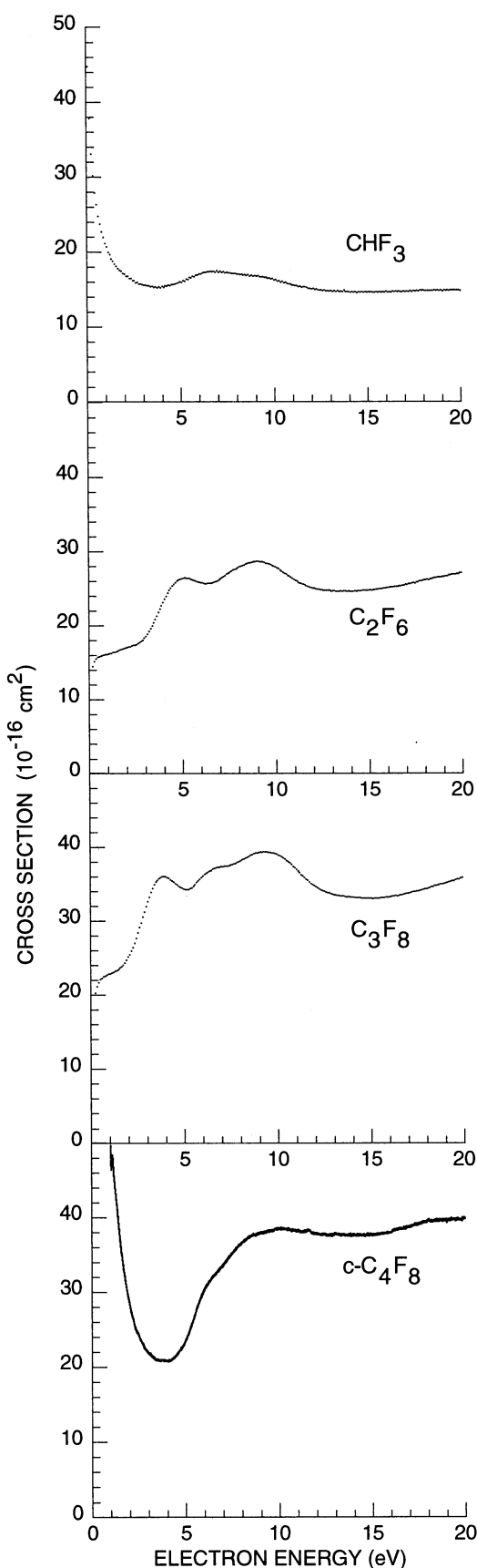


FIG. 1. Total electron scattering cross sections for CHF_3 , C_2F_6 , C_3F_8 , and cyclo- C_4F_8 .

features at 3.34 and 6.00 eV in the derivative electron transmission spectrum⁸ and to peaks at 3.0 and 6.0 eV in the total attachment cross section (i.e., the fragment negative ion yield).¹⁵

The shape of the total scattering cross section for *c*- C_4F_8 is quite different from that of the linear fluoroalkanes. There is only a suggestion of a resonance at about 6 eV corresponding to a feature at 5.8 eV reported in the derivative electron transmission spectrum.⁸ Below 1 eV the cross section becomes so large that we are unable to make reliable measurements, since to maintain single-collision conditions would require target pressures too low for us to measure. Electron attachment rates below 1 eV have been found to rise steeply as the electron energy approaches 0 eV.^{16,17} Ishii *et al.* argue that the strain of cyclization greatly stabilizes the LUMO of the perfluoroalkanes.⁸ The deep minimum in the cross section near 3.5 eV suggests a Ramsauer–Townsend minimum and the steep rise of the cross section for electron energies approaching 0 eV is consistent with the existence of a very-low-energy resonance or even the possibility of a stable ground-state ion. Indeed, Miller *et al.* have estimated an electron affinity of +0.63 eV from electron attachment experiments.¹⁸

As expected we find the total scattering cross sections for CHF_3 , C_2F_6 , C_3F_8 , and cyclo- C_4F_8 to increase in magnitude with increasing molecular size. Prominent temporary-negative-ion resonances appear with the lowest energy resonance presumably corresponding to electron capture into the LUMO. The energy of the LUMO decreases with the length of the carbon backbone in the linear molecules and is greatly stabilized in the highly-strained cyclic compound. In an attempt to determine the symmetry of the LUMO we have performed static MO calculations, however, we find these to be so sensitive to the basis set as to be unreliable. It appears that only large dynamic scattering calculations or detailed differential cross section measurements like those of Takagi *et al.* will suffice to determine the nature of the molecular orbitals involved in the resonant enhancement of the scattering cross sections and the attendant dissociation processes.

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