

Absolute Electron Scattering Cross Sections for the CF₂ Radical

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Using a crossed electron-molecular beam experiment, featuring a skimmed nozzle beam with pyrolytic radical production, absolute elastic cross sections for electron scattering from the CF₂ molecule have been measured. A new technique for placing measured cross sections on an absolute scale is used for molecular beams produced as skimmed supersonic jets. Absolute differential cross sections for CF₂ are reported for incident electron energies of 30–50 eV and over an angular range of 20–135 deg. Integral cross sections are subsequently derived from those data. The present data are compared to new theoretical predictions for the differential and integral scattering cross sections, as calculated with the Schwinger multichannel variational method using the static-exchange and static-exchange plus polarization approximations.

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Molecular radicals are key components of many gas discharge and low-temperature plasma environments. They are typically formed by electron impact dissociation or dissociative attachment and their highly reactive nature is often used to advantage for material or surface modification or deposition. A prime example of such technology is the plasma processing of semiconductors where fluorocarbon feedstock gases such as C₂F₄ or C₄F₈ are dissociated to produce a range of radical products (e.g., CF_x, x = 1, 2, 3) and/or their negative ions. These species are then responsible for much of the surface etching used in the large-scale production of semiconductor circuits.

The molecular properties that render these radicals so reactive (e.g., open shell structure, large dipole moments and dipole polarizabilities, high electronegativity) also imply that they become important constituents of the gas discharge itself. These properties are also consistent with very large low-energy cross sections for a variety of electron-collision processes, and even small concentrations of such radicals can therefore have a profound effect on the overall behavior of the discharge.

Results of calculations for electron interactions with fluorocarbon radicals have recently become available in the literature [1–3] and are indicative of their potential importance in gas discharge environments. To date there have been no experimental measurements of absolute elastic cross sections for such molecules. In this Letter we report measurements of absolute elastic cross sections for electron scattering from the CF₂ molecule, with these data also being supplemented by new calculations.

Flash pyrolysis of C₂F₄ molecules [Eq. (1)] was used to produce a clean source of jet-cooled CF₂ molecules for the

experimental measurements. Flash pyrolysis is an efficient method for breaking the relatively weak double carbon-carbon bond [4] in C₂F₄ [5].



The apparatus used to perform the CF₂ cross section measurements is depicted in Fig. 1. The experiment is a crossed-beam electron scattering experiment comprising four differentially pumped chambers. The first chamber contains the solenoid valve, the pyrolytic nozzle, and the

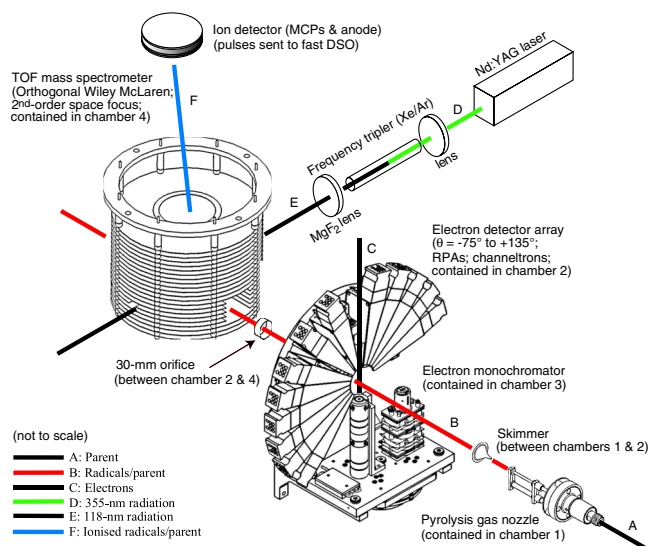


FIG. 1 (color online). Schematic diagram of the apparatus used to measure absolute electron scattering cross sections for the CF₂ radical.

skimmer, and is pumped by a 10 in. diffusion pump. The nozzle diameter is 0.8 mm and the skimmer aperture is 1.0 mm. The pyrolysis tube, constructed from Hexoloy SE SiC, has a 1-mm bore and a length of 25 mm. The second chamber, separated from the first by the skimmer, houses the fixed-angle electron detectors, and is pumped by a 156 l/s turbomolecular pump. Nine detectors were used in the fixed array, spanning an angular range of 20–135 deg. The third chamber contains the electron monochromator, and is differentially pumped by a 50 l/s turbomolecular pump to shield the monochromator from the gas pulse. The fourth chamber, separated from the second by a 30-mm aperture, houses the time-of-flight mass spectrometer and is evacuated by a 6 in. diffusion pump.

The pyrolysis nozzle, based on a Chen-type design [6], was resistively heated through the application of an ac voltage. Following pyrolysis the heated products underwent cooling through supersonic expansion. A skimmer was placed downstream from the pyrolytic nozzle to collimate the beam for passage through the scattering chamber. The electron monochromator produces a monoenergetic electron beam which is scattered from the collimated beam, and an array of up to 13 fixed-angle detectors is used to determine the scattering intensities for those angles. The composition of the beam was monitored using a time-of-flight mass spectrometer (TOFMS) with 118-nm radiation used to ionize species through single-photon ionization. The temperature of the pyrolysis nozzle was measured with an optical pyrometer. Differential cross section (DCS) data were placed on an absolute scale by using a modified form of the skimmed supersonic relative density method (SSRDM) [7].

With C_2F_4 pulsing through the system, the production of CF_2 radicals was observed by monitoring the combined outputs of the electron spectrometer, the TOFMS, and the pyrometer (Fig. 2). With the pyrolysis tube at room temperature, a strong C_2F_4 peak was observed in the TOFMS and a strong scattering signal was detected. When the pyrolysis temperature was increased to 900 °C the C_2F_4 TOFMS peak began to decline indicating the onset of C_2F_4 pyrolysis, a result consistent with previous measurements [5,8]. As the pyrolysis temperature was further increased, the C_2F_4 TOFMS peak diminished until the C_2F_4 peak vanished at 1250 °C. Over this same temperature range the scattering signal remained strong. Consequently, C_2F_4 was being fully pyrolyzed by 1250 °C. A previous study [5] also measured full pyrolysis of C_2F_4 at this temperature and found CF_2 to be the predominant (>99%) pyrolysis product. In the present study, CF_2 radicals could not be directly observed in the TOFMS as the ionization energy of this species (IE = 11.44 eV [9]) is in excess of the single-photon energy of 118-nm radiation ($E = 10.5$ eV). Also, according to the TOFMS spectrum at 1250 °C there was no evidence for presence in the beam of CF (IE = 9.11 eV [9]) (a result also found in a previous study [5]), CF_3 (IE =

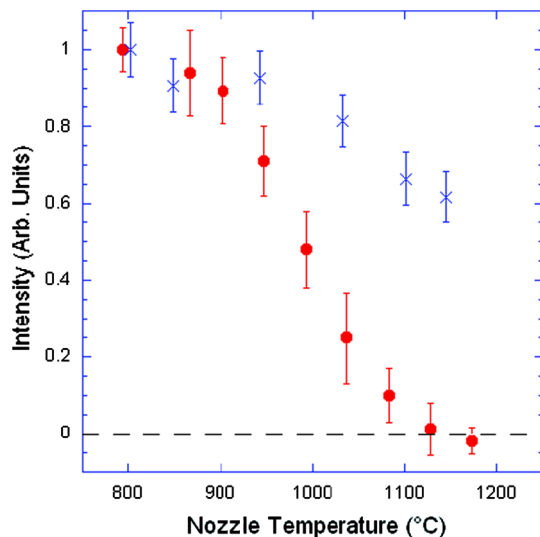


FIG. 2 (color online). Method for determining the pyrolysis temperature for C_2F_4 into CF_2 . The amount of C_2F_4 was monitored in the TOFMS (●) and compared with the scattering counts in the electron spectrometer (×).

8.5 eV [10]), or C_2F . The present authors conclude that for flash pyrolysis of pure C_2F_4 at 1250 °C the resultant supersonic expansion consists almost exclusively of CF_2 radicals.

The reference species chosen to normalize the CF_2 cross sections was CF_4 , because this molecule does not undergo flash pyrolysis at a temperature of 1250 °C. Because of the tendency of CF_2 to adhere to the chamber walls, pumping speeds for CF_2 and CF_4 were explicitly measured rather than calculated in terms of molecular mass. The chamber pressure P is related to the pumping speed S and elapsed time t by $P(t) = P_i \exp(-t \frac{S}{V})$, where V is the volume of the chamber and P_i is the initial pressure when the pulsed nozzle was shut off. The chamber pressure was logged immediately after shut off, and then the ratio of the pumping speeds determined as input to the SSRDM normalization. To demonstrate the effectiveness of SSRDM, the DCS of C_2F_4 was measured relative to CF_4 with the pyrolytic tube set at a temperature of 850 °C, well under the temperature required to commence pyrolysis of C_2F_4 yet hot enough to test the validity of SSRDM when used with beams heated through the pyrolysis tube. No significant difference was observed between the 850 °C C_2F_4 absolute DCS measurement and the corresponding result at room temperature. Furthermore, both these results were in very good agreement with those obtained in independent effusive beam studies using a traditional relative flow technique [11].

Schwinger multichannel [12] calculations of the elastic electron scattering cross section were carried out in the static-exchange (SE) and static-exchange plus polarization (SEP) approximations. Both calculations used the 6–311G basis set as contained in GAMESS [13] with a $1s1p3d$

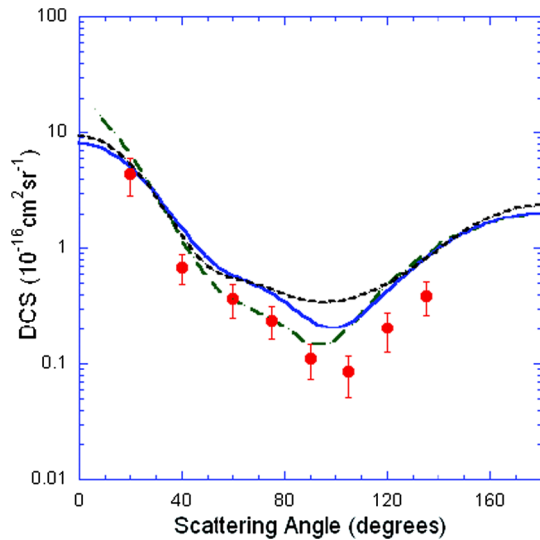


FIG. 3 (color online). Absolute elastic DCS for CF_2 at 30-eV incident electron energy: present experimental (\bullet) and SE (solid line) and SEP (short-dashed line) theoretical results, and the ISM-DWA calculation of Lee *et al.* [1] (dashed line).

diffuse and polarization supplement ($3s$ d functions excluded) for which GAMESS default exponents were used. The geometry was optimized in C_{2v} symmetry at the level of second-order Møller-Plesset perturbation theory in the 6–31G(d) basis, again using GAMESS. The variational space for the SE calculation included only doublet configuration state functions (CSFs) built by coupling the Hartree-Fock ground state of CF_2 with every virtual orbital. The SEP space included, in addition, all doublet CSFs that could be built by coupling any modified virtual orbital (MVO) [14] to the singlet single excitations out of the 9 valence occupied orbitals into the 30 lowest-energy MVOs for a +6 core, as well as to the triplet excitation out of the highest occupied orbital into the lowest MVO.

The present experimental, SEP- and SE-level theoretical results for the absolute elastic differential cross sections of CF_2 are presented in Figs. 3–5. Also shown in these figures, where possible, are the results of Lee and colleagues [1], calculated using the iterative Schwinger variational method combined with the distorted-wave approximation (ISM-DWA). It is clear from Figs. 3–5 that the present experiment and theory are strongly peaked at the more forward scattering angles, possibly reflecting the permanent dipole moment of CF_2 . It is also clear that the present experiment and calculations are in quite good accord, in terms of the shape and magnitude of these DCS, at each of the energies studied. If anything, the ISM-DWA calculation of Lee *et al.* [1] is in even better agreement with the current measured DCS, at both 30 and 50 eV, probably reflecting the importance, at these energies, of coupling to open inelastic channels, including the ionization channel. The calculation of Lee *et al.* [1] included such coupling through an absorbing potential, whereas it is neglected in

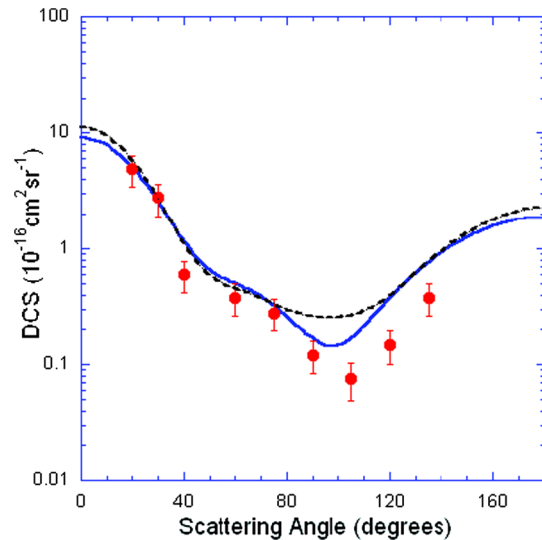


FIG. 4 (color online). Absolute elastic DCS for CF_2 at 40-eV incident electron energy: present experimental (\bullet) and SE (solid line) and SEP (short-dashed line) theoretical results.

the SE approximation. Similarly, the SEP calculation includes excitation channels but treats all of them as closed, which probably explains why the SE calculation appears to give better results at these energies. Nonetheless, it is encouraging that an SE-level calculation does so well in reproducing the measured elastic DCS at these intermediate energies.

Experimental elastic integral cross sections (ICSs) for CF_2 were deduced (Fig. 6) from the absolute DCS measurements, determined according to a phase-shift analysis method [15]. Again, the present measured results are con-

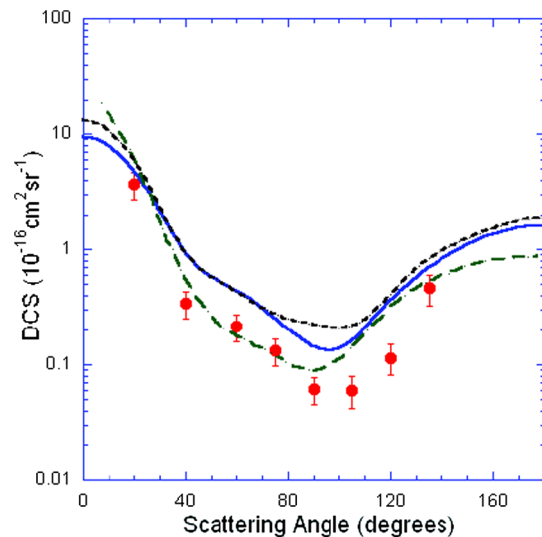


FIG. 5 (color online). Absolute elastic DCS for CF_2 at 50-eV incident electron energy: present experimental (\bullet) and SE (solid line) and SEP (short-dashed line) theoretical results, and the ISM-DWA calculation of Lee *et al.* [1] (dashed line).

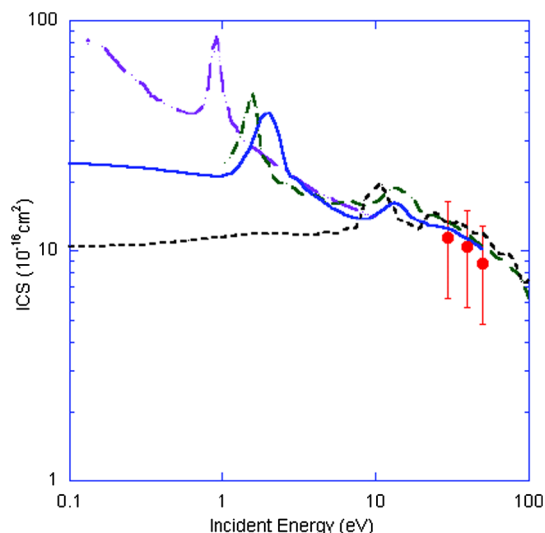


FIG. 6 (color online). Absolute elastic ICS for CF_2 at incident electron energies of 30, 40, and 50 eV: present experimental (\bullet) and SE (solid line) and SEP (short-dashed line) theoretical results, the ISM-DWA calculation of Lee *et al.* [1] (dashed line), and the *R*-matrix calculation of Rozum *et al.* [3] (long-dashed line).

sistent with present and previous [1] theoretical results. We believe this is an important result for the modelling community, where the ICS are the critical data, as it demonstrates that an SE-level calculation can provide an accurate description of the elastic electron- CF_2 scattering process at intermediate energies. At energies below 10 eV, however, there is a significant difference in our calculated ICS between the present SEP and SE results. While one expects the inclusion of polarization to affect low-energy cross sections strongly, the changes are unusually extensive in this case. The large difference in magnitude between the present SEP result and earlier calculations [1,3] is partly due to our omission of a correction for dipolar scattering; however, polarization effects also appear to play a significant role. In future work, the uncertainty on the experimental ICS data should be reduced through the inclusion of more forward angle measurements.

Future experiments are also planned at lower incident electron energies. The rationale for this is clear from Fig. 6, where the work of Lee *et al.* [1] and the present SE calculation suggest a strong resonance in the elastic channel between 1–2 eV. Such a resonance is also observed in the *R*-matrix calculation [3], at a slightly lower energy, and was found still lower in the unpublished SEP calculation of Lee, at about 0.2 eV [16]. In the present SEP calculation, which is somewhat more extensive than that of Lee [16], the resonance is extremely narrow and occurs at 0.01 eV,

below the lower energy limit of Fig. 6, again indicating a stronger influence of polarization than seen in earlier calculations. Hence experimental clarification is desirable here. In the near future, an electron ionizer will be introduced into the TOFMS to provide a continuously variable ionization energy to cater for species that cannot be ionized by the 118 nm photons. In particular, the electron ionizer will allow CF_2 to be directly observed in the TOFMS. Finally, other CF_x species will be studied with the pyrolysis of C_2F_6 into CF_3 radicals being an interesting possibility.

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