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Electron impact vibrational excitation cross sections of SiF₄

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Electron drift velocities in mixtures of SiF₄ and Ar have been measured using a pulsed-Townsend type drift tube. A set of vibrational excitation cross sections of electron scattering in SiF₄ has been subsequently determined by the swarm analyses of measured transport data in highly dilute SiF₄-Ar mixtures. The derived cross sections are consistent with the electron transport properties over an order of magnitude in SiF₄ concentration in gas mixtures, thus providing evidence that the main features of their near threshold behavior, and of their absolute magnitude have been captured.

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Electron collisional processes and transport in Group IV tetrafluorides (CF₄, SiF₄) are of considerable interest due to their wide application in dry etching for the fabrication of microelectronic devices. The ν_3 fundamental vibrational mode of SiF₄ is of special interest in the field of laser spectroscopy due to the possibility of achieving measurements with sub-Doppler resolution on single transitions coinciding with CO₂ laser lines.¹ SiF₄ is also of interest in laser photochemistry,² and has been the subject of investigations in fundamental IR spectroscopy.³

While there exists in the literature, considerable information on the low energy electron collision cross sections in CF₄,^{4,5} the corresponding data for SiF₄, especially the momentum transfer and vibrational excitation cross sections are not known. Absolute cross sections for the electron impact dissociation of SiF₄ (>10 eV) into neutral radicals, ionization,⁶ and electron attachment⁷ have been measured. Electron energy loss spectra for the energy loss range of 10-30 eV,⁸ and photoabsorption studies in SiF₄ above 10 eV have also been reported.^{9,10} In this communication, we infer a set of vibrational excitation cross sections of SiF₄ from the measurements and analyses of electron drift velocity (w_d) data in highly dilute mixtures of SiF₄ in Ar. This choice is made to obviate the need to know the low energy momentum transfer cross section of SiF₄, and to take advantage of electron transport sensitivities in Ramsauer rare gas-molecular gas mixtures.

The experimental apparatus is a classical pulsed-Townsend type drift tube described in detail in Ref. 11. Briefly, a photoelectron swarm is initiated by the laser irradiation (pulse duration 6 ns) of a gold-palladium photocathode using a 266 nm quadrupled Nd Yag laser. The laser initiated swarm drifts under the influence of a uniform applied electric field across a drift distance of 6.455 cm. The charge swarm is collected at the anode with an integrating amplifier. The averaged charge ramp (over 128 repetitions of the swarm) is then analyzed for the arrival time of the swarm. The w_d are determined from the ratio of the drift distance to the arrival time, and are not corrected for the effects of diffusion, ionization or attachment.

The w_d measurements were made in gas mixtures from 0.1% to 4.8% SiF₄ in Ar. The gas mixtures were made by

volume mixing in the drift tube using a pre-prepared mixture of 4.8% SiF₄ in Ar with pure Ar (both Matheson Semiconductor Grade). The mixing ratios were determined by pressure measurements using 10 Torr and 1000 Torr capacitance manometers. The w_d measurements have an accuracy of 2% based on the measurement uncertainties of the pressure, voltage, temperature, mixture ratio, and swarm arrival time.

The electron transport in the swarm analyses was obtained by conventional "two-term" solution of the collisional Boltzmann transport equation (BTE).¹² A set of *trial* cross sections was constructed as the input to the numerical solution of the BTE. The calculated w_d were then compared with the experimental data. If the differences between the experimental and calculated w_d were greater than the experimental error margins, then the cross sections were adjusted in the mean energy range of the deviations. The comparisons and modifications of the cross sections were repeated till a satisfactory agreement between the calculated and the experimental data was achieved (see Ref. 13 for further details). The collision cross sections of Ar were taken from Ref. 14, and were fixed throughout this study.

The wide range of concentrations of SiF₄ considered in the gas mixtures permits different regions of the electron energy distribution function (EEDF) to be probed in the swarm analysis. For the highest dilutions (0.1% and 0.2%), the elastic scattering events are essentially controlled by the momentum transfer cross section (q_m) of Ar, and the inelastic scattering events are determined by the vibrational excitation collisions of electrons with SiF₄. The respective energy losses associated with the four infrared active vibrational modes of SiF₄ are: ν_1 (0.099 eV), ν_2 (0.032 eV), ν_3 (0.126 eV), and ν_4 (0.052 eV).¹⁵ In order to reduce the parameter space of the solutions, the vibrational modes ν_1 and ν_3 (which are relatively close in threshold energies) were lumped together as one process with a energy loss threshold of 0.099 eV.

Figure 1 presents the comparisons between the experimental, and the calculated w_d in %SiF₄-Ar mixtures. The converged vibrational excitation cross sections of SiF₄ resulting from the unfolding procedure are shown in Fig. 2. At low E/N, the w_d data for mixtures show large increases over the corresponding data in either constituent gas, and are domi-

FIG. 1. Electron drift velocities in Ar and %SiF₄–Ar mixtures. Points represent experimental data. Lines represent calculations using the converged vibrational excitation cross sections derived from the swarm analyses.

nated by the well known phenomenon of Negative Differential Conductivity¹⁶ (see Ref. 17 for w_d measurements in pure SiF₄). The demanding requirements to achieve agreement with the experimental w_d -E/N-concentration *surface* result in (and illustrate) consistency in the present derived vibrational cross sections. As expected, the measured data are consistent with the calculations for 0.1 and 0.2% mixture compositions since the cross sections were essentially derived from these gas mixtures. However systematic deviations of magnitudes greater than the experimental error margins between the calculated and the measured data begin to appear for gas mixture compositions higher than 0.5%. The reasons for these discrepancies are twofold:

- (1) For mixture compositions greater than 0.5%, the q_m of SiF₄ also have to be included in the cross section unfolding procedure. We have made an estimate of the q_m of SiF₄ from the swarm analyses (using ‘two-term’ Boltzmann calculations)¹⁸ of the measured w_d data in pure SiF₄.¹⁷ The results indicate a large cross section ($\approx 10^{-14}$ cm²) at very low electron energies accompanied by a Ramsauer-Townsend minimum in the cross section at around 0.4 eV.
- (2) More importantly, consider the relative anisotropy in the EEDF in gas mixtures. Figure 3 presents the ratio f_1/f_0 , where f_1 and f_0 are the anisotropic (due to inelastic scattering) and isotropic (due to elastic scattering) components of the EEDF respectively. The ratios presented in Fig. 3 were calculated at the E/N values corresponding to the maximum in the w_d curves where their values are expected to be the highest. We point out that for these typical conditions, the w_d can become comparable to the electron thermal velocities. Figure 3 shows that the EEDF in gas mixture compositions exceeding 0.5% are highly anisotropic and therefore the ‘two-term’ solutions of the BTE are no longer valid for accurate description of electron transport in these gas mixtures. The deviations between the measured and the calculated data near the w_d maxima are therefore enhanced by the inadequate description of electron transport in these gas mixtures.¹³ Further, in pure SiF₄, the magnitude of the vibrational excitation cross sections is larger than that of

FIG. 2. Swarm derived vibrational excitation cross section set of SiF₄. Refer to text for denoted symbols.

momentum transfer near its Ramsauer-Townsend minimum leading to a complete breakdown of the ‘two-term’ approximation.¹⁸

Following the above, the q_m of SiF₄ has to be rederived by obtaining the electron transport through ‘multi-term’ solutions of the BTE or Monte-Carlo calculations in pure SiF₄, in conjunction with higher fractional SiF₄ composition mixture w_d data, and the present derived vibrational cross sections. We point out that the electron transport in highly dilute mixtures of SiF₄ and Ar reported here is analogous to that occurring in fluorine based Si etching reactors where SiF₄ is the *by-product* of the etching processes. Therefore the results reported here are directly applicable towards accurate estimations of electron transport, and of power deposition in plasma etching reactors.

In conclusion, the present measurements and analyses have resulted in important guidelines for deriving the low energy electron impact cross sections of SiF₄. The vibrational excitation cross sections derived in this work can now be used to derive the momentum transfer cross sections of SiF₄. The established data base can then be extended to include attachment, dissociation, and ionization cross sections.

FIG. 3. Relative anisotropy (f_1/f_0) in %SiF₄–Ar mixtures. The E/N values at which the ratios have been calculated are also shown in the legend box (1 Td = 10^{-17} V cm²).

The above extensions and analyses are currently in progress and will be reported.

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