Electron Collision Cross Sections Derived from Critically Assessed Data

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1. Introduction

Electron-molecule collisions are among the most fundamental processes in gas discharges. They are also the precursors of the ions and the radicals which drive the etch, cleaning, or deposition processes in plasma reactors. Hence, there is a need for a quantitative understanding of the fundamental electron collision processes in terms of cross sections. Unfortunately, cross sections for critical electron-collision processes often are not known. In this paper cross sections are reported for indirect (resonance enhanced) electron-impact vibrational excitation of the plasma processing gases CF_4 and Cl_2, and for total electron scattering for CF_4 below ~1 eV. None of these cross sections are presently known from direct measurements. Their determination was made by a critical assessment of other electron collision cross sections for these molecules. Also reported are swarm-adjusted electron-beam attachment cross sections for Cl_2 .

2. Indirect vibrational excitation cross sections for CF_4 and Cl_2

Critically assessed electron collision data for CF_4 [1] and Cl_2 [2] allow deduction of cross sections for total indirect vibrational excitation, $\sigma_{vib,\,indir,\,t}(\varepsilon)$, for CF_4 and Cl_2. These deduced cross sections are shown in Fig. 1 by the solid lines.

For CF_4, this cross section has been determined from

$$\sigma_{vib,\,indir,\,t}(\varepsilon) = [\sigma_{sc,\,t}(\varepsilon) - \sigma_{e,\,int}(\varepsilon)] - [\sigma_{vib,\,dir,\,t}(\varepsilon) + \sigma_{da,\,t}(\varepsilon)]. \qquad (1)$$

In Eq. (1), $[(\sigma_{sc,\,t}(\varepsilon) - \sigma_{e,\,int}(\varepsilon)]$ is the difference between the recommended total electron scattering cross section $\sigma_{sc,t}(\varepsilon)$, and the recommended integral elastic cross section $\sigma_{e,\,int}(\varepsilon)$ determined in Ref. [1]; $\sigma_{vib,\,dir,\,t}(\varepsilon)$ is the sum of the cross sections for direct vibrational excitation for the two infrared active modes ν_3 and ν_4 of CF_4 as calculated in the Born-dipole approximation [3]; and $\sigma_{da,\,t}(\varepsilon)$ is the assessed [1] total dissociative electron attachment cross section. The data shown in the figure by the open circles were not considered since the values of $\sigma_{e,\,int}(\varepsilon)$ are uncertain above 10 eV. The derived cross section shows that indirect vibrational excitation of CF_4 is significant in the energy range from ~7 eV to ~13 eV. This process exerts a significant influence on the electron energy distribution function [4].

For Cl_2, $\sigma_{vib,\,indir,\,t}(\varepsilon)$ was estimated from

$$\sigma_{vib,\,indir,\,t}(\varepsilon) = \sigma_{sc,\,t}(\varepsilon) - [\sigma_{e,\,t}(\varepsilon) + \sigma_{i,\,t}(\varepsilon) + \sigma_{diss,\,neut,\,t}(\varepsilon) + \sigma_{da,\,t}(\varepsilon)], \qquad (2)$$

where $\sigma_{sc,\,t}(\varepsilon)$, $\sigma_{e,\,t}(\varepsilon)$, $\sigma_{i,\,t}(\varepsilon)$, $\sigma_{diss,\,neut,\,t}(\varepsilon)$, and $\sigma_{da,\,t}(\varepsilon)$ are the assessed values [2] of the cross sections for total electron scattering, total elastic electron scattering, total ionization, total dissociation into neutrals, and total dissociative electron attachment. The $\sigma_{vib,\,indir,\,t}(\varepsilon)$ derived this way is taken [2] equal to the cross section for total vibrational excitation, $\sigma_{vib,\,t}(\varepsilon)$, and is compared in Fig. 1b with $\sigma_{vib,\,t}(\varepsilon)$ values of Cl_2 from two Boltzmann-code analyses [5, 6]. Our deduced values bare no similarity to them. In spite of the uncertainty involved in the present derivation of $\sigma_{vib,\,indir,\,t}(\varepsilon)$, the derived cross section clearly shows that the indirect vibrational excitation cross section of Cl_2 is large. In the absence of any direct measurement of $\sigma_{vib,\,t}(\varepsilon)$, the present cross section $\sigma_{vib,\,indir,\,t}(\varepsilon)$ derived from the assessed data is to be preferred to those provided by the Boltzmann codes.

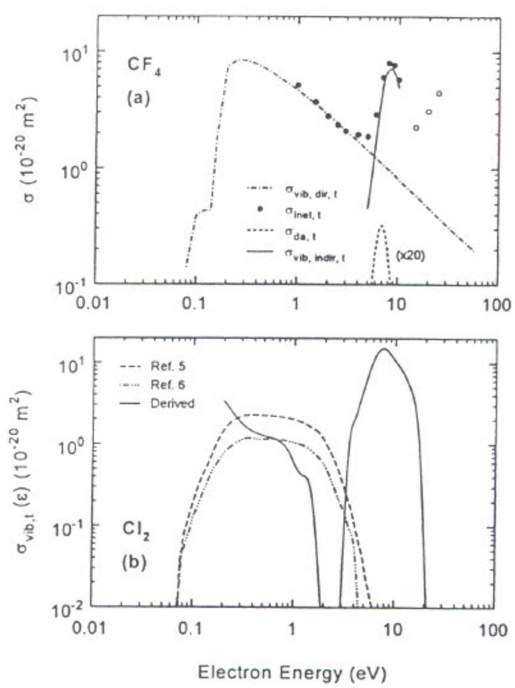

Figure 1. (a) $\sigma_{vib,\,indir,\,t}(\varepsilon)$ for CF_4 (__ , see text). Also shown are: $\sigma_{vib,\,dir,\,t}(\varepsilon)$ (-.-); $\sigma_{sc,\,t}(\varepsilon) - \sigma_{e,\,int}(\varepsilon)$ (•,∘); $\sigma_{da,\,t}(\varepsilon)$ (---). (b) $\sigma_{vib,\,t}(\varepsilon)$ for Cl_2 derived from assessed cross sections (___ , see text); results of Boltzmann-code analyses: (--- , Ref. [5]), (-.- , Ref. [6]).

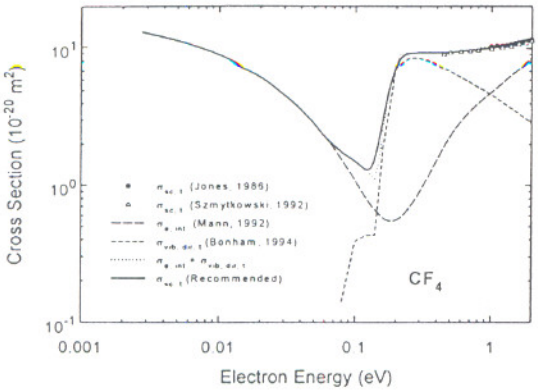

Figure 2. Determination of the recommended $\sigma_{sc,t}(\varepsilon)$ of CF_4 below ~1eV (see text).

3. Determination of the total electron scattering cross section, $\sigma_{sc,t}(\varepsilon)$, for CF_4 below ~1 eV

While recommended values for the $\sigma_{sc,t}(\varepsilon)$ of CF_4 have been derived from multiple measurements above 1 eV [1], there are no direct measurements of the $\sigma_{sc,t}(\varepsilon)$ below ~1 eV for CF_4. Nevertheless, we have determined and recommended values for the $\sigma_{sc,t}(\varepsilon)$ of CF_4 down to 0.003 eV (solid line, Fig. 2) as follows. Firstly, the measurements of $\sigma_{sc,t}(\varepsilon)$ above ~0.5 eV by Jones [7] (solid circles, Fig. 2) and by Szmytkowski et al. [8] (open triangles, Fig. 2) were accepted as reliable high-energy reference data points. Secondly, the measurements of Mann and Linder [9] for $\sigma_{e,int}(\varepsilon)$ below ~2 eV (long-dash curve, Fig. 2) were accepted. Thirdly, below the lowest vibrational threshold of CF_4 at 0.054 eV, $\sigma_{sc,t}(\varepsilon)$ was taken equal to $\sigma_{e,int}(\varepsilon)$. Fourthly, since there are no known negative ion states of CF_4 below ~2 eV [1], it was assumed that all vibrational excitation below ~2 eV is due to the direct excitation of the ν_3 and ν_4 infrared active modes of CF_4. Furthermore, since in this energy range electronic excitation is absent and rotational excitation is negligible (the CF_4 molecule has neither a dipole nor a quadrupole moment) it was assumed that between ~0.06 eV and 2 eV, $\sigma_{sc,t}(\varepsilon) = \sigma_{e,int}(\varepsilon) + \sigma_{vib,dir,t}(\varepsilon)$, where $\sigma_{vib,dir,t}(\varepsilon)$ is the sum of the cross sections for direct excitation of the ν_3 and ν_4 (short-dash curve, Fig. 2). The dotted curve in Fig. 2 is $\sigma_{sc,t}(\varepsilon) = \sigma_{e,int}(\varepsilon) + \sigma_{vib,dir,t}(\varepsilon)$ and was obtained using the recommended values for $\sigma_{e,int}(\varepsilon)$ and $\sigma_{vib,dir,t}(\varepsilon)$ [1]. The cross section $\sigma_{sc,t}(\varepsilon)$ estimated in the manner outlined above from 0.08 eV to 2 eV was used, along with the measurements of Jones [7] and Szmytkowski et al. [8] for $\sigma_{sc,t}(\varepsilon)$ above ~0.5 eV to obtain a best estimate (solid line) of $\sigma_{sc,t}(\varepsilon)$ from 0.003 eV to ~1 eV.

4. Swarm-adjusted electron beam dissociative attachment cross section, $\sigma_{da,t}(\varepsilon)$, for Cl_2

The $\sigma_{da,t}(\varepsilon)$ of Cl_2 has been measured by Kurepa and Belić [10] using an electron beam apparatus. This cross section has been adjusted upward by 30% based on the absolute electron swarm measurements of the rate constant for electron attachment as a function of the mean electron energy $\langle\varepsilon\rangle$, $k_a(\langle\varepsilon\rangle)$, made by McCorkle et al. [11] and on three sets of calculated values of $k_a(\langle\varepsilon\rangle)$ [11-13]. McCorkle et al. [11] calculated $k_a(\langle\varepsilon\rangle)$ using the electron energy distributions in N_2 and the total electron attachment cross section of Kurepa and Belić [10]. Kurepa et al. [12] and Chantry [13] calculated $k_a(\langle\varepsilon\rangle)$ using the Kurepa and Belić [10] cross section and a Maxwellian electron energy distribution function for the electron energies. Near 0.1 eV all three calculated values of $k_a(\langle\varepsilon\rangle)$ using the Kurepa and Belić [10] total electron attachment cross section have a similar energy dependence to the directly measured rate constants, but they are all lower in magnitude by ~30%. Hence the measured cross section is deemed too low, and the swarm-based adjustment of 30% was applied to the electron-beam data for Cl_2.

5. Conclusion

These examples help illustrate the value of critically assessed knowledge on electron collision reactions in deriving needed data which are not available at the time.

6. References

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