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Calculated absolute electron impact ionization cross-section for the molecules CF_3X (X = H, Br, I)

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Abstract

We report calculated total single ionization cross-sections for the three molecules—CFH_3, CF_3Br, and CF_3I using the Deutsch–Märk (DM) formalism. In the case of CF_3H, our calculated cross-sections are in good agreement with the BEB calculation of Kim et al. and with the recent measurement of Iga et al., but disagree with earlier experimental data. Our calculated cross-sections for CF_3Br and CF_3I are in good agreement with recent experiments, which reported measured data for these two molecules for the first time. (Int J Mass Spectrom 214 (2002) 53–56) © 2002 Elsevier Science B.V. All rights reserved.

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The CF_3H molecule is widely used in the semiconductor industry as a plasma processing gas instead of CF_4. Even though CF_3H has a higher global warming potential than CF_4, the lifetime of CF_3H in the atmosphere is about 50 times shorter than that of CF_4 [1], so that its destructive effect on the ozone layer is much reduced compared to CF_4. A recent review of electron interactions with this molecule [2] revealed that there are large uncertainties (roughly a factor of 2) in the measured and calculated total ionization cross-sections that have been reported by various groups [3–6]. Christophorou et al. [2] on the basis of earlier experiments [4,5], suggested a total ionization cross-section function in the energy range from threshold to 100 eV which peaks at a value of about 8×10^{-16} cm^2 and exceeds the very early measurement [3] and the calculated cross-section of Kim et al. [6] using the BEB method [7] by almost a factor of 2. A subsequent measurement by Iga et al. [8], however, supported the lower maximum total cross-section value, their values for partial cross-sections being in good agreement with another recent study by Haaland and co-workers [9]. Thus, an independent calculation using a different theoretical approach such as the Deutsch–Märk (DM) formalism [10] seemed to be desirable to shed additional light on this discrepancy. In the case of the molecules CF_3Br and CF_3I, which are widely used as fire suppressants and in plasma-assisted processing applications [11,12], the recently reported measured ionization cross-sections [13] are

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the only ionization data that are available for these molecules.

A detailed discussion of the DM formalism can be found in the recent review of Deutsch et al. [10] to which we refer the reader for an in-depth discussion of the DM method. Briefly, the DM formula for the calculation of the absolute electron-impact ionization cross-section σ of an atom has the form

$$\sigma = \sum_{n,l} g_{nl}\pi(r_{nl})^2 \xi_{nl} f(U) \quad (1)$$

where $(r_{nl})^2$ is the square of the radius of maximum radial density of the atomic sub-shell characterized by the quantum numbers n and l (as listed in column 1 in the tables of Desclaux [14]), ξ_{nl} refers to the number of atomic electrons in the (n,l) sub-shell, and the g_{nl} are appropriately chosen weighting factors [10]. The function $f(U)$ (for details see [10]) describes the energy dependence of the ionization cross-section where U is the reduced collision energy, $U = E/E_{nl}$. E denotes the energy of the incident electron and E_{nl} refers to the ionization energy in the (n,l) sub-shell.

The function $f(U)$ has the explicit form

$$f(U) = d(1/U)[(U-1)/(U+1)]^a \times \{b + c[1-(1/2U)]\ln[2.7 + (U-1)^{0.5}]\} \quad (2)$$

where the parameters a, b, c, and d have different values for s-, p-, d-, and f-electrons as one might expect on the basis of the different angular shapes of atomic s-, p-, d-, and f-orbitals (see [10] for further details). In the case of molecular targets, it was found advantageous [10] to reduce the molecular ionization cross-section calculation to the atomic cross-section formula of Eq. (1). This requires a Mulliken population analysis [15,16] or an equivalent method that expresses the molecular orbitals in terms of the atomic orbitals of the constituent atoms and determines the atomic orbital populations. Orbital ionization energies were calculated via outer-valence Green's functions [17,18] and atomic orbital populations of the valence molecular orbitals of CF_3X (X = H, Br, I) were derived from Hartree–Fock calculations using the SDD basis set and effective core potentials [19].

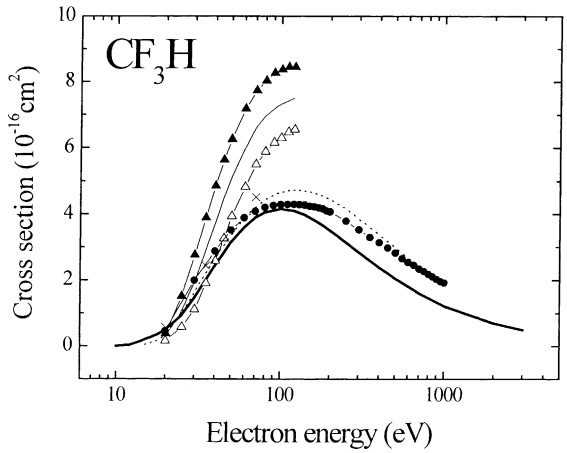

Fig. 1. Calculated ionization cross-section for CF_3H using the DM formalism (thick solid line) in comparison with various measured and calculated data. The various symbols refer to the measured data of [3] (crosses), [4] (filled triangles), [5] (open triangles), [8] (filled circles), the calculated data of [6] (dashed line), and the suggested cross-section of [2] (thin solid line).

Fig. 1 shows the present DM calculation of the total single ionization cross-section of CF_3H in comparison with the four available sets of experimental data [3–5,8], the calculated cross-section of Kim et al. [6] and the suggested cross-section of Christophorou et al. [2]. Our calculated cross-section agrees quite well with the very early data of [3] and the most recent measurements of [8] (which are supported by the other recent measurements on partial cross-sections [9]) as well as with the calculated cross-section of Kim et al. [6] over the entire range of impact energies. The DM calculations do not reproduce the much larger maximum cross-section values reported in [4,5] which on the one hand served as the basis for the suggested cross-section advocated in [2] and on the other hand have been measured with methods less reliable than the ones used in the more recent studies [8,9] (see the detailed discussion in [8] about possible sources of errors in [4,5]). Our calculation (whose reliability has been demonstrated in [10] in many examples, see also other recent examples [20–22]) thus clearly supports the notion of a maximum cross-section value around $4 \times 10^{-16}\,\mathrm{cm}^2$.

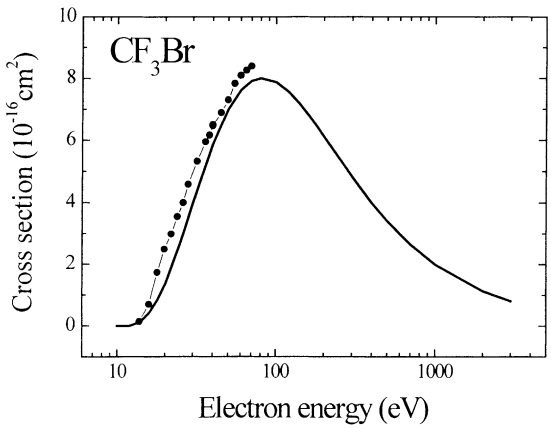

Fig. 2. Calculated ionization cross-section for CF_3Br using the DM formalism (thick solid line) in comparison with measured data [13] (filled circles).

Figs. 2 and 3 show the present DM calculations for respectively CF_3Br and CF_3I in comparison with the recently measured ionization cross-sections of Jiao et al. [13]. In the case of CF_3Br, the calculated cross-section lies somewhat below the measured data over the range of impact energies for which experimental data are available, but the discrepancy is rather insignificant (less than 8% at the position of the cross-section maximum). The agreement between calculated and measured cross-section is essentially perfect for CF_3I at all impact energies.

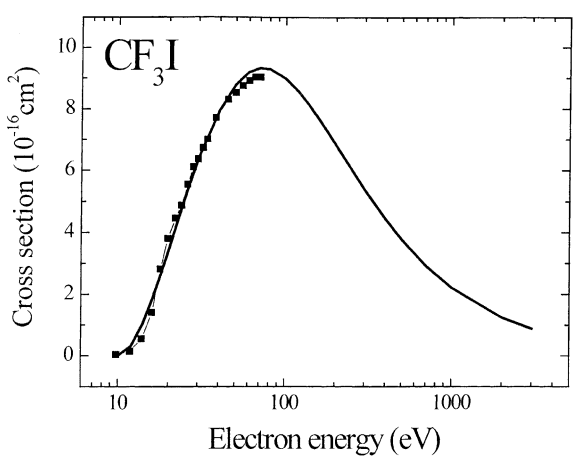

Fig. 3. Calculated ionization cross-section for CF_3I using the DM formalism (thick solid line) in comparison with measured data [13] (filled squares).

In summary, the present DM calculations of total single ionization cross-sections for the molecules CF_3X (X = H, Br, I) shed light on the discrepancy in the previously reported ionization cross-sections for CF_3H and support the lower maximum cross-section value measured by Iga et al. [8] and calculated by Kim et al. [6]. In the case of CF_3Br and CF_3I, our calculations are in excellent agreement with the recently measured cross-sections for these two molecules [13] thus lending added credibility to the reliability of these cross-sections.

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