Evaluation of the computational methods for electron-impact total ionization cross sections: Fluoromethanes as benchmarks

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The experimental electron-impact total ionization cross sections (TICSs, ICSs) of CF_4, CHF_3, CH_2F_2, and CH_3F fluoromethanes reported so far and a new set of data obtained with a linear double focusing time-of-flight mass spectrometer have been compared with the *ab initio* and (semi)empirical based ICS available methods. TICSs computational methods include: two approximations of the binary-encounter dipole (BED) referred to hereafter as Kim (Kim-BEB) and Khare (Khare-BEB) methods, the Deutsch and Märk (DM) formalism, also requiring atomic and molecular *ab initio* information, the modified additivity rule (MAR), and the Harland and Vallance (HV) methods, both based on semiempirical or empirical correlations. The molecular *ab initio* information required by the Kim, Khare, and DM methods has been computed at a variety of quantum chemistry levels, with and without electron correlation and a comprehensive series of basis sets. The general conclusions are summarized as follows: the Kim method yields TICS in excellent agreement with the experimental method; the Khare method provides TICS very close to that of Kim at low electron-impact energies (<100 eV), but their Mott and Bethe contributions are noticeably different; in the Kim and Khare approximations the electron correlation methods improve the fittings to the experimental profiles in contrast with the large basis sets, that leads to poorer results; the DM formalism yields TICS profiles with shapes similar to the experimental and the BEB methods, but consistently lower and with the profiles maxima shifted towards lower incident electron energies; the MAR method supplies very good ICS profiles, between those of BEB and DM methods; finally, the empirical HV method provides rather poor fittings concomitant with the simplicity and the few empirical parameters used. © *2001 American Institute of Physics.*
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I. INTRODUCTION

The electron-impact total ionization cross sections (TICSs, ionization cross section, ICS) of molecules, crucial to the modeling of a variety of industrial, fusion edge, low temperature, and laboratory plasmas, has witnessed an upsurge of interest in both the experimental measurements and the development of reliable *ab initio* and semiempirical computational predictive methods. Among the chemical species more extensively used in industrial plasmas one should highlight the family of fluoromethanes and a few other fluorine derivative molecules. Upon electron collision these molecules yield highly reactive ions and neutrals fragments extensively used in the semiconductor industry for plasma etching.[1] Parallel to the experimental determination of the molecular ICS a number of computational approaches have appeared.[2] The sum of known weighted atomic ICS has been suggested to add up to that of the molecule in the additivity rule,[3] later modified analytically[4] and geometrically.[5] Deutsch *et al.* have proposed overcoming large-scale quantum chemistry molecular calculations by using a limited number of parameters or explicit relationships, giving rise to the so-called modified additivity rule (MAR).[6] Harland and Vallance (HV)[7] have also proposed an empirical method based on the correlation between the maximum molecular ICS profile and the ground state molecular polarizability[8] and further adding guessed analytical profiles above and below the ICS maximum. As in most (semi)empirical methods, their application is straightforward and yields acceptable estimates of the ICS with modest computational effort. However, the most rigorous method proposed so far evaluates the molecular orbitals' ICS and adds them to compute the molecular TICSs, directly [binary-encounter dipole (BED)] or including a sensible approximation for the continuum dipole oscillator strength and leading to either the Kim-BEB[9–11] or the Khare-BEB[12] methods. The ICS profiles computed with the BEB methods are in good agreement with the experimental results and have been previously applied to a series of

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small size molecules,[10] molecules of atmospheric interest,[13] and CF_4, C_2F_6, and C_3F_8 fluoroalkanes.[14] Deutsch and Märk[15] have derived an electron-impact ICS relationship based on the classical binary encounter approximation and recently[16] reported a comparative study of the DM and BEB TICS calculations of a large number of molecules, free radicals, and their experimental profiles.

In this work a study of the above TICS calculation methods and the influence of the computational level and the basis sets in the Kim, Khare, and DM methods have been applied to the fluoromethane family CF_4, CHF_3, CH_2F_2, and CH_3F. The parallel experimental study reported is justified to include a set of consistent measurements and permits an evaluation of the relative scatter of the data, essential in a subject where the reported ICSs have a considerable dispersion.[17–19] ICSs and other electron-impact related properties of the CF_4, one of most studied and best known molecules due to its industrial plasma applications, have been reviewed recently.[17,19] CHF_3 has also been studied, although to a lesser extent, and reviewed recently.[18] Vallance *et al.* have reported the TICSs of CH_3X (X=H, F, Cl, Br, and I) comparing the Kim, the DM, and the HV calculations.[20] To the best of our knowledge no cross-section experimental data on CH_2F_2 has been reported until recently.[21]

II. EXPERIMENT

The experimental setup used to determine the experimental cross sections has been described elsewhere[21] and only a brief summary will be given here. A pulsed supersonic molecular beam of the selected fluoromethane collides at a right angle with a pulsed electron beam [0.5 eV full width at half maximum (FWHM) at 10 μA electron intensity, energy up to 100 eV] in the ''extraction region'' of a linear double focusing time-of-flight (TOF) mass spectrometer (R. M. Jordan). 300 ns after the collisions are over, a negative voltage pulse is applied to the extraction grid, creating an electric field that drives the ions onto the 86.5 cm long flight tube, perpendicular to both molecular and electron beams, where a set of *x*-*y* plates focuses the ions onto a three-stage microchannel plate (MCP) (C-07001, $\phi=18$ mm) detector. The detector response is routed to a digital oscilloscope (Tektronix TDS360) and later to a computer for further analysis and storage.

Reference and/or target gases were stored in a stainless steel cylinder at a stagnant pressure of 3 bar (MKS-baratron 750B, 1% accuracy) connected to the TOF mass spectrometer through a pulsed valve. The supersonic expansion beam was skimmed and further crossed with a well-characterized energy electron beam (calibrated with the appearance potential of Ar^+). Ions resulting from the beam collisions were selected by their characteristic TOF and their partial ICS converted to absolute scale by comparison with the ICS of close-in-mass Ar (40 amu) or Kr (84 amu) reference gases, to minimize the mass effect on the extraction and flight steps. The absolute partial ICS for the CF_2^+ ion, chosen as an illustration of the method, is given by the equation:

$$\sigma_{CF_2^+}(E)=\frac{I_{CF_2^+}\cdot n_{Ar}}{I_{Ar^+}\cdot n_{CH_2F_2}}\cdot\sigma_{Ar^+}(E), \tag{1}$$

where $I_{CF_2^+}$ and I_{Ar^+} are the detector currents for CF_2^+ and Ar^+ ions, respectively, and $n_{CH_2F_2}$ and n_{Ar} the gas density of the precursor and the reference gas, respectively. The Ar^+ and Kr^+ ICSs[22,23] were used as references following Syage's method.[24] Total ionization (counting) cross sections of the CF_4, CHF_3, CH_2F_2, and CH_3F molecules were determined by adding up the partial ICSs of all the ions observed.

III. TOTAL IONIZATION CROSS-SECTION COMPUTATIONAL METHODS

Electron-impact TICSs have been computed by the Kim-BEB and the Khare-BEB methods, the Deutsch-Märk (DM) formalism, the modified additivity rule (MAR), and the Harland and Vallence (HV) methods. Although the BEBs and DM methods include some type of additivity, they are not related to atomic additivity but to the molecular orbital ICSs. None of these methods regards the contributions of the neutral dissociation and multiple ionization (autoionization and Auger processes) to the total ICSs. In the following we present a succinct summary of the methods, highlighting their approximations.

A. The Kim-BEB and Khare-BEB methods

BEB[9–12] methods are approximations of the analytical binary-encounter dipole (BED) method. In order to calculate the BED electron-impact ICS profile, the molecular orbital continuum dipole oscillator strength (df/dw) (CDOS) must be experimentally known or computed. Unfortunately the available CDOS of atoms and molecules reported is very limited. Hence Hwang *et al.*[11] proposed a simplified version of the method based on the H, He, and H_2 CDOS experimental shapes, whose first term of the expansion conveniently handled leads to an analytical integration of the differential cross section. In a Kim-BEB TICS calculation three physical parameters are required: the electron binding energy *B*, the average kinetic energy *U*, and the orbital occupation number *N*. The integrated cross section per molecular orbital is

$$\sigma_{BEB}=\frac{S}{t+u+1}\left[\frac{\ln t}{2}\left(1-\frac{1}{t^2}\right)+1-\frac{1}{t}-\frac{\ln t}{t+1}\right], \tag{2}$$

where, besides *B*, *U*, and *N*, the following parameters are used: *T* as the incident electron energy, $t=T/B$; $u=U/B$; $S=4\pi a_0^2R^2N/B^2$; $a_0=0.5292$ Å; and $R=13.61$ eV. The cross section is the sum of two terms, the first, the Bethe term, associated with the first logarithm function, stands for the soft or large impact parameter collisions and is dominated by the dipole interaction, while the residual terms, i.e., $1-1/t-(\ln t)/(t+1)$, represent the hard or close impact parameter collision cross section as described by Mott. The logarithm term of the Mott contribution originates from the interference of the incident and the scattered electron. In consequence, the σ_{BEB} is the sum of the molecular orbital contributions that in turn are determined as their Bethe and Mott cross-sections contributions.

In the calculation of a molecule TICSs by Eq. (2) the greatest contribution term by far, up to 80% of the cross section in halomethanes, is the first ionization energy (IE). The use of Koopmans' theorem, known to overestimate by ca. 15%[13] the experimental IEs, produces low and shifted TICS profiles. Indeed, the use of experimental IE significantly improves the overall TICS profile. For practical reasons, except for the first ionization energy of the highest molecular orbital, the set of molecular orbital binding energies, *B*, have been taken from the *ab initio* computations.

The molecular orbital energies of the fluoromethanes studied were computed with the GAUSSIAN 98W package,[25] initially at the HF/6-311G level to match the computations by Hwang *et al.*[11] In addition, systematic computations have also been conducted at other levels, including those at HF/6-311G, MP2/6-311G, MP4(SDQ)/6-311G, CC/6-311G, and CISD 6-311G. It is worth noting that computations with the minimum basis set at the HF/STO-3G level yield very high cross-section profiles and are depicted only for reference (cf. Fig. 1). Basis sets 6-31G(d), 6-31G(d,p), 6-311G, 6-31$+G(d,p)$, and 6-311+G(d,p) have also been explored to study the TICS dependence on the polarization and diffuse functions. Furthermore, the computed TICSs differ among themselves by some 5% (Fig. 1), a figure smaller than the 10%–15% estimated error of the experimental measurements. Tables I–IV collect the calculated molecular orbital electron occupation number *N*, orbital binding *B*, and orbital kinetic energy *U* of CF_4, CHF_3, CH_2F_2, and CH_3F. Experimental and computational studies on the CF_4 molecule have been recently reported[13] and the results agree and validate those presented here.

A significant limitation of the Kim-BEB method is associated with the production of one single ion, neglecting either multiple ionization or neutral dissociation. In many cases, including fluoromethanes,[26] a number of neutral dissociation channels are opened following the creation of excited and superexcited states over the ionization potential. It has been suggested that multiple ionization contributions be corrected by doubling the contributions of the inner shell orbitals with binding energies of 40–150 eV,[14] and neutral dissociation contributions, leading to overestimate the ICS, by taking the computed TICS as upper limits.[14] In fluoromethanes the estimated contribution of the multiple ionization increases the TICS by about 5%, shifting concomitantly (doubling the inner shell contributions) toward higher electron incident energies and improving the fitting to the experimental results. Given the empirical nature of the corrections and the limited range of electron-impact energy studied here, no attempt of application to the ICS profiles has been considered, in the understanding that they may be readily computed from the molecular orbitals' binding energies, kinetic energies, and occupation numbers depicted in Tables I–IV.

Khare *et al.*[12] have developed a method combining the BED[10] approach and the plane wave Born approximation (PWBA).[27] The contributions of the Bethe cross section (soft collisions) and the Mott (hard collisions) differ considerably from those of the Kim-BEB method[13] although, surprisingly, their sums are very close over the whole electron energy range. The grounds for the compensation are unclear. For the CH_4 molecule the TICS difference between both methods is less than 3%.[28] In this paper TICS for CF_4, CHF_3, CH_2F_2, and CHF_3 molecules have been computed by the Khare-BEB method and Fig. 2 shows, as an illustration, the CF_4 ICS profiles. Kim's and Khare's computations of the TICS profiles of CHF_3, CH_2F_2, and CHF_3 have a similar behavior, i.e., differences of TICS of 4% near energy threshold and an improvement up to 1% for electron-impact energies higher than 40 eV. The small differences make the display of both ICS profiles unjustified.

B. The Deutsch and Märk formalism

The method[15] is an extension to molecular species of earlier models for the electron-impact ionization of ground state atoms.[29,30] In the present version it has been successfully applied to atoms,[31] radicals,[32] molecules,[33] and clusters.[34] In the DM formalism, the electron-impact ICS calculation requires the weighting factors of the orbitals identified by their *n* anl *l* quantum numbers, the maximum radial density radius, the effective occupation numbers taken from a population analysis, the incident electron energy *T*, and the ionization energy of the jth subshell E_j. In addition, the DM cross-section formula requires a number of semiempirical parameters *a*, *b*, *c*, and *d* characteristic for the *s*-, *p*-, *d*-, or *f*-electron orbitals.[32] Due to the lack of experimental vertical ionization energies of the jth subshell, E_j, the electron binding energies were taken from *ab initio* computations, except for the lower orbital energy where the first experimental ionization energy is used.

In this work the contribution of the atomic orbitals to the molecular ones has been weighted with the population analysis computed either by the Löwdin or the Mulliken methods.[35] Since both population analysis methods for CF_4 yield very close cross sections, the calculations were conducted with the simplest one, i.e., that of Mulliken. The population analysis was conducted at the HF/6-311G**, MP2/6-311G, MP4(SDQ)/6-311G, CC/6-311G, CISD/6-311G, and HF/STO-3G levels, yielding results close to within 5% and, thus, the method is less sensitive to the computational level. However, the population analysis was systematically carried out at the HF/STO-3G level. Tables I–IV collect the computed parameters required for the DM method calculations for CF_4, CHF_3, CH_2F_2, and CHF_3 molecules and Fig. 3 shows the TICS profiles for the indicated computation levels. Energy calculations were carried out at the MP2/6-311G level but in the computed ICS the lower energy was substituted by the experimental first ionization energy.

C. The modified additivity rule (MAR) method

The well-known overestimation of the molecular ICS by adding the atomic ICS contributions[5] has stimulated the suggestion of empirical corrections to improve the fittings. One of the successful ones is the modified additivity rule (MAR) for A_xB_y, $A_xB_yC_z$, and $A_pB_sC_tD_u$ type molecules.[6] For the case of hydride CH_yF_z molecules the cross-section additivity rule is

$$\sigma^+(CH_yF_z) = f_C\sigma^+(C) + f_H y\sigma^+(H) + f_F z\sigma^+(F), \qquad (3)$$

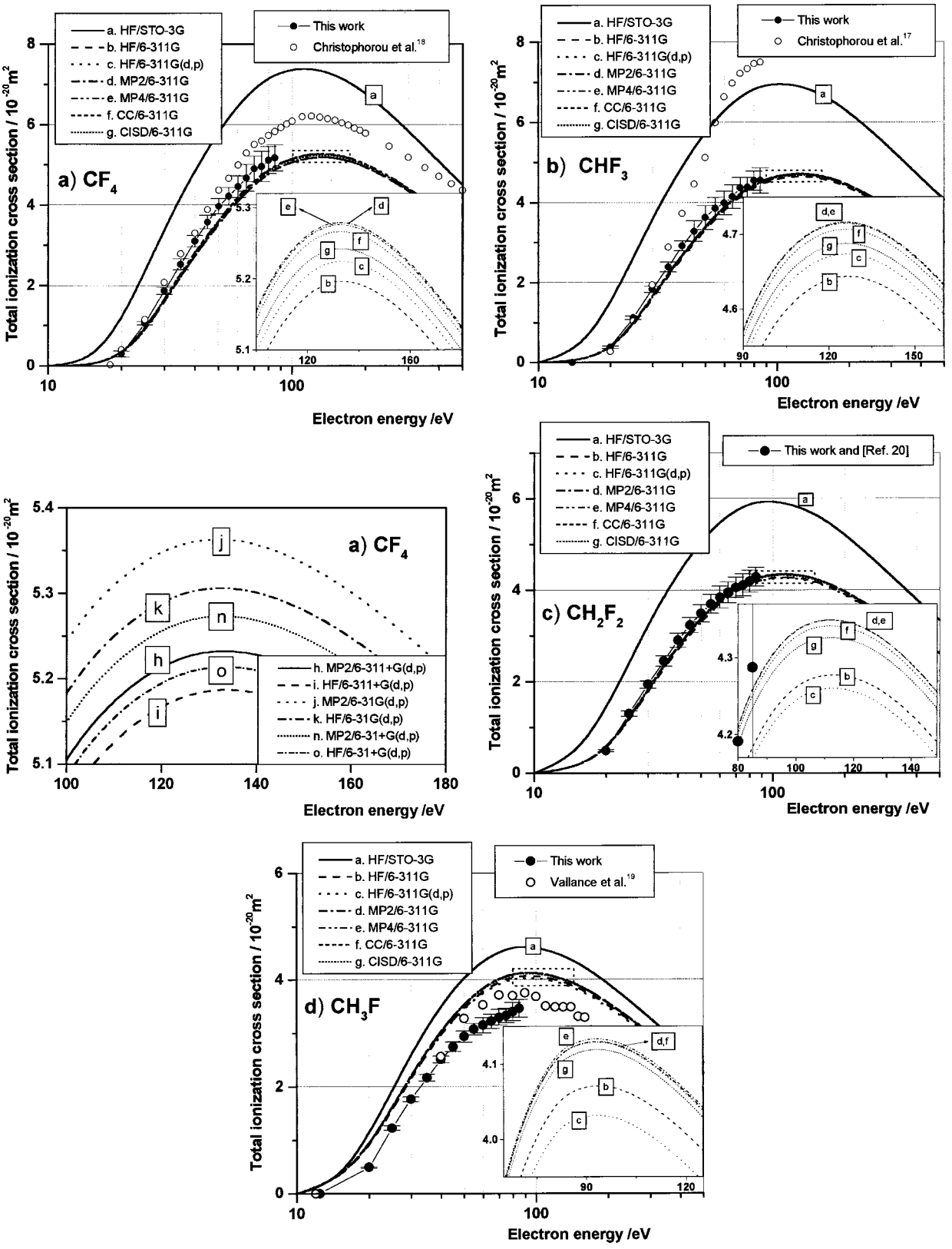

FIG. 1. Experimental and computed total ionization cross-section (TICS) profiles by the Kim method for the following fluoromethane: CF_4 (a), CHF_3 (b), CH_2F_2 (c), and CH_3F (d). The molecular orbital binding energies *B*, kinetic energies *U*, and electron occupation numbers *N*, were calculated at the *ab initio* levels, method and basis set, displayed in the insets (cf. Tables I–IV). Calculations were carried out using the calculated molecular orbital energies except for the external one that was substituted by the first ionization energy.

TABLE I. Molecular orbital irreducible representation, orbital binding energy *B*, kinetic energy *U*, electron occupation number *N*, maximum radial density radius $r_{A,nl}$, effective occupation number $\xi^j_{A,nl}$ (from Mulliken population analysis), and weighting factors $g^j_{A,nl}$ of the CF_4 molecule calculated at the MP2/6-311G level. The molecular orbital energy marked with an asterisk is the experimental first ionization potential, IE (cf text).

Molecular level and energy, *B*/eV	*U*/eV	*N*	$r_{A,nl}$	Atomic orbital	$\xi^j_{A,nl}$	$g^j_{A,nl}$
$(1t_1)$ 16.20*	94.549	6	3.81E−09	F(2*p*)	6	1.852
$(4t_2)$ 19.395	88.899	6	6.44E−09	C(2*p*)	0.186	1.547
			3.81E−09	F(2*p*)	5.814	1.547
$(1e)$ 20.931	84.900	4	3.81E−09	F(2*p*)	4	1.433
			6.44E−09	C(2*p*)	1.706	1.249
$(3t_2)$ 24.024	73.552	6	4.06E−09	F(2*s*)	0.348	0.832
			3.81E−09	F(2*p*)	3.946	1.249
			6.46E−09	C(2*s*)	0.657	0.719
$(4a_1)$27.812	85.000	2	4.06E−09	F(2*s*)	0.422	0.719
			3.81E−09	F(2*p*)	0.921	1.079
			6.44E−09	C(2*p*)	0.483	0.652
$(2t_2)$ 45.991	104.748	6	4.06E−09	F(2*s*)	5.457	0.435
			3.81E−09	F(2*p*)	0.060	0.652
			6.46E−09	C(2*s*)	0.427	0.408
$(3a_1)$49.061	88.832	2	4.06E−09	F(2*s*)	1.501	0.408
			3.81E−09	F(2*p*)	0.072	0.611

TABLE II. Molecular orbital irreducible representation, orbital binding energy *B*, kinetic energy *U*, electron occupation number *N*, maximum radial density radius $r_{A,nl}$, effective occupation number $\xi^j_{A,nl}$ (from Mulliken population analysis), and weighting factors, $g^j_{A,nl}$ of the CHF_3 molecule calculated at the MP2/6-311G level. The molecular orbital energy marked with an asterisk is the experimental first ionization potential, IE (cf. text).

Molecular level and energy, (eV)	*U*/eV	*N*	$r_{A,nl}$	Atomic orbital	$\xi^j_{A,nl}$	$g^j_{A,nl}$
			6.44E−09	C(2*p*)	0.151	2.160
$(6a_1)$ 13.86*	72.904	2	5.29E−09	H(1*s*)	0.408	2.750
			3.81E−09	F(2*p*)	1.441	2.160
$(1a_2)$18.150	93.775	2	3.81E−09	F(2*p*)	2	1.653
$(5e)$ 18.199	90.231	4	6.44E−09	C(2*p*)	0.126	1.648
			3.81E−09	F(2*p*)	3.874	1.648
$(4e)$ 19.311	86.527	4	3.81E−09	F(2*p*)	4	1.553
			6.44E−09	C(2*p*)	1.095	1.365
$(3e)$ 21.972	74.470	4	4.06E−09	F(2*s*)	0.204	0.910
			3.81E−09	F(2*p*)	2.701	1.365
			6.44E−09	C(2*p*)	0.692	1.307
$(5a_1)$22.961	59.765	2	5.29E−09	H(1*s*)	0.250	1.663
			3.81E−09	F(2*p*)	1.058	1.307
			6.46E−0.9	C(2*s*)	0.787	0.731
$(4a_1)$27.369	69.060	2	5.29E−09	H(1*s*)	0.323	1.396
			4.06E−09	F(2*s*)	0.313	0.731
			3.81E−09	F(2*p*)	0.567	1.096
$(2e)$ 44.600	105.171	4	6.44E−09	C(2*p*)	0.323	0.673
			4.06E−09	F(2*s*)	3.677	0.448
			6.46E−09	C(2*s*)	0.361	0.427
$(3a_1)$46.893	91.973	2	4.06E−09	F(2*s*)	1.578	0.427
			3.81E−09	F(2*p*)	0.061	0.640

where f_C, f_H, and f_F are parameters related to the number of atoms, the atomic radii (r_C, r_H, r_F), and the number of electrons (ξ_C, ξ_H, ξ_F), and are fixed by empirical fitting to the experimental ICS of a few benchmark molecules. For CHF_3, CH_2F_2, and CH_3F molecules the smaller size of the fluorine atom with respect to the hydrogen makes it necessary to apply the rule for hydrides, where the ICSs are exclusively determined by geometric factors, and the coefficients are set to one. The calculation of the fluoromethanes' ICSs requires the knowledge of the ICSs of the C, H, and F atoms' ICSs that have been reported elsewhere.[36–38] Very good agreement has also been achieved by starting from the computed ICSs of the C, H, and F atoms computed by the BEB methods.

D. Harland and Vallance method

The correlation between the TICS profile maximum and the molecular polarizability volume, α (Å^3), has been justified by simple electrostatic arguments[8] and applied by Harland and Vallance[7] to estimate TICS profiles. The correlation

$$\sigma_{\max} \propto \left(\frac{\alpha}{E_0}\right)^{1/2}, \tag{4}$$

where E_0 is the ionization potential (eV) gives the ICS maxima, while the profile is[7] the sum of two empirical terms:[39]

$$\sigma = \frac{\sigma_{\max}}{2}\left[\left(\frac{E_{\max}}{E_{\max}-E_0}\right)\left(\frac{E-E_0}{E}\right)+1-\frac{|\lambda-\lambda_{\max}|}{\lambda_{\max}}\right], \tag{5}$$

where $E_{\max}$ stands for the electron-impact energy at $\sigma_{\max}$ and λ and $\lambda_{\max}$ are the de Broglie wavelength at the electron-impact energies E and $E_{\max}$, respectively.

Although a considerable number of atoms and molecules seem to fit the $\sigma_{\max}/\alpha$ correlation, the prediction of the TICS profiles in the range of electron-impact is very poor. Harland *et al.*[7] have reported cross-section profiles for N_2, CO, CO_2, NH_3, CH_3F, and CH_3Cl, and the results are limited by the accuracy of the polarizability volume.[40] In the application to the fluoromethane studied in this work, the polarizability of CH_2F_2 is unknown and has been calculated at the MP2/STO-3G level as the best suited simple method to reproduce the polarizability of the other members of the family: CF_4, CHF_3, and CH_3F. The computed value of 3.30 Å^3 seems to be a sensible figure, also matching the experimentally interpolated value of the series.

IV. RESULTS AND DISCUSSION

Electron-impact TICS calculated by the methods described in Sec. III are compared in Figs. 4–7 with the more reliable experimental data reported in the literature so far and those measured in this work. The source of experimental uncertainties in setups based on time-of-flight (TOF) systems

TABLE III. Molecular orbital irreducible representation, orbital binding energy B, kinetic energy U, electron occupation number N, maximum radial density radius $r_{A,nl}$, effective occupation number $\xi^j_{A,nl}$ (from Mulliken population analysis), and weighting factors, $g^j_{A,nl}$ of the CH_2F_2 molecule calculated at the MP2/6-311G level. The molecular orbital energy marked with an asterisk is the experimental first ionization potential, IE (cf. text).

Molecular level and energy (eV)	U (eV)	N	$r_{A,nl}$	Atomic orbital	$\xi^j_{A,nl}$	$g^j_{A,nl}$
			6.4E−09	C(2p)	0.214	2.358
($2b_1$) 12.72*	64.013	2	5.2E−09	H(1s)	0.520	3.003
			3.8E−09	F(2p)	1.266	2.358
			3.8E−09	C(2p)	0.132	1.792
($6a_1$) 16.738	75.861	2	5.29E−09	H(1s)	0.202	2.282
			3.81E−09	F(2p)	1.666	1.792
($4b_2$) 16.965	90.453	2	3.81E−09	F(2p)	2	1.768
($1a_2$) 17.897	88.225	2	3.81E−09	F(2p)	2	1.676
($3b_2$) 19.627	75.744	2	6.44E−09	C(2p)	0.555	1.528
			3.81E−09	F(2p)	1.445	1.528
			6.44E−09	C(2p)	0.608	1.480
($5a_1$) 20.273	66.035	2	5.29E−09	H(1s)	0.162	1.884
			3.81E−09	F(2p)	1.230	1.480
			6.44E−09	C(2p)	0.838	1.428
($1b_1$) 21.007	51.299	2	5.29E−09	H(1s)	0.482	1.818
			3.81E−09	F(2p)	0.680	1.428
			6.46E−09	C(2s)	1.000	0.748
($4a_1$) 26.741	57.070	2	5.29E−09	H(1s)	0.498	1.428
			4.06E−09	F(2s)	0.211	0.748
			3.81E−09	F(2p)	0.291	1.121
($2b_2$) 43.128	105.308	2	6.44E−09	C(2p)	0.137	0.696
			4.06E−09	F(2s)	1.863	0.464
($3a_1$) 44.525	96.060	2	6.46E−09	C(2s)	0.247	0.449
			4.06E−09	F(2s)	1.753	0.449

TABLE IV. Molecular orbital irreducible representation, orbital binding energy B, kinetic energy U, electron occupation number N, maximum radial density radius $r_{A,nl}$, effective occupation number $\xi^j_{A,nl}$ (from Mulliken population analysis), and weighting factors, $g^j_{A,nl}$ of the CH_3F molecule calculated at the MP2/6-311G level. The molecular orbital energy marked with an asterisk is the experimental first ionization potential, IE (cf. text).

Molecular level and energy, (eV)	U (eV)	N	$r_{A,nl}$	Atomic orbital	$\xi^j_{A,nl}$	$g^j_{A,nl}$
			6.44E−09	C(2p)	0.187	2.406
($2e$)12.47*	59.571	4	5.29E−09	H(1s)	0.121	3.063
			3.81E−09	F(2p)	3.692	2.406
($5a_1$)17.204	67.207	2	6.44E−09	C(2p)	0.328	1.744
			3.81E−09	F(2p)	1.672	1.744
			6.44E−09	C(2p)	1.184	1.631
($1e$)18.394	54.801	4	5.29E−09	H(1s)	0.274	2.077
			3.81E−09	F(2p)	2.542	1.631
			6.46E−09	C(2s)	1.046	0.763
($4a_1$)26.201	44.402	2	5.29E−09	H(1s)	0.240	1.458
			4.06E−09	F(2s)	0.348	0.763
			3.81E−09	F(2p)	0.366	1.145
($3a_1$)42.193	100.636	2	4.06E−09	F(2s)	2.00	0.474

essentially comes from the inaccuracy of the lightest fragments partial ICSs, released with a considerable kinetic energy so that a non-negligible portion of ions is lost during their flight to the detector.[21] Moreover, their contribution to the TICS is small and the experimental accuracy in our measurements is estimated to be better than ±10%.[21] In the following a detailed discussion of the results for the specific fluoromethanes is presented.

A. CF_4

The CF_4 molecule is by far the best and most studied fluoromethane either at the theoretical or experimental levels and Fig. 4 collects the most reliable sets of reported experimental measurements,[41–43] as well as Christophorou *et al.*'s[17,19] recently ''recommended'' values, an averaging of former reliable determinations, and the Kim-BEB TICS calculation.[13] In addition, the plot includes our own measurements, which may be regarded as a study of the set of fluoromethanes carried out under identical conditions and methods and which are, in fact, in excellent agreement with the latest recommended profiles.[19] TICS calculation profiles were conducted with the standard methods already referred to and the results are also plotted in Fig. 4. By far the method that best fit the experimental results over the whole incident electron energy range considered is the Kim-BEB (and the Khare-BEB, not plotted but similar) computed at the MP2/6-31G(d) level, in preference to the MP2/6-31G(d,p) > MP2/6-311G > MP2/6-31+G(d,p) > MP2/6-311+G(d,p). A concomitant shift towards higher energies, of c.a. 1.8 eV, is also observed [Fig. 1(a)]. With the 6-311G basis set the sequence of the good fittings levels are MP2≈MP4 > CC > CISD > HF. At the HF level the quality of the fitting follows the sequence 6-31G(d) [≈6-31G(d,p)] > 6-311G > 6-31+G(d,p) > 6-311+G(d,p). For the Khare-BEB computed profiles the trends are very similar to those of Kim-BEB and their results have not been drawn in Figs. 4–7 for simplification purposes.

The TICS profiles computed by the DM method have maxima lower than the experimental ones and the results computed by the Kim-BEB method (cf. Fig. 4). The overall difference and maximum energy shift to lower incident electron energies is substantial. The empirical MAR and to a lesser extent the HV methods, as in most cases for semiempirical approximations, provide satisfactory rough results if compared with the computational effort and straightforward application.

B. CHF_3

The expected lower maximum of the TICS CHF_3 profile compared to that of CF_4 is not confirmed by the experimental measurements,[19] some of them considerably higher [in the range $>8.0\times10^{-20}\,m^2$ (Ref. 44) and $>6.0\times10^{-20}\,m^2$ (Ref. 45)] and others much lower, ca. $4.5\times10^{-20}\,m^2$.[46,47] The big differences of these TICS in one of the best characterized simple molecules illustrates the large discrepancies in the

reported experimental results. Our own determinations for CHF_3, with the experimental setup calibrated with CF_4, Ar, and Kr atoms yield a profile with maximum at 4.5 $\times 10^{-20}\,m^2$, are presented in Fig. 5 along with our theoretical calculations. Furthermore, the scarce available experimental data shows notable discrepancies as reflected in the recommended ICS by Christophorou *et al.* in their first[18,44,45] and second review[19,46] which point out the necessity of new experiments to assess the TICS. Indeed, the experimental determinations obtained in this work provide a new set in excellent agreement with those reported by Jiao *et al.*[46]

Kim's method calculations on the CHF_3 TICS profiles are in good agreement with those of Jiao *et al.* and those provided in the present work. In fact, at an electron-impact energy of 80 eV the computed TICS is $4.2\times10^{-20}\,m^2$, that matches very well to the experimental value of $4.5(\pm0.5)$ $\times 10^{-20}\,m^2$. The best fits for calculation basis sets and levels follow the same trends as the full fluorinated CF_4 molecule. The empirical MAR method yields a TICS profile very close to that of the Kim-BEB method, their profiles cross at ca. 35 eV and the ICS difference at the maxima is but 0.5 $\times 10^{-20}\,m^2$. Systematic lower values than those of Kim-BEB are provided by the DM formalism ($\Delta ICS = 0.4\times10^{-20}\,m^2$ for 25 eV$<$electron energy$<$90 eV) with a significant electron energy shift in the maximum. Finally, the HV method grossly overestimates the TICS at low energies (15 eV$<E<$100 eV) and also again over 300 eV.

C. CH_2F_2

Both experimental and theoretical TICSs profiles for the CH_2F_2 molecule are plotted in Fig. 6, and the fitting for the series of basis set and calculation level studied are shown in Fig. 1(c). The experimental partial and total ICSs for the molecule have recently been reported elsewhere.[21] Although the two hydrogen atoms in the molecule suggest the appearance of high kinetic energy light ion products following electron collision, the fitting of the experimental data to the Kim-BEB profiles is excellent in the whole energy range studied.

The DM calculation yields considerable differences with the Kim-BEB profile and the same trends as other halomethanes already reported. While the differences at energies lower than 80 eV may be considered small or acceptable, at higher energies the difference increases considerably. Compared to the Kim-BEB, the MAR profile is very good for a semiempirical method while the HV grossly overestimates the ICS.

D. CH_3F

Vallance *et al.*[20] have reported the TICSs of a series of halomethanes CH_3X (X=H, F, Cl, Br, and I) at an electron impact of 0–180 eV using the total ion current method (no mass selection). Their data for the CH_3F molecule together with those obtained in this work by mass-resolved TOF spectroscopy are plotted for comparison purposes in Fig. 7. The TICS computed with the reliable Kim's method, using electron orbitals, kinetic and binding energies calculated at the same levels as for other fluoromethanes, yield the same sequence in the profiles, of which only the MP2/6-311G profile is plotted in Fig. 7.

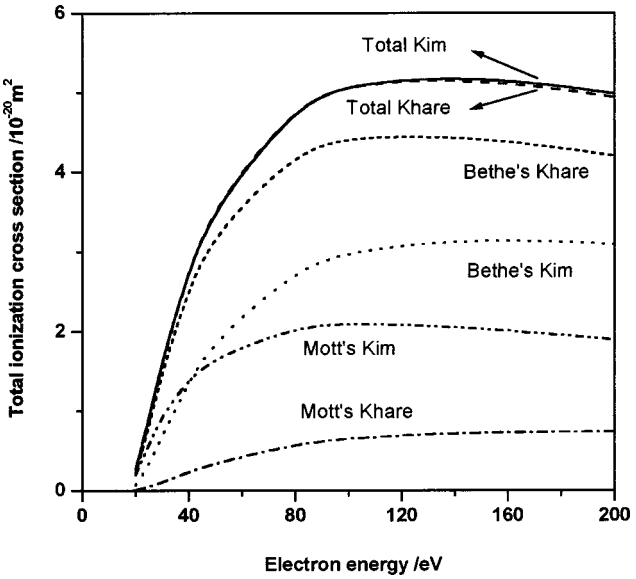

FIG. 2. Electron-impact total ionization cross sections for the CF_4 molecule, as calculated by the Kim and Khare methods. The Mott and Bethe contributions to the TICS are also indicated.

An overall comparison of our TICS experimental results and the Kim-BEB computed profiles for the family of fluoromethanes (Figs. 4–7) leads to the trend that the higher the number of H atoms in the molecule, the lower the experimental TICS profiles with respect to the calculated ones. The expected effect has its origin in the TICS decrease with the number of electrons and in the large kinetic energy of the ejected lightweight fragments. In fact it has been shown[21,48] that following the electron impact the lightweight fragments are ejected with much higher kinetic energies than heavier mass ones, and thus special care should be taken to avoid

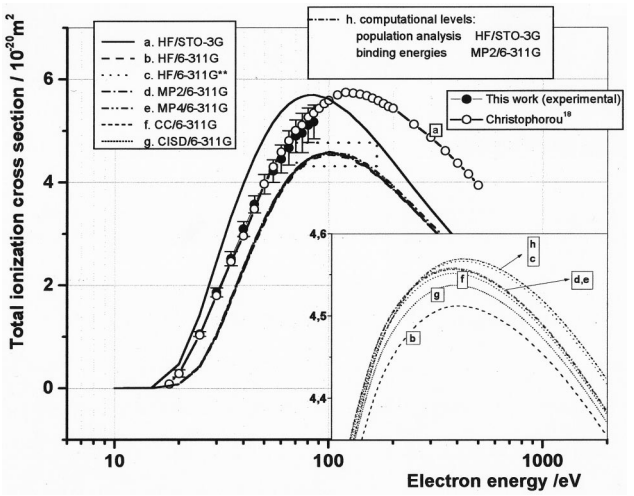

FIG. 3. Experimental and DM computed total ionization cross-section profiles for the CF_4 molecule. Similar dependences with the calculation method and basis set are observed for CHF_3, CH_2F_2, and CH_3F molecules. Calculations were carried out using the calculated molecular orbital energies except for the external one that was substituted by the first ionization energy.

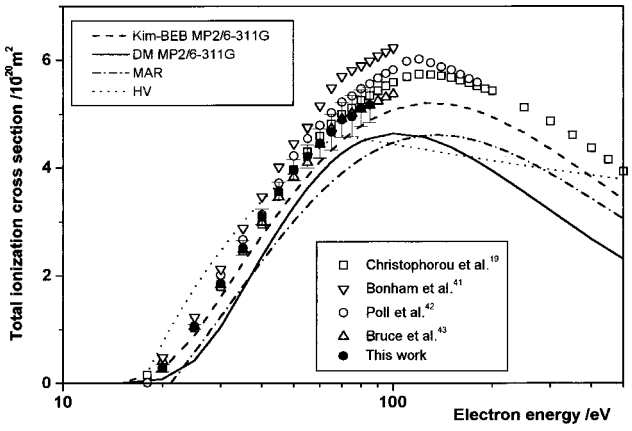

FIG. 4. Experimental electron-impact total ionization cross sections of the CF_4 benchmark molecule as a function of electron-impact energy (Refs. 19, 41–43). The calculated profiles were carried out with the following methods: Kim (dashed line), DM (thick solid line), MAR (dash-dot line), and HV (dotted line).

loss of atoms flying to the detector. In general, corrections to the TOF method must be included to avoid systematic errors, which obviously increase at higher electron impact energies (over 40 eV, cf. Fig. 7). In consequence, the TICSs reported by Vallance *et al.* should be regarded, in principle, as more reliable than our own results without corrections, although in contrast it neglects other effects such as field inhomogeneities near the edge extraction plates, which may lead to an overestimation of the ICS. Studies on experimental corrections are being pursued in our laboratory. The same arguments apply to the discrepancies between the Kim calculation and our experimental results.

Figures 1(a)–1(d) show that the electron correlation methods produce an increase in the TICS, with an apparent saturation limit. In addition, the computed profiles systematically fit better to the experimental results when the external electron energy is substituted by the experimental ionization potential. It is also noticeable for all the fluoromethanes studied that for the MP2 method the smaller the basis set the better it reproduces the TICS profiles, according to the

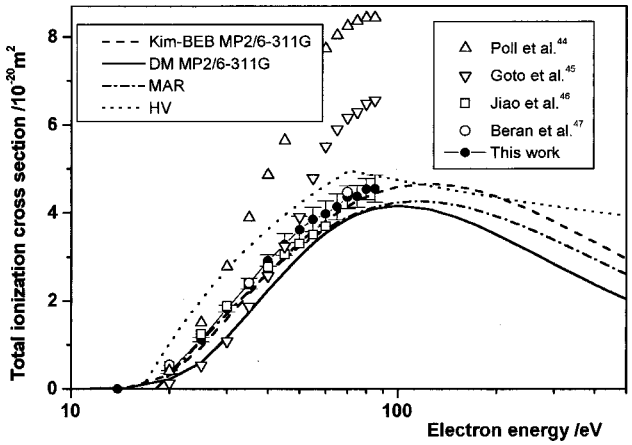

FIG. 5. Experimental electron-impact total ionization cross-section profile of the CHF_3 molecule as a function of the electron-impact energy (Refs. 44–47). The calculation methods were the following: Kim (dashed line), DM (thick solid line), MAR (dash-dot line), and HV (dotted line).

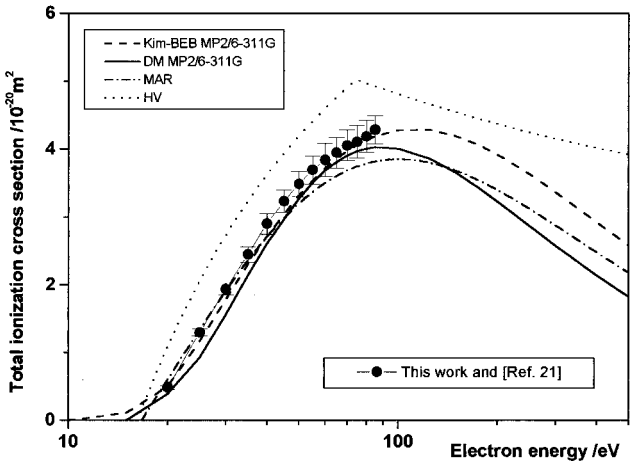

FIG. 6. Experimental electron-impact total ionization cross-section profile of the CH_2F_2 molecule as a function of electron-impact energy. The only experimental data available for this molecule has been reported recently (Ref. 21) (closed circles). The calculation profiles were determined by the following methods: DM (thick solid line), Kim (dashed line), HV (dotted line), and MAR (dash-dot line).

series 6-311G>6-31G(d)≈6-31G(d,p)>6-31+G(d,p)>6-311+G(d,p), while MP4 yields better but close fits (MP4≈MP2>CC>CISD>HF). Furthermore, the Kim TICSs fit the experimental results better if diffuse and polarization functions are not included in the computation. The effect seems to be related to the balance between hard and soft collision contributions. As the basis set is enlarged the TICS contribution of the Bethe term increases and the Kim approach underestimates the Mott cross section.

The comparison of TICS profiles supplied by the DM and the Kim-BEB methods leads to the following conclusions: DM underestimates the TICS and shifts their maxima towards lower electron-impact energies. In the DM calculation reported by Vallance *et al.* the weighting factors g_{nl} for all the atomic orbitals are considered identical, neglecting the

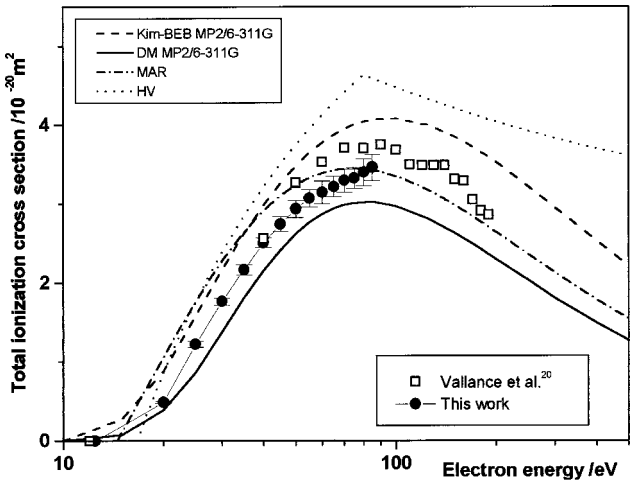

FIG. 7. Experimental electron-impact total ionization cross-section profile of the CH_3F molecule as a function of electron-impact energy. The experimental determinations are from Vallance *et al.* (Ref. 20) (open squares) and this work (closed circles). The calculation profiles were determined by the following methods: Kim (dashed line), DM (thick solid line), MAR (dash-dot line), and HV (dotted line).

energy of the molecular orbital originating from their combination (cf. Table IV[20]). In consequence, the TICS are considerably higher than those properly computed, e.g., 5 Å^2 versus 3.7 Å^2 at an electron-impact energy of 80 eV. As in the other cases studied so far, the MAR method yields a good approximation for the type of method and easy application. The HV method provides very poor profiles.

V. CONCLUSIONS

The comparison between experimental and computed TICS of the CF_4, CHF_3, CH_2F_2, and CH_3F molecules leads us to conclude that the Kim- and the Khare-BEB methods are far superior to predict the experimental profiles. Although both methods yield very close TICS profiles their Mott's and Bethe's contributions are significantly different. The best *ab initio* levels to compute the molecular parameters in both methods follows the sequence MP2≅MP4>CISD>CC>HF with basis sets without diffuse or polarization functions. For CF_4, CHF_3, CH_2F_2, the Kim-BEB model slightly underestimates the TICS as the number of fluorine atoms is increased, (cf. Fig. 4) CF_4 being the most conspicuous case. This fact may be a consequence of the Kim-BEB approximation itself that takes the optical oscillator strength shape of the ground state of atomic hydrogen regardless of the molecular orbital and molecule considered, which might not be very accurate for molecules containing heavy atoms. In short, one must be extremely cautious in predicting TICSs of large molecules.

With the basis set used in the work the profiles provided by the DM formalism slightly underestimate the TICSs and shifts the electron-impact profile maximum to lower energies. In the intermediate molecule in the series, CH_2F_2, the Kim-BEB and DM methods provide close results at impact energies lower than 100 eV. The MAR method provides intermediate BEB and DM profiles for all targets and may be recommended for standard species and as a first approximation. Finally, the HV method gives the poorest results overall, overestimating TICSs of light molecules and shifting the maximum to higher electron energies. However, because of its simplicity of application, requiring only two empirical parameters, it may be occasionally worthwhile.

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