Absolute total-cross-section measurements for intermediate-energy electron scattering on CF_4, $CClF_3$, CCl_2F_2, CCl_3F, and CCl_4

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The total cross sections of chlorofluoromethane molecules were measured in the 75–4000-eV range. A comparison is given with existing experimental and theoretical data. The present data and previous measurements in the 15–50-eV range were fitted with a Born-like formula. This simple fit allows the cross sections to be reproduced within experimental errors. Phenomenological double Yukawa scattering potentials can be derived from the formula. A short discussion for the total-cross-section partitioning is given for CF_4, CF_2Cl_2, and CCl_4.

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I. INTRODUCTION

Halogenated methanes are artificial gases of wide technological diffusion. Large-scale use has been made of them in refrigeration machines, in the manufacture of plastic foams, and as propeller gases. More sophisticated uses range from plasma (reactive ion beam) etching in the semiconductor industry [1] to discharge switches [2]. The high electron-attachment cross sections of chlorofluoromethanes make them particularly suitable as dielectrics in high-voltage equipment [3].

Only in recent years has the responsibility of halogenated methanes in the destruction of high-troposphere ozone been recognized [4]. At about the same time, the high potential of these gases for greenhouse warming was evidenced [5]. The atmospheric chemistry, the optical properties and the macroscopic behavior of these gases is obviously related to their molecular structure. This in turn is reflected in the electron-scattering cross sections. Apart from a number of electron-attachment experiments [6–8], relatively few cross-section measurements exist for these gases, and semiempirical approaches [9–11] are frequently used to model the discharge parameters.

The total cross sections for electron scattering on CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, and CF_4 at low energies (1–50 eV) have been obtained in a time-of-flight experiment by Jones [12]. Normalized total cross sections up to 400 eV have been published by Sueoka and co-workers for CCl_4 [13] and CF_4 [14]. Differential elastic cross sections at several energies between 75 and 400 eV have been measured for CCl_4 [15] and in a recent experiment [16] for CF_4 up to 700 eV. The relatively simple molecular structure of halogenated methanes allows them to be suggested as a benchmark for comparison between theory and experiment. In spite of this, a few theoretical calculations concern mainly elastic scattering in the low-energy range [17,18]. The recent calculation of Baluja *et al.* [19] has been performed for intermediate energies.

In the present work, absolute total cross sections for CCl_4, CCl_3F, CCl_2F_2, $CClF_3$, and CF_4 have been measured by the transmission method in the 75–4000-eV energy range.

II. APPARATUS AND METHOD

The apparatus used to perform the present measurements has already been described in our previous works [22–22]. We will only summarize the parameters relevant to the quality of the measurements. The apparatus was a modified version of the Ramsauer setup. A two part scattering chamber allowed an angular acceptance of 3.4×10^{-4} sr to be reached. Both the current transmitted to the collector and the scattered current were measured to obtain the cross-section value. This technique decreases the sensitivity of the apparatus to external disturbances and noise. The apparatus was differentially pumped and a diverter valve [23] was used to produce a constant background pressure during the measurement cycle. The cross section was computed with a modified de-Beers law (see [20]). The measurements were made at room temperature; the temperature of the capacitance-manometer head followed the temperature of the scattering chamber within 0.1 °C.

The absolute errors are evaluated as in Ref. [20]. The quadratic sum of all the systematic errors (apart from the angular resolution error) yields less than 3% for all gases. The lack of differential cross-section measurements for energies above 1000 eV did not allow the magnitude of the angular resolution error at the high-energy limit of our data to be evaluated. On the basis of existing data we were able to evaluate this error as 0.4% of the total cross section at 700 eV for CF_4 and about 0.4% at 400 eV for CCl_4. The assumption of a $1/E$ dependence of this error is reasonable [24]. The angular resolution error may be slightly higher for $CFCl_3$, CF_2Cl_2, and CF_3Cl, which are polar molecules.

The random errors were less than 2.5% for CF_4, CF_3Cl, and CF_2Cl_2. They were higher (within 3%) for CCl_4 and CCl_3F, which showed a larger pressure-reading instability. For these gases, longer evacuation times were necessary and statistical fluctuations affected our data to a higher extent. We should also stress that, due to the small values for the vibrational constants in the CCl_4 molecule [25], at ambient temperature a considerable fraction of the molecules is in nonzero vibrational states.

TABLE I. Total cross sections for electron scattering from the present experiment (in units of 10^{-20} m^2). In parentheses are given standard deviations of the mean values (in %).

Energy (ev)	CCl_4	CCl_3F	Cl_2CF_2	$CClF_3$	CF_4
75	38.2 (1.8)	35.0 (0.4)	30.9 (0.8)	24.0 (1.1)	19.9 (1.1)
80	37.0 (1.9)	24.0 (0.6)	29.9 (0.8)	23.5 (0.8)	19.9 (1.1)
90	36.1 (2.1)	33.0 (0.7)	28.6 (0.8)	22.5 (0.9)	19.2 (1.2)
100	36.6 (1.4)	31.3 (1.2)	27.4 (1.1)	22.7 (0.4)	18.5 (0.6)
110	35.0 (1.3)	31.0 (1.9)	26.2 (1.0)	22.0 (0.7)	18.2 (0.7)
125	34.2 (1.3)	29.9 (1.4)	24.6 (1.4)	20.8 (0.6)	17.0 (0.7)
150	31.0 (1.2)	27.3 (2.5)	22.9 (1.0)	19.3 (0.7)	16.3 (1.4)
175	28.9 (1.2)	26.1 (2.6)	21.7 (0.4)	18.1 (0.9)	15.5 (1.2)
200	28.0 (1.6)	23.9 (2.1)	20.7 (0.4)	17.0 (0.9)	14.4 (1.4)
225	25.6 (1.1)	22.5 (0.7)	19.1 (0.8)	16.0 (1.0)	13.2 (0.9)
250	24.4 (1.0)	21.2 (0.7)	18.4 (0.3)	15.0 (0.6)	12.7 (0.7)
275	23.5 (1.5)	20.7 (1.3)	17.7 (0.3)	14.4 (0.2)	12.1 (1.0)
300	22.6 (1.3)	20.0 (1.1)	17.0 (1.2)	13.9 (1.1)	11.6 (1.2)
350	20.8 (0.5)	17.7 (1.3)	15.2 (0.3)	12.4 (0.3)	10.8 (0.5)
400	19.4 (0.7)	16.7 (1.5)	14.1 (0.2)	11.5 (0.3)	10.0 (0.6)
450	17.9 (0.5)	16.0 (2.5)	13.1 (0.4)	10.7 (0.5)	9.37 (0.6)
500	16.4 (1.9)	14.6 (2.2)	12.2 (0.5)	9.92 (0.4)	8.47 (0.4)
600	14.7 (1.8)	13.0 (1.4)	10.8 (0.4)	8.90 (0.4)	7.48 (0.4)
700	13.3 (2.2)	11.8 (1.8)	9.77 (0.3)	7.98 (0.3)	6.74 (0.4)
800	12.5 (2.8)	10.6 (0.8)	8.98 (0.5)	7.27 (0.5)	6.22 (0.7)
900	11.1 (2.8)	9.65 (0.6)	8.21 (0.3)	6.79 (1.0)	5.71 (0.8)
1000	10.3 (2.1)	9.02 (0.7)	7.61 (0.3)	6.45 (1.1)	5.26 (0.9)
1100	9.41 (3.4)	8.58 (1.5)	7.01 (0.4)	6.05 (1.1)	4.87 (0.9)
1250	8.69 (1.8)	7.72 (1.0)	6.34 (0.2)	5.56 (1.0)	4.37 (0.6)
1500	7.55 (2.1)	6.71 (0.8)	5.45 (0.2)	4.86 (1.1)	3.81 (0.6)
1750	6.79 (2.2)	5.88 (1.0)	4.80 (0.3)	4.19 (1.1)	3.21 (0.4)
2000	5.95 (0.8)	5.17 (0.7)	4.32 (0.2)	3.72 (0.6)	2.94 (0.6)
2250	5.48 (0.9)	4.63 (0.9)	3.85 (0.2)	3.29 (1.3)	2.64 (0.7)
2500	5.00 (1.0)	4.21 (1.3)	3.50 (0.2)	3.05 (1.3)	2.39 (0.7)
2750	4.60 (1.1)	4.01 (1.1)	3.20 (0.3)	2.82 (1.2)	2.21 (0.9)
3000	4.32 (1.6)	3.59 (1.1)	2.96 (0.3)	2.63 (1.1)	2.03 (1.1)
3250	3.96 (1.6)	3.39 (0.8)	2.74 (0.6)	2.50 (0.5)	1.88 (1.0)
3500	3.70 (1.7)	3.19 (0.8)	2.59 (0.3)	2.35 (1.1)	1.77 (1.3)
4000	3.40 (1.3)	2.87 (2.3)	2.31 (0.3)	2.04 (0.3)	1.51 (0.4)

As in several low-energy experiments for CO_2 and SF_6, some dependency of the total cross section on temperature has been observed [26–28] and one could expect a similar effect for CCl_4. Test runs performed at different temperatures showed no detectable effect in our energy range. Statistical errors are shown for each measured point in Table I.

III. RESULTS

Table I gives the values of the cross sections measured for the five halogenated methanes from 75 to 4000 eV. The cross sections investigated fall monotonically in the entire energy range. Between 100 and 4000 eV their absolute values change by a factor larger than 10. At any given energy, the cross sections diminish going from CCl_4 to CF_4, the latter molecule showing values roughly half of those of CCl_4.

Present results for CCl_4, CCl_2F_2, and CF_4 are compared with other total-cross-section data and with available partial cross sections in Figs. 1–3. Figures for

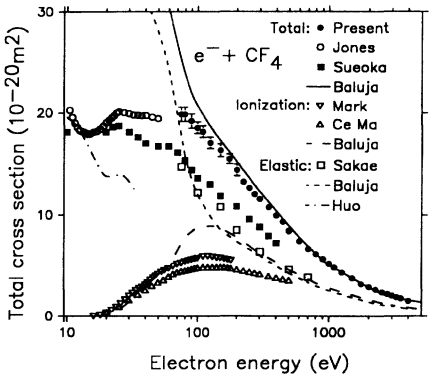

FIG. 1. Total and partial cross sections for electron-CF_4 scattering. Experimental data on total cross sections: present, absolute; Jones (Ref. [12]), absolute, corrected for the energy-dependent error, as explained in the text; Sueoka, Mori, and Katayama (Ref. [14]) normalized. Ionization: Märk *et al.* (Ref. [29]), absolute; Ma, Bruce, and Bonham (Ref. [30]), absolute. Elastic: Sakae *et al.* (Ref. [16]), absolute. Theory: Huo (Ref. [17]); Baluja *et al.* (Ref. [19]).

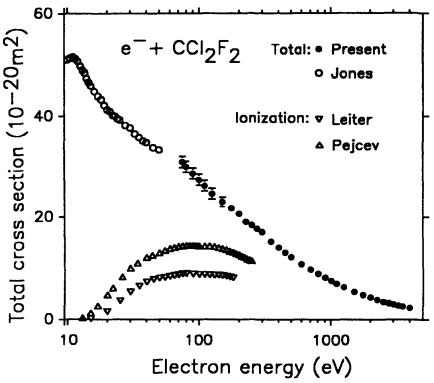

FIG. 2. Total and partial cross sections for electron-CCl_2F_2 scattering. Total cross sections as in Fig. 1. Experimental ionization: Leiter *et al.* (Ref. [31]), absolute; Pejčev, Kurepa, and Čadež (Ref. [32]), absolute.

$CClF_3$ and CCl_3F are not given since no other measurements or theories are available for these gases. The results of Jones [12] at the high-energy limit of his apparatus are influenced by scattering on the exit apertures; this (together with an angular resolution error) causes an underestimation of his total cross sections [34]. Therefore, in Figs. 1–3 we present the data of Jones, which has been corrected by an energy-dependent coefficient. We adopted a coefficient changing linearly with the energy, from 0.9% at 10 eV to 7% at 50 eV, in accordance with the systematical uncertainty bars given by Jones [12].

A direct comparison with the results of Jones [12] is difficult, since the two data sets do not overlap. We tried to measure CCl_3F down to 50 eV, which is practically outside the energy range of our apparatus. At such low energies, stray magnetic fields and beam current instabilities cause higher statistical errors, which usually tend to overestimate the real cross-section value. At 50 eV, we found a cross-section value of 40.2×10^{-20} m^2, which is 5% higher than the corrected Jones results. Taking into account the combined error, the agreement between these two measurements is quite satisfactory. For the remaining gases, a visual extrapolation of our results down to 50 eV suggests a good matching with the measurements of Jones, as can be seen from Figs. 1–3.

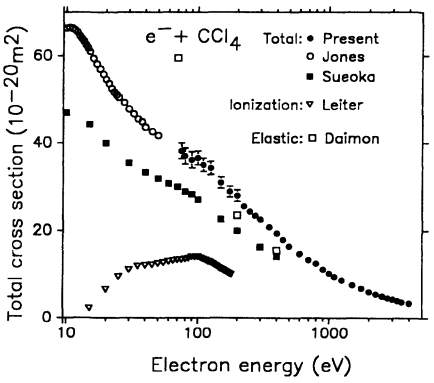

FIG. 3. Total and partial cross sections for electron-CCl_4 scattering. Total as in Fig. 1. Experimental ionization: Leiter *et al.* (Ref. [33]), renormalized by the authors (see text). Elastic: Daimon, Kondow, and Kuchitsu (Ref. [15]) normalized differential cross sections, integrated by the authors.

CCl_4 and CF_4 total cross sections were measured by Sueoka and co-workers [13,14] in the 1–400-eV energy range. The data of Sueoka is 15–20% lower than the present data in the whole overlap energy range. At lower energies, the same disagreement is observed between the data of Sueoka and the results of Jones in [12]. This discrepancy, constant versus energy, can be explained by an ambiguity of the normalization procedure in the experiments of Sueoka and co-workers.

In the case of CF_4, our data are in good agreement with the optical model results of Jain and co-workers [19] in the whole energy range. The agreement for this relatively large molecule is even better than the agreement found between our measurements and Jain's previous calculations for NH_3, CH_4, and SiH_4 (see Ref. [22]). However, at low energies, the calculations of Jain and co-workers [19] substantially exceed the experimental values of Jones [12]. As existing calculations for CF_4 in the low-energy region [17–19] give results differing by a factor of 2, much room remains for possible improvements in the theory.

IV. PHENOMENOLOGICAL FIT TO THE CROSS-SECTION DATA

In our previous work for intermediate-energy electron scattering on hydride molecules (CH_4, SiH_4, NH_3, H_2O, H_2S) [22], we reported that the total cross sections of these gases can be well approximated by the formula

$$\sigma(E)=\frac{1}{A+BE} \tag{1}$$

for energies higher than 200 eV. An attempt to use the same formula to fit the experimental points for chlorofluoromethanes showed that only the CF_4 cross section is described accurately by Eq. (1) down to our lowest measured energy (75 eV). The cross sections of our four chlorofluoromethanes show this simple behavior at higher energies only.

It is known that Eq. (1) has the same energy dependence of the Born approximation for the elastic scattering on a Yukawa potential [35]. The shape of the cross sections of the four heavier chlorofluoromethanes suggests that the cross section sums up from a Born-like term dominating at energies higher than a few hundred eV plus a second term significant at the low energy only. If the hypothesis is made that both terms can be described by a Born-like approximation to the scattering from a double Yukawa potential,

$$V(r)=\frac{V_1}{r}\exp\left[-\frac{r}{a_1}\right]+\frac{V_2}{r}\exp\left[-\frac{r}{a_2}\right], \tag{2}$$

the resulting formula for the cross section contains two

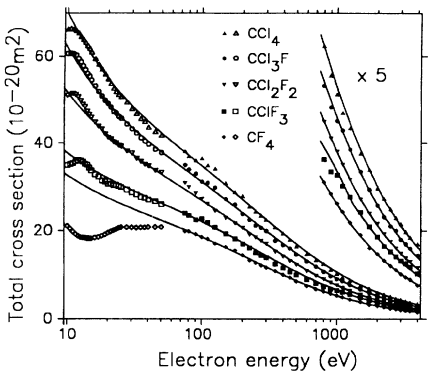

FIG. 4. Comparison of the total cross sections for electron-chlorofluoromethanes scattering in the 10–4000-eV energy range. Experimental points, closed symbols; present, open symbols; Jones (Ref. [12]), corrected. Curves: semiempirical fit [see Eq. (3)], with parameters as in Table I.

terms of the form (1) plus a cross term:

$$\sigma(E)=\frac{1}{A_1+B_1E}+\frac{1}{A_2+B_2E}+\frac{2}{E}\frac{(A_1A_2)^{1/2}}{A_2B_1-A_1B_2}\ln\frac{1+B_1E/A_1}{1+B_2E/A_2}\ , \qquad (3)$$

where

$$A_i=\frac{\hbar^4}{16\pi m^2a_i^4V_i^2}\ , \quad B_i=\frac{\hbar^2}{2\pi ma_i^2V_i^2}\ .$$

Equation (3) closely reproduces the measured total cross sections of the chlorinated halomethanes down to a few tens of eV. The best fitting curves lie entirely within our error bars and within the symmetrized (see preceding paragraph) error bars of Jones. The curve on the CF_4 cross-section data was obtained by fitting Eq. (3) to the present results. The fit reproduces our measurements within the error bars: it fails to reproduce the experimental data below 75 eV.

The best fit values A_i,B_i allow the corresponding V_i,a_i values to be reconstructed in Eq. (2). We noted that the best fit values for a_2 range from less than 2 to about 50 a.u. Values in this range are compatible with the measurement errors for all chlorofluoromethanes. In particular, a_2 values in the range of a few atomic units are acceptable for all the gases. Based on this indetermination, we have arbitrarily constrained the fitting algorithm to keep the a_2 values fixed at the molecular radii as derived from the coefficients of van der Waals [36] (see Table II, column 1). The following discussion is not biased in its qualitative aspects by this arbitrary choice. Column 2 gives the polarizabilities of the five halocarbons. Columns 3–6 report the a_i,B_i values obtained with the fitting procedure described above; columns 7–9 give the corresponding values for V_1,V_2, and a_1. The V_1 and a_1 values obtained with the unconstrained fitting procedure are very nearly the same as those reported in Table II.

V. PARTITIONING OF THE TOTAL CROSS SECTION

A number of processes, both elastic and inelastic, contribute to the total cross sections (TCSs) at intermediate energies. Both the energy dependencies and the magnitudes of partial cross sections differ for every specific process. Different semiempirical expressions describing these dependencies are still far from being commonly acknowledged [37]. Usually, the partial cross sections obtained from experiments have to be normalized in order to get absolute values. Additionally, the precision of the measurements is inferior to that achieved in total-cross-section experiments. The comparative analysis of the partitioning of the total cross sections can help to verify absolute values of the partial cross sections, to understand more fully the interactions between specific channels and to point out common features for groups of targets.

In our recent study on hydrides (CH_4, NH_3, H_2O, SiH_4) [22], we noticed that, in spite of the fact that the absolute values of total and of partial cross sections for different gases differ significantly, the relative contributions of separate processes to the total cross section exhibit common features. The relative contribution of ionization rises rapidly from the threshold up to about 200 eV. This rise is accompanied by a rapid fall of the elastic contribution. Around an energy of 200 eV both elastic and ionization cross sections amount to about 40% of the TCS; above this energy the ionization cross section is predominant. At higher energies the changes in partitioning are less rapid.

Experimental results for chlorofluoromethanes are only fragmentary; nevertheless, the agreement between

TABLE II. Coefficients of the fit of the total cross section from the present experiment to Eq. (3), as explained in the text (A_i in units of 10^{20} m^{-2}, B_i in units of 10^{20} keV^{-1} m^{-2}); coefficients of the derived phenomenological potential; columns 1 and 2 give molecular radii derived from van der Waal's coefficients (Ref. [36], Table 6.48) and polarizabilities (from [36]).

	Mol. radii	Polarizability	Fit parameters				Potential parameters		
Molecule	(a.u.)	(a.u.)	A_1	B_1	A_2	B_2	V_1 (a.u.)	a_1 (a.u.)	V_2 (a.u.)
CF_4	3.48	25.9	0.043	0.16	0.013	47.8	101	0.110	0.189
CF_3Cl	3.79	37.7	0.037	0.12	0.0098	41.7	127	0.104	0.186
CF_2Cl_2	4.02	52.7	0.030	0.11	0.0038	18.3	129	0.108	0.266
$CFCl_3$	4.20	65.7	0.027	0.087	0.0022	12.0	151	0.103	0.313
CCl_4	4.38	75.6	0.025	0.074	0.0017	10.2	168	0.0996	0.325

different sets of data is better than for hydrides. The available partial cross sections are reported in Figs. 1–3. The recent ionization-cross-section measurements of Märk *et al.* for CF_4 [29] and CF_2Cl_2 [31] allowed normalization factors to be obtained, also bringing former data [33,38] into agreement with both other experiments [30] and the semiempirical calculations [37].

According to the data of Märk and co-workers [29,31,33], the relative contribution of the ionization cross sections to the 175-eV TCS is equal for all three gases CCl_4, CCl_3F, and CF_4: about 37%. An even smaller contribution results from the most recent measurements of Ma, Bruce, and Bonham [30]: 31% for CF_4 at 175 eV. The ionization share is smaller for chlorofluoromethanes than for CH_4, where, according to different sets of data, the ionization contributes between 45 and 50% (see Ref. [22] and recent data by Djurić [39]). This difference can be explained by the fact that no stable parent molecular ions have been observed for chlorofluoromethanes, whereas for hydrides the parent ionization is predominant.

The elastic-scattering contribution was evaluated for CF_4 from differential-cross-section measurements of Sakae *et al.* [16]. It diminishes from about 70% at 75 eV to 60% at 200 eV and 55% at 700 eV. As a possible error in the measurements of Sakae *et al.* is 9%, one has to conclude that, within the experimental uncertainties, the recent elastic- and ionization-cross-section data sum up to the upper limit set by our total-cross-section values. The contribution from the elastic channel at 700 eV is surprisingly high. For H_2O and CH_4, elastic scattering at this energy amounts to only 40% of the total cross section (see [22]). This comparison also indicates that the contribution from electronic excitation is negligible at energies above 100 eV. In fact, the measurements of electron impact excitation cross sections [40–42] show that electronic excitations contribute less than 4% of TCS at 100 eV and less than 1% at 400 eV.

For CCl_4, to our knowledge, the only measurements of elastic scattering are the data of Daimon, Kondow, and Kuchitsu [15]. As this data is normalized to the independent-atom-model calculations, they tend to be more reliable at high energies. According to these results, the 400-eV elastic cross section amounts to almost 80% of the total. This is in some disagreement with the ionization measurements. At lower energies, the results of Daimon, Kondow, and Kuchitsu are evidently overestimated: at 75 eV they exceed the measured total-cross-section value.

In spite of the experimental uncertainties, there is enough evidence to assess a different partitioning scheme for hydrides and chlorofluoromethanes. For the latter gases, elastic scattering is the dominant part of TCS's, at least up to energies of several hundred eV. Most probably, this results from the electronegative character of fluorine and chlorine, which are the outer atoms in the examined molecules. The measurements of ionization cross sections for different chlorofluoromethanes at energies of several hundred eV would be especially useful to confirm this particular partitioning scheme.

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[1] J. W. Butterbough, D. C. Gray, and H. H. Sawin, J. Vac. Sci. Technol. B **9**, 1461 (1991).
[2] S. R. Hunter, J. G. Carter, and L. G. Christophorou, J. Appl. Phys. **58**, 3001 (1985).
[3] R. E. Wootton, S. J. Dale, and N. J. Zimmerman, in *Gaseous Dielectrics II*, edited by L. G. Christophorou (Pergamon, New York, 1980).
[4] R. S. Eckman, J. D. Haigh, and J. A. Pyle, Nature **329**, 616 (1987).
[5] V. Ramanatham, L. Callis, R. Cess, J. Hansen, I. Isaksen, W. Kuhn, A. Lacis, F. Luther, J. Mahlmann, R. Reck, and M. Schlesinger, Rev. Geophys. **25**, 1441 (1987).
[6] S. H. Alajajian and A. Chutjian, J. Phys. B **20**, 2117 (1987).
[7] D. L. McCorkle, A. A. Christodoulides, L. G. Christophorou, and I. Szamrej, J. Chem. Phys. **72**, 4049 (1980).
[8] D. Smith, N. G. Adams, and E. Alge, J. Phys. B **17**, 461 (1984).
[9] K. Mašek, L. Láska, R. d'Agostino, and F. Cramarossa, Contrib. Plasma Phys. **27**, 15 (1987).
[10] B. Stefanov, N. Popkirova, and L. Zarkova, J. Phys. B **21**, 3989 (1988).
[11] J. P. Novak and M. F. Fréchette, J. Appl. Phys. **57**, 4368 (1985).
[12] R. K. Jones, J. Chem. Phys. **84**, 813 (1986).
[13] O. Sueoka, citing M. Hayashi, in *Swarm Studies and Inelastic Electron-Molecule Collisions, Proceedings of the Meeting of the Fourth International Swarm Seminar, Tahoe City, 1985,* edited by L. C. Pitchford, B. V. McKoy, A. Chutjian, and S. Trajmar (Springer, New York, 1985), p. 101.
[14] S. Mori, Y. Katayama, and O. Sueoka, At. Coll. Res. Jpn. Prog. Rep. **11**, 19 (1985).
[15] H. Daimon, T. Kondow, and K. Kuchitsu, J. Phys. Soc. Jpn. **52**, 84 (1983).
[16] T. Sakae, S. Sumiyoshi, E. Murakami, Y. Matsumoto, K. Ishibashi, and A. Katase, J. Phys. B **22**, 1385 (1989).
[17] W. M. Huo, Phys. Rev. A **38**, 3303 (1988).
[18] J. A. Tossell and J. W. Davenport, J. Chem. Phys. **80**, 813 (1984); **83**, 4824(E) (1985).
[19] K. L. Baluja, A. Jain, V. DiMartino, and F. A. Gianturco, Europhys. Lett. **17**, 139 (1992).
[20] A. Zecca, S. Oss, G. Karwasz, R. Grisenti, and R. S. Brusa, J. Phys. B **20**, 5157 (1987).
[21] A. Zecca, G. Karwasz, R. S. Brusa, and R. Grisenti, J. Phys. B **23**, 2737 (1991).

[22] A. Zecca, G. Karwasz, and R. S. Brusa, Phys. Rev. A **45**, 2777 (1992).
[23] M. Basta, I. Lazzizzera, and A. Zecca, J. Phys. E **9**, 6 (1976).
[24] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics, Non-relativistic Theory* (Pergamon, Oxford, 1965), p. 483.
[25] G. Herzberg, *Molecular Spectra and Molecular Structure II: Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand, Princeton, 1966), p. 167.
[26] S. J. Buckman, M. T. Elford, and D. S. Newman, J. Phys. B **20**, 5157 (1987).
[27] J. Ferch, C. Masche, W. Raith, and L. Wiemann, Phys. Rev. A **40**, 5407 (1989).
[28] K. L. Stricklett and P. D. Burrow, J. Phys. B **24**, L149 (1991).
[29] H. U. Poll, C. Winkler, D. Margreiter, V. Grill, and T. D. Märk, Into. J. Mass Spectrosc. Ion Proc. **112**, 1 (1992).
[30] Ce Ma, M. R. Bruce, and R. A. Bonham, Phys. Rev. A **44**, 2921 (1991).
[31] K. Leiter, P. Scheier, G. Walder, and T. D. Märk, Int. J. Mass Spectrosc. Ion Proc. **82**, 209 (1989).
[32] V. M. Pejčev, M. V. Kurepa, and I. M. Čadež, Chem. Phys. Lett. **63**, 301 (1979).
[33] K. Leiter, K. Stephan, E. Märk, and T. D. Märk, Plasma Chem. Plasma Process **4**, 235 (1984).
[34] R. K. Jones, J. Chem. **82**, 5424 (1985).
[35] Ch. J. Joachain, *Quantum Collision Theory* (North-Holland, Amsterdam, 1975), p. 174.
[36] *CRC Handbook of Chemistry and Physics*, 71st ed., edited by D. R. Lide (CRC, Boca Raton, 1990).
[37] D. Margreiter, H. Deutsch, M. Schmidt, and T. D. Märk, Int. J. Mass Spectrosc. Ion Proc. **100**, 157 (1990).
[38] K. Stephan, H. Deutsch, and T. D. Märk, J. Chem. Phys. **83**, 5712 (1985).
[39] N. Djurić, I. Čadež, and M. Kurepa, Int. J. Mass Spectrosc. Ion Proc. **108**, R1 (1991).
[40] H. A. van Sprang, H. H. Brongersma, and F. J. de Heer, Chem. Phys. **35**, 51 (1978).
[41] K. A. Blanks, A. E. Tabor, and K. Becker, J. Chem. Phys. **86**, 4871 (1987).
[42] M. B. Roque, R. B. Siegel, K. E. Martus, V. Tarnovsky, and K. Becker, J. Chem. Phys. **94**, 341 (1991).