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Halogenation effects in electron scattering from CHF_3, CH_2F_2, CH_3F, $CHCl_3$, CH_2Cl_2, CH_3Cl, $CFCl_3$, CF_2Cl_2, and CF_3Cl

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We report differential elastic cross sections for low-energy electron scattering by CHF_3, CH_2F_2, CH_3F, $CHCl_3$, CH_2Cl_2, CH_3Cl, $CHCl_3$, CF_2Cl_2, and CF_3Cl, obtained with the Schwinger multichannel method with norm-conserving pseudopotentials. Our results are in excellent agreement with available experimental and theoretical data. We compare the present results with our previous results for CH_4, CF_4, and CCl_4 and show that the oscillatory behavior of the cross sections is related to electron scattering from heavier centers (F or Cl), which favors the coupling of high partial waves. We also include a table with momentum-transfer cross sections. [S1050-2947(99)02801-2]

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We present theoretical differential cross sections for low-energy electron scattering by fluoromethanes (CHF_3, CH_2F_2, and CH_3F), chloromethanes ($CHCl_3$, CH_2Cl_2, and CH_3Cl), and chlorofluoromethanes ($CClF_3$, CCl_2F_2, and CCl_3F), compared to our previous results for CH_4 [1], CF_4 [2], and CCl_4 [3]. We have been studying the theoretical features of low-energy electron collisions with molecules that are of industrial and environmental importance [4] and this work represents one more step towards a full understanding of these processes.

Our cross sections were obtained using the Schwinger multichannel method [5] implemented with Bachelet-Hamann-Schlüter pseudopotentials [6]. This combined method allows calculations of low-energy electron scattering by molecules containing heavy atoms with reduced computational effort [1]. Our calculations were carried out in the fixed-nuclei, static-exchange approximation. Polarization effects are not included, but they are known to be of little importance for the impact energies we study (8–30 eV). The cross sections are averaged over all molecular orientations and rotational levels are not resolved.

All molecules studied have permanent dipole moments. However, the present calculations do not include any correction to account for this long-range potential. Based on previous studies on the inclusion of these corrections through the Born approximation, we found that this procedure does not affect the final results in a significant way, especially for energies above 8 eV and angles above 20°–30°.

Our differential cross sections for CF_2Cl_2, CF_3Cl, CH_3Cl, CHF_3, and CH_3F are shown in Figs. 1 and 2, at different impact energies, in good agreement with experimental data of Refs. [7–11], respectively, and with the theory of Ref. [12] (the complex Kohn variational method). The slightly different shape of our differential cross section for CH_3Cl compared to the experiment [9] and to the theoretical result of Ref. [12] is due to the absence of a description of polarization effects in our calculations, which is important at lower energies. Figure 3 shows our momentum-transfer cross section for CH_3Cl, in good agreement with the static-exchange result of Ref. [12]. Our momentum-transfer cross sections for all molecules are shown in Table I for energies above 10 eV.

Figure 4 compares our results at 20 eV for fluoromethanes, chloromethanes, and chlorofluoromethanes so that we can see the influence of the outer atoms in the differential cross sections for each set of molecules. For the fluoromethanes of Fig. 4(a) we reproduce the shoulder that begins to appear experimentally at 60°–65° [11] for molecules containing F atoms. The magnitude of these structures increases as the number of fluorine atoms in the molecule goes from 0 to 4, as pointed out by the experiment. In Fig. 4(b), however, we show that the differential cross sections for chloromethanes present exactly the same behavior, except that the shoulder now begins to appear around 30°–40°. These two figures show that this type of undulation in the differential cross sections is a halogenation effect (confirming the fluorination effects observed by Tanaka *et al.* [11]) and it is due to the presence of heavier atoms that are better scattering centers than hydrogen. These effects are much

TABLE I. Momentum-transfer cross sections (10^{-16} cm^2).

Energy (eV)	$CHCl_3$	CH_2Cl_2	CH_3Cl	CH_3F	CH_2F_2	CHF_3	$CClF_3$	CCl_2F_2	CCl_3F
10	31.01	21.87	19.71	18.41	14.90	15.51	15.72	22.74	22.80
15	26.05	17.56	16.50	12.51	11.35	12.39	15.55	19.25	21.96
20	21.40	14.67	12.77	9.80	10.56	11.37	13.70	15.40	18.56
25	17.68	11.74	10.18	8.54	10.16	10.54	12.12	13.32	18.33
30	14.82	9.64	8.65	7.64	9.22	10.13	11.31	12.04	17.13

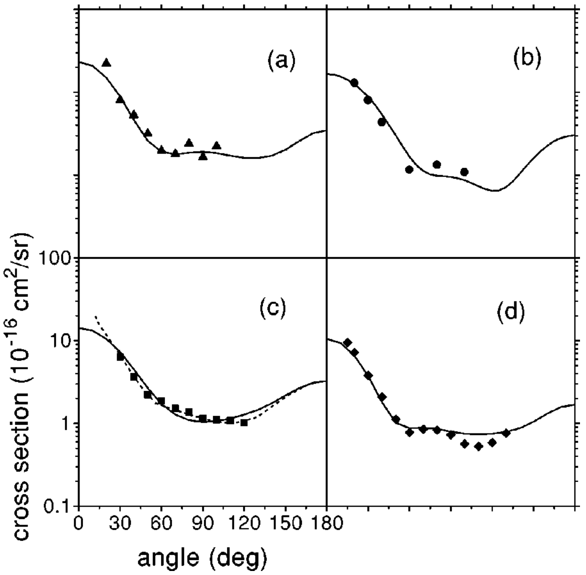

FIG. 1. Differential cross sections for (a) CCl_2F_2 at 9 eV, (b) $CClF_3$ at 10 eV, (c) CH_3Cl at 8 eV, and (d) CHF_3 at 20 eV. Full lines, our theoretical result; dashed line, complex Kohn result [12]; triangles, experimental results [7]; filled circles, experimental results [8]; squares, experimental results [9]; diamonds, experimental results [10].

more prominent for chloromethanes than for fluoromethanes (Cl atoms are heavier than F atoms).

In Fig. 4(c) we compare differential cross sections for chlorofluoromethanes at 20 eV. We could not identify any clear characteristic behavior in the cross sections for this set of halomethanes as we could clearly see for the two other sets above. The undulations vary in position and magnitude with no apparent relation to the type of the outer atoms, but they are always present in the cross sections (also for other impact energies between 8 eV and 30 eV), as a result of the electron interaction with heavier scattering centers.

It is known from the study of potential scattering [13] that, since the scattering amplitude can be written in terms of Legendre polynomials, oscillations in the differential cross sections can be related to polynomials of high degree, i.e., to the coupling of many partial waves. Table II shows the partial-wave contribution for the cross sections at 20 eV. The partial cross sections were obtained for collision processes of

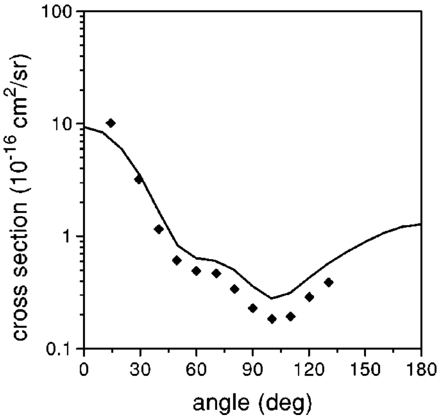

FIG. 2. Differential cross sections for CH_3F at 30 eV. Full line, our theoretical result; diamonds, experimental results [11].

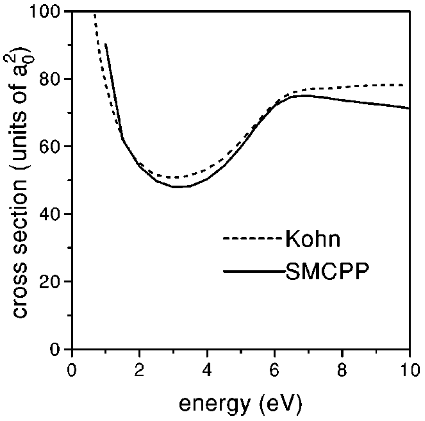

FIG. 3. Momentum transfer cross sections for CH_3Cl. Full line, our theoretical result; dashed line, complex Kohn static exchange result [12].

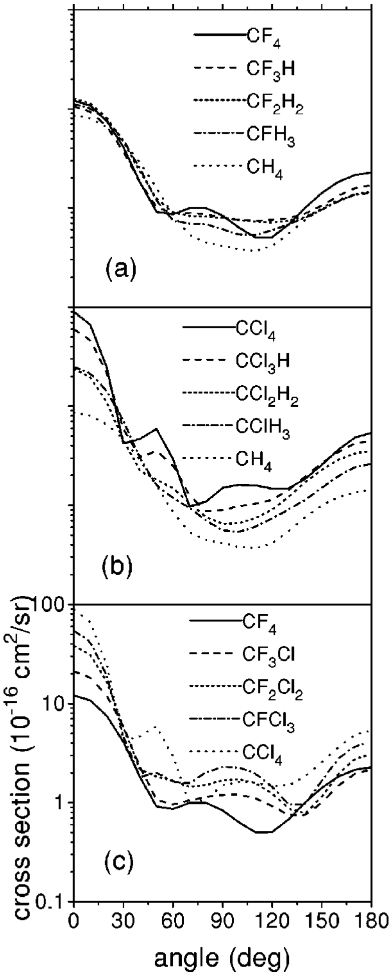

FIG. 4. Differential cross sections. (a) Fluoromethanes at 20 eV. Full lines, CF_4 [2]; long dashed lines, CHF_3; dashed lines, CH_2F_2; dot-dashed lines, CH_3F; dotted lines, CH_4 [1]. (b) Chloromethanes at 20 eV. Full lines, CCl_4 [3]; long-dashed lines, $CHCl_3$; short-dashed lines, CH_2Cl_2; dot-dashed lines, CH_3Cl; dotted lines, CH_4 [1]. (c) Chlorofluoromethanes at 20 eV. Full lines, CF_4 [2]; long-dashed lines, $CClF_3$; short-dashed lines, CCl_2F_2; dot-dashed lines, CCl_3F; dotted lines, CCl_4 [3].

TABLE II. Partial-wave contribution for the cross sections at 20 eV.

ℓ	CCl_4	$CHCl_3$	CH_2Cl_2	CH_3Cl	CH_4	CH_3F	CH_2F_2	CHF_3	CF_4	$CClF_3$	CCl_2F_2	CCl_3F
0	2%	2%	4%	6%	12%	10%	9%	10%	12%	8%	5%	4%
1	4%	4%	10%	15%	33%	28%	21%	24%	24%	17%	11%	9%
2	13%	18%	24%	32%	45%	26%	33%	27%	27%	22%	20%	18%
3	22%	26%	26%	21%	9%	26%	23%	21%	24%	17%	23%	19%
4	28%	25%	21%	16%	1%	8%	12%	15%	11%	21%	22%	25%
5	22%	18%	11%	8%	0%	2%	2%	3%	2%	11%	14%	18%
6	8%	6%	3%	2%	0%	0%	0%	0%	0%	3%	4%	6%
7	1%	1%	1%	0%	0%	0%	0%	0%	0%	1%	1%	1%

incoming electrons in a plane wave to outgoing electrons in partial waves (ℓ, m_ℓ), summed over m_ℓ and averaged over all molecular orientations. The percentage is made with respect to an integral cross section summed up to $\ell = 7$. The highest partial wave with significant contribution (more than 10%) increases with the number of heavy atoms in the molecule for chloromethanes and for fluoromethanes, except for one inversion (CF_4 and CHF_3) that we do not consider to be significant. In general, chloromethanes show higher partial-wave coupling than fluoromethanes. This is the reason for the more intense changes in the cross sections shown in Fig. 4(b). In addition, low-angle scattering is highly influenced by high partial waves, which may cause the shoulder to appear at lower angles for chloromethanes than for fluoromethanes. In general, the coupling of $\ell = 5$ is important only when there is Cl in the molecule and among chlorofluoromethanes it is more important for CCl_3F.

Another important feature in the scattering process is the molecular size. Hydrogen atoms, which are typically placed 1.1 Å from the carbon atom for all molecules shown here, are poor scatterers. The internuclear distance between a fluorine atom and the carbon atom is on the order of 1.35 Å, while the typical distance between chlorine and carbon is 1.78 Å. When hydrogen atoms are replaced by fluorine and/or chlorine atoms, the molecules become larger and therefore better scattering centers.

To summarize, we may say that our calculation techniques can produce cross sections for these molecules in remarkable agreement with experiment. The differential cross sections present oscillations due to the high-partial-wave coupling introduced by the presence of external larger atoms in these molecules. The larger the outer atom, that is, Cl larger than F and F larger than H, the richer the undulations in the differential cross section plots. The same feature is observed in the cross sections for other impact energies in the range 8–30 eV. In other words, these effects are expected to be observed when hydrogen atoms are replaced by any other heavier atoms.

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[1] M. H. F. Bettega, L. G. Ferreira, and M. A. P. Lima, Phys. Rev. A **47**, 1111 (1993).

[2] A. P. P. Natalense, M. H. F. Bettega, L. G. Ferreira, and M. A. P. Lima, Phys. Rev. A **52**, R1 (1995).

[3] M. T. do N. Varella, A. P. P. Natalense, M. H. F. Bettega, and M. A. P. Lima (private communication).

[4] L. G. Christophorou, J. K. Olthoff, and M. V. V. S. Rao, J. Phys. Chem. Ref. Data **25**, 1341 (1996); **26**, 1 (1997); L. G. Christophorou, J. K. Olthoff, and Y. Wang, *ibid.* **26**, 1205 (1997).

[5] K. Takatsuka and V. McKoy, Phys. Rev. A **24**, 2473 (1981); **30**, 1734 (1984); M. A. P. Lima and V. McKoy, *ibid.* **38**, 501 (1988).

[6] G. B. Bachelet, D. R. Hamann, and M. Schlüter, Phys. Rev. B **26**, 4199 (1982).

[7] A. Mann and F. Linder, J. Phys. B **25**, 1633 (1992).

[8] A. Mann and F. Linder, J. Phys. B **25**, 1621 (1992).

[9] X. Shi, V. K. Chan, G. A. Gallup, and P. D. Burrow, J. Chem. Phys. **104**, 1855 (1996).

[10] H. Tanaka (private communication).

[11] H. Tanaka, T. Masai, M. Kimura, T. Nishimura, and Y. Itikawa, Phys. Rev. A **56**, R3338 (1997).

[12] T. N. Rescigno, A. E. Orel, and C. W. McCurdy, Phys. Rev. A **56**, 2855 (1997).

[13] C. J. Joachain, *Quantum Collision Theory* (American Elsevier, New York, 1975), p. 72.