

Fluorination effects in electron scatterings from CH₄, CH₃F₁, CH₂F₂, CH₁F₃, and CF₄

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A conspicuous fluorination effect, prominent structures in elastic differential cross sections below 100 eV, in electron-methane and fluoromethanes (CH₄, CH₃F₁, CH₂F₂, CH₁F₃, and CF₄) collisions has been found in a systematic manner. The effect becomes more prominent when the number of fluorine atoms increases. Further, a systematic undulation due to F atoms at small-angle scatterings has also been observed, and the case has been studied in detail, in which we have found it to be due to interferences of a scattered electron from different scattering centers. Therefore, we have examined a possibility of utilizing the undulation as a means for molecular structure analysis. For these observed features, a simple, intuitively correct interpretation based on the underlying molecular structure and scattering physics has been given. [S1050-2947(97)50811-0]

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Due to basic interest in the fundamental nature of molecular electronic structures and scattering processes as well as their applications in plasma chemistry and material sciences, a study on total, elastic, and inelastic processes for electron scattering from methane and fluoromethanes (CH₄, CH₃F₁, CH₂F₂, CH₁F₃, and CF₄) has become increasingly important in recent years, and thus has attracted a great deal of interest [1]. Comparative studies of the electronic structure and scattering process from CH₄ to CF₄ by sequentially replacing a H atom in a methane molecule with a F atom would be expected to provide a much deeper insight into the basics of atomic and molecular physics of hydrocarbons and their dynamical interaction mechanisms. Furthermore, a set of cross-section data for electron scattering from partially fluorinated-methane gases is urgently needed in plasma processing, material sciences, and earth sciences, since these molecules, which have a shorter lifetime than that of CF₄ in the atmosphere, are considered to be "environmentally acceptable, next generation plasma-processing gases" [2]. Although there have been earlier studies for these systems using the electron-energy-loss technique to experimentally identify electronic states [3,4], as well as theoretical approaches for CH₄ and CF₄ [5,6], to the best of our knowledge, no complete study based on electron-scattering elastic differential cross sections (DCS's), i.e., a more suitable object for a detailed and accurate study, has been carried out to date. For a different system, Jones [7] and Zecca *et al.* [8] have measured total elastic cross sections for CCl₄ and their F-substituted molecules, but no theoretical interpretation of their findings has been provided. Therefore, we have initiated the present joint experimental and theoretical investigation of electron scattering of these molecules to learn more basic and systematic physics, and, possibly, to search for any signature of the fluorination effect of these molecules on DCS's, which may possess a wider potential for a further understanding of interactions and a possible application for molecular structure analysis.

The present experimental apparatus and method have been shown in detail earlier [9], and only some specific features of that study are briefly explained here. The apparatus consists of an electron-scattering spectrometer, gas flow system, and a multichannel analyzer for detecting and storing the scattered electron signal. The scattering spectrometer contains an electron gun and hemispherical monochromator, which produce a nearly monoenergetic electron beam of the desired energy, a detector with a hemispherical energy analyzer, a channeltron for the detection of scattered electrons, and a nozzle through which target gas effuses to produce a well-defined beam of these molecules. Both the monochromator and the detector are enclosed in differentially pumped boxes to, respectively, reduce the effect of background gases and to minimize the stray electron background. The lens properties of the multicomponent lens system are carefully calculated with an electron trajectories program. For some lens elements, the driving voltages are, therefore, controlled by the programmable power supplies to keep the transmission of the scattered electrons constant. The incident electron's beam crosses the molecular beam at 90° and the scattered electrons can be detected in the angular region between 15° and 135° with respect to the incident electron beam. During the present measurements, the overall energy and angular resolutions of the spectrometer were 35–40 meV and ±15°, respectively. Rotational structures are not resolved. The incident electron energy is calibrated against the 19.35-eV resonance of He. The cross-section calibration method employs a measurement of the ratio of the elastically scattered intensity of either molecular gas to that of He under the same experimental conditions, and the details given earlier [9]. Experimental errors are estimated at 15–30%. Note that the data for CH₄ and CF₄ were taken earlier by that group [10].

Figures 1(a)–1(c) present elastic DCS's observed for all molecules at 1.5, 30 (35 for CF₄), and 100 eV. We tentatively divide the molecules treated here into two groups for later discussion: (i) one for CH₄ and CF₄, nonpolar mol-

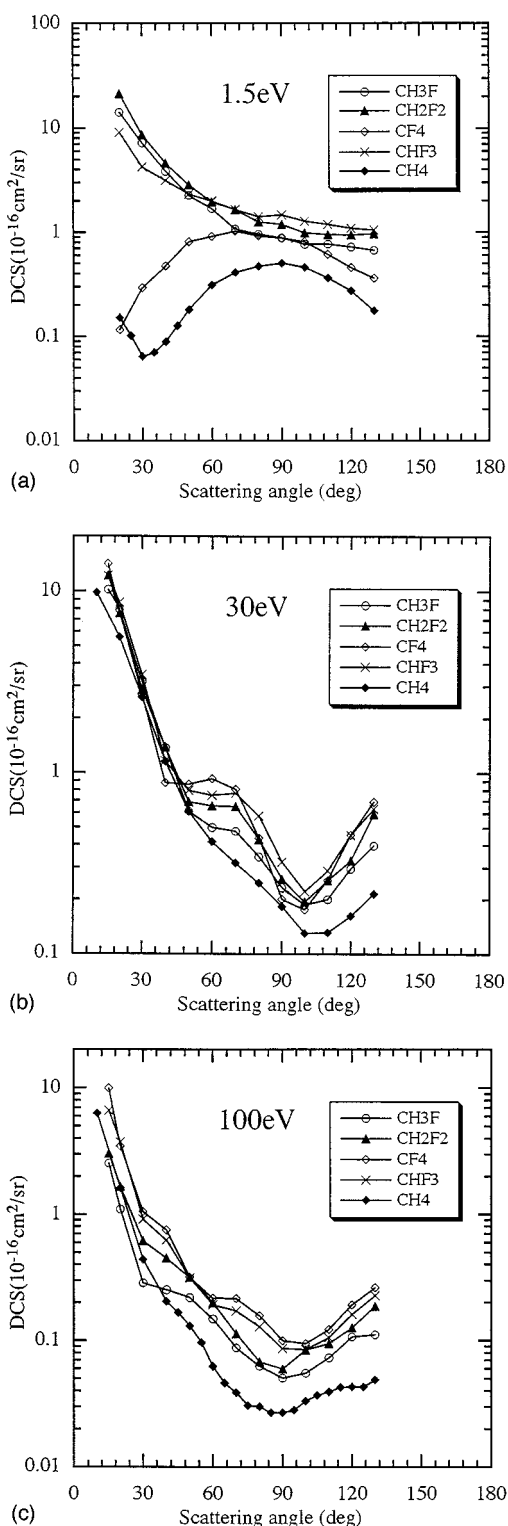


FIG. 1. Elastic differential cross sections for CH_4 , CH_3F , CH_2F_2 , CHF_3 , and CF_4 molecules at (a) 15 eV, (b) 30 eV, and (c) 100 eV. Note that the data for the DCS's for CF_4 are obtained for 35 eV.

ecules; and (ii) another for CH_3F , CH_2F_2 , and CHF_3 , polar molecules. Salient features in the present results are summarized here. (a) At 1.5 eV, DCS's for class (i) show a decreasing trend toward smaller angles below 70° , while those for class (ii), i.e., all partially F-substituted (polar) methanes,

TABLE I. Ratios of DCS's at 60° and 30° eV.

Ratio of the number of F atoms	Ratio of DCS's	
1.3–1.5	$\frac{\text{CF}_4}{\text{CHF}_3} = 1.2$	$\frac{\text{CHF}_3}{\text{CH}_2\text{F}_2} = 1.14$
2	$\frac{\text{CH}_2\text{F}_2}{\text{CH}_3\text{F}_1} = 1.31$	$\frac{\text{CF}_4}{\text{CH}_2\text{F}_2} = 1.37$
3	$\frac{\text{CHF}_3}{\text{CH}_3\text{F}} = 1.49$	
4	$\frac{\text{CF}_4}{\text{CH}_3\text{F}} = 1.79$	

rapidly continue to grow in small angles, resulting in a strong forward peak, a typical characteristic due to a long-range dipole interaction of polar molecules. (b) At larger angles above 100° , again, these two classes of molecules show a deviation in DCS's, causing a less strong backward scattering for class (i). (c) At 30 eV, the sharp forward peaking in DCS's at small angle scattering below 50° is very similar and a common feature to all molecules, indicating the lesser effectiveness of the dipole interaction at this energy. (d) Within each class of molecules, DCS's are similar in shape with respect to the scattering angle at all energies, and as the energy increases above 20 eV the shapes of all DCS's become more similar (except for a structure at 60° ; see below), although the magnitude is rather different. (e) The conspicuous shoulder begins to appear around 60° – 65° as each hydrogen is replaced by a fluorine atom, and the magnitude of the structure is proportional to the number of F atoms in a molecule, the *fluorination effect*. (f) At higher energies above a few tens of eV, the order of the magnitude of the DCS shows more complicated features and does not appear to depend strongly on molecular natures (the number of F atoms in a molecule, for example). Particularly, it shows a much more complicated trend both for small-scattering ($<50^\circ$) and large-scattering ($>100^\circ$) angles. (g) Lastly, at above 30–50 eV, more undulations at small angles below 50° can be seen, especially for those molecules that contain many F atoms, suggesting another type of *fluorination effect* due to the interference from multicenter scattering.

In order to obtain a better understanding of the interesting features above, a few simulations based on the continuum multiple-scattering (CMS) method [11] and *ab initio* molecular structure calculations by using the GAMESS program [12] have been carried out. Note that when the atomic size goes from H to F atoms, it increases a mere 11%, and this size difference is unlikely to account for a majority of the characteristics in the DCS discussed above. First, we have focused on the origin of the shoulder at the intermediate angle region as exemplified in Fig. 1(b). Ratios of all DCS's at 60° and 30 eV are tabulated in Table I. These results show that when the ratio of the number of fluorine atoms is similar; for example, in the range 1.3–1.5, then the ratio of the DCS is found to be nearly identical to the value of 1.2; and when the ratio of the number of F atoms increases to a factor of 2, then the ratio of the DCS also increases to a value of ~ 1.3 . This trend also holds for the case of a larger ratio. One would

expect that when the size of the atom increases by a factor of 1.2, for example, the corresponding cross section should increase roughly $(1.2)^2$, which is consistent with the present measurement. This apparently suggests that the characteristic is due to the fluorine atom in a molecule, because no shoulder is observed for CH_4 , and to the fact that the shoulder at 60° grows as the number of fluorine atoms increases in a molecule, as in the case where the additivity rule of a F atom holds. Generally, a H atom is known to be a weak scatterer, and makes a small contribution to the scattering process. These features that are due to a F atom in a molecule are strongly visible, and appeared in all the energy regions we studied.

A test CMS calculation reveals that this shoulder arises because of a combination of, primarily, a mixing of many partial waves, particularly a mixing of d - and f -partial waves and a background, and, secondarily, the effect of the a_1 , b_2 , e , and T_2 resonances seen at above 20 eV. As the number of fluorine atoms increases causing the stronger deviation from the spherical symmetric shape, consequently the large number of partial waves contributes to scattering events resulting in a stronger mixing of these partial waves and, hence, an occurrence of the prominent structure. The present CMS calculations reproduce a general trend of the measured DCS's, except for the magnitude, as a function of the number of F atoms for intermediate energies. In the 30-eV calculation, by artificially turning the exchange and polarization potentials on and off in the CMS, we have observed that the small ($<30^\circ$) and large ($>90^\circ$) angle scattering regions are more sensitively affected, while intermediate angle regions are rather weakly sensitive to these changes of the potential. This clearly indicates that the incoming electron is influenced mainly by the static potential, i.e., the charge distribution of the target molecule, and therefore the structure owes much to this potential. This is the signature of the target's electronic structure reflecting more sensitivity from the fluorine atom. A hydrogen atom is a weak scatterer and its effect on scattering observables may be considered to be less significant.

For a resonance, we have examined electronic structures by using the *ab initio* method, and orbital energies thus obtained are shown in Fig. 2. Note that we have fixed molecular geometries at each equilibrium position in the calculation. All orbitals with negative values are occupied orbitals, and the highest (smallest in value) of all corresponds to the highest occupied molecular orbital (HOMO), while those with positive energies are unoccupied orbitals, and the one in the lowest corresponds to the lowest unoccupied molecular orbital (LUMO). All unoccupied molecular orbitals (UMO's) are known to cause shape resonances, which are seen experimentally as broad humps in total cross section, normally in the region around 2–15 eV. In the present calculation, a series of UMO's is found in the energy region of a couple of eV's and above, and they are more densely populated around 20–30 eV, resulting in more shape resonances at higher-energy regions. These a_1 , b_2 , and e resonances are generally observed experimentally at above a few eV to the 15-eV region [1], which is consistent with the present molecular calculations. Even when only one F atom is replaced by a H atom in CH_4 , the characteristics of CH_4 and CH_3F_1 are found to differ rather substantially at higher UMO's, as is obvious

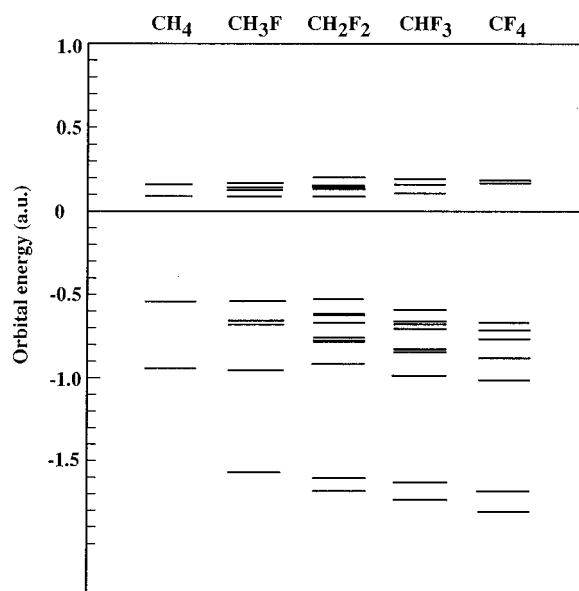


FIG. 2. Orbital energies for CH_4 , CH_3F_1 , CH_2F_2 , CH_1F_3 , and CF_4 .

in Fig. 2, indicating, again, a strong F-atom effect. (As a measure of the present precision, the LUMO's are found to be located at 2.503, 2.503, 2.626, and 2.775 eV for CH_4 , CH_3F_1 , CH_2F_2 , and CH_1F_3 , in the a_1 symmetry, and 4.634 eV for CF_4 in the T_2 symmetry, respectively.)

It should be interesting to discuss the similarity and dissimilarity between the present DCS's, particularly for CH_4 and CF_4 , and those of a neon atom [13], which is expected to lead us to some clues to an understanding of more underlying physics of electron scattering from these polyatomic molecules. As for the number of electrons in a target, Ne and CH_4 have ten electrons forming isoelectron systems, and hence some similarities in various physical quantities like the photoionization cross section have been pointed out earlier in these two targets [14]. Intuitively, one would expect a similarity in both DCS's in shape (angle and energy dependencies), at least for higher energies because of the similar electronic structure and the spherical symmetric shape. When a F atom is replaced with one of the H atoms in methane, the F atom tends to be more negatively charged because of its stronger electron affinity than that of a carbon atom, and as the number of F atoms (and hence, the total number of electrons) increases, one might expect that it should quickly begin to depart from the feature seen in the Ne atom. However, surprisingly, the general shape of the DCS's for fluoromethanes and methane is found to look quite similar in all angles at intermediate energies. This observation leads us to speculate that for smaller scattering angle (that is, a larger impact parameter) than a few tenths of a degree, an incident electron may "see" primarily a negatively charged F ion (Ne-like electronic structure), and this view may become more realistic when all H atoms are replaced with F atoms, i.e., the formation of CF_4 . Scattering effects from C and H atoms are rather weak, and may make a secondary contribution, as noted earlier, while the contribution from F atoms dominates rather overwhelmingly. The DCS of Ne shows a weak shoulder near 60° , which appears to coincide well with that seen in all F-substituted methanes above, followed by a

sharp dip near 100° before it steeply rises again at much larger angles. The origin of the sharp drop near 100° for the Ne-DCS, known as a "critical minimum," may be similar in nature to that seen in CH_4 . However, the dip in Ne and CH_4 may be different from that in fluoromethanes because of different electron charge distributions and molecular structures "seen" by the impinging electron. Nevertheless, it is very intriguing to observe the similar sharp dip at the nearly identical scattering angles in all molecules studied, which also suggests strongly that the incoming electron appears in fact to "see" the dominant atom in a molecule, in this case a F atom. It is quite important to recognize that the similarity of this feature still remains, even after the rotational averaging; that is, a strong influence of a F atom and a weak contribution from a H atom in these molecules [15].

In conjunction with the atomic residue in a molecule, the DCS's at small angle below 40° at 100 eV, for example, show some undulations, or wavy structures, particularly for CHF_3 and CF_4 . We have suspected that these undulations arise from the interferences, due to the multiple-scattering center, by F atoms in CF_4 , which may be used as a tool for structural analysis. By using a simple analysis based on the independent-atom model [16], in which the scattering can be expressed as a superposition of complex spherical amplitudes from each atomic center, the DCS is the sum of the term from all single atomic parts and that of a molecular interference would be yielded. Then, by taking the Fourier transformation of the DCS, one would obtain a radial distribution that relates to the interatomic distance and connects

directly to the experimental information of the position of the F atom in a molecule. This approach is valid for high-energy scattering above a few tens of eV. We have applied the procedure to the present case. The result obtained by using the DCS at 100 eV for CF_4 is that a F-atom position is found to be at about 1.33 \AA from a carbon atom in the molecular center; compared with experimentally determined value of 1.32 \AA [17], which is in reasonable accord. This reasonable agreement of the position of the F atom seems to support the validity of our simple model and the possible use of this technique for molecular structure analysis. Therefore, a more careful and systematic analysis of these structures would be important and interesting for establishing this method.

We add one last additional note that vibrational excitation processes for these molecules have also been investigated, and clearer and more pronounced structures in DCS's have been observed, as expected, because of a strong mass disparity between H and F atoms. These findings should also offer much knowledge of vibrational motion in molecules and their couplings with other freedoms of motion, and study along these lines is underway.

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