Theoretical study of electron scattering from CH_2F_2 molecules

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Abstract. Vibrationally elastic cross sections for electron scattering from difluoromethane (CH_2F_2) are calculated at the collision energies 3–30 eV. No elaborate study for the system has been published to date. Present calculation is based on the fixed-nuclei approximation. As for an interaction potential, effects of an *ab initio* electrostatic, electron-exchange and target polarization are taken into account. The latter two effects are considered by means of a model potential approximately. The closure formula is employed to obtain a converged cross section. The agreement between the present differential cross section and the experimental one is generally good. The integral and momentum transfer cross sections are estimated theoretically for the first time.

1. Introduction

Electron scatterings from hydrocarbon (C_mH_n), fluorocarbon (C_mF_n) and fluorohydrocarbon ($C_lH_mF_n$) molecules are fundamental processes in various fields, such as gaseous electronics, plasma chemistry, planetary science and astrophysics [1, 2]. From a practical point of view, a series of cross sections for these molecules are especially in great demand because of the application to plasma processing in the semiconductor industry. Responding to the demand, vibrationally elastic and inelastic cross sections have been measured for a number of molecules (see e.g. [3]) though the range of the collision energy and the target molecules treated are very limited.

   In the present paper, a theoretical work on the vibrationally elastic scattering of electrons from difluoromethane (CH_2F_2) molecules is reported. No elaborate study for the $e^- + CH_2F_2$ system has been published to date to the best of the author's knowledge, although many theoretical approaches for CH_4 (see [4] and references therein) and several ones for CF_4 (see [5] and references therein) have been reported. A CH_2F_2 molecule belongs to the C_{2v} point group, as H_2O and H_2S molecules do but with a more complicated molecular structure. Previously, the elastic scatterings of electrons for two kinds of polar molecules H_2O and H_2S have been studied by the group of the present author [6, 7]. The resulting differential cross sections (DCSs) were both in very good agreement with the corresponding experimental data by Johnstone and Newell [8] for H_2O and Gulley *et al* [9] for H_2S. Since a CH_2F_2 molecule has a very strong dipole moment and two bulky fluorine atoms, the contribution of a non-spherical effect to the resulting cross sections must be considered sufficiently.

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In practice, the availability of DCSs for the $e^- + CH_2F_2$ system measured by Tanaka's group [10, 11] and a remarkable development of computational capacity enable the author to apply the present theory to the collision system. Because of the experimental difficulty, the DCSs employed for comparison have been measured for scattering angles (θ) neither smaller than $15°$ nor larger than $130°$. Theoretical studies therefore play an important role in understanding the complete picture of the elastic scattering. In particular, data of integral and momentum transfer cross sections (abbreviated as ICSs and MTCSs, respectively, from now on) for the system are given theoretically for the first time in the present paper.

2. Theory

The details of the present theory have already been reported [6]. The present calculation is based on the fixed-nuclei approximation. In order to properly consider the molecular symmetry, the wavefunction of the scattered electron (F) is expanded in terms of the symmetry-adapted angular basis functions X_l^ν [12] as follows:

$$F(\boldsymbol{r}) = \frac{1}{r} \sum_{l\nu} f_{l\nu}(r) \, X_l^\nu(\hat{\boldsymbol{r}}) \tag{1}$$

where $\boldsymbol{r}$ denotes the position vector of the incident electron. The index ν denotes indices collectively specifying an irreducible representation (IR) and those distinguishing the degenerate members of the same l and IR. Throughout this paper, atomic units (au) are used unless otherwise stated.

The interaction potential between an electron and a target molecule is constituted of three terms, that is, electrostatic, electron exchange and polarization ones. The electrostatic potential is obtained from an *ab initio* target wavefunction. As for the electron exchange, use is made of the Hara version of the free-electron gas exchange model potential originally introduced by Hara [13]. The effect of polarization is described through the parameter-free correlation-polarization model. The detailed form of the model is given by Padial and Norcross [14]. For the latter two terms of the potential, the same electron density obtained from the target wavefunction is used as for the electrostatic potential. In a manner similar to equation (1), the interaction potential V is expanded as

$$V(\boldsymbol{r}) = \sum_{\lambda\mu} V_{\lambda\mu}(r) \, X_\lambda^\mu(\hat{\boldsymbol{r}}). \tag{2}$$

Then, the radial part $f(r)$ in equation (1) satisfies a set of coupled differential equations:

$$\left\{ \frac{d^2}{dr^2} - \frac{l(l+1)}{r^2} + k^2 \right\} f_{l\nu}(r) = 2 \sum_{l'\nu'} \langle l\nu|V|l'\nu' \rangle \, f_{l'\nu'}(r) \tag{3}$$

where $\langle l\nu|V|l'\nu' \rangle$ denotes the interaction matrix as

$$\langle l\nu|V|l'\nu' \rangle = \int d\hat{\boldsymbol{r}} \, X_l^{\nu*}(\hat{\boldsymbol{r}}) \, V X_{l'}^{\nu'}(\hat{\boldsymbol{r}}). \tag{4}$$

By solving equation (3) with an appropriate boundary condition, we can obtain the scattering matrix. In general, DCS (q) expanded in terms of the partial-wave expansion converges very slowly for a polar molecule, because of a strong interaction caused by the permanent dipole moment. To avoid this difficulty, the closure formula for the quantity calculated by the Born approximation for the dipole interaction is employed as

$$q(\theta) = q^{\text{Born dip}}(\theta) + \sum_L \left(A_L - A_L^{\text{Born dip}} \right) P_L(\cos\theta). \tag{5}$$

Here, P_L is the Legendre function with Lth order and A_L defined by equation (7) in Okamoto *et al* [6]. $q^{\text{Born dip}}$ depends on the rotational state of the target molecule (for details, see [6]).

3. Numerical calculations

The present calculation of the target wavefunction is made at the equilibrium geometry [15]. The CH₂F₂ molecule is placed by the Cartesian coordinates (in au) as H($\pm 1.706\,20$, 0.0, 2.161 00), C(0.0, 0.0, 1.027 41) and F(0.0, $\pm 2.037\,17$, $-0.439\,41$). In order to generate a multicentred wavefunction of the target molecule in its electronic ground state, the molecular orbital code GAMESS [16] is employed in the self-consistent field approximation. A Gaussian-type-orbital basis set proposed by Lie and Clementi [17] is used for the present calculation. The total energy obtained is $-238.011\,854$ au. The permanent dipole moment given by the target wavefunction is $\mu_z = 0.809$ au, which is compared with the experimental value of 0.778 au [18]. For the long-range part of the polarization potential, calculational values of the polarizability from the target wavefunction are adopted (i.e. $\alpha_{xx} = 14.34$, $\alpha_{yy} = 15.53$ and $\alpha_{zz} = 14.90$ au). In the expansion of equation (2), the terms are retained up to $\lambda = 40$ to sufficiently take the non-spherical effect into consideration. To obtain the cross sections consider the diopole interaction correctly, the dipole term ($\lambda = 1$) is adjusted to have the asymptotic form which gives the
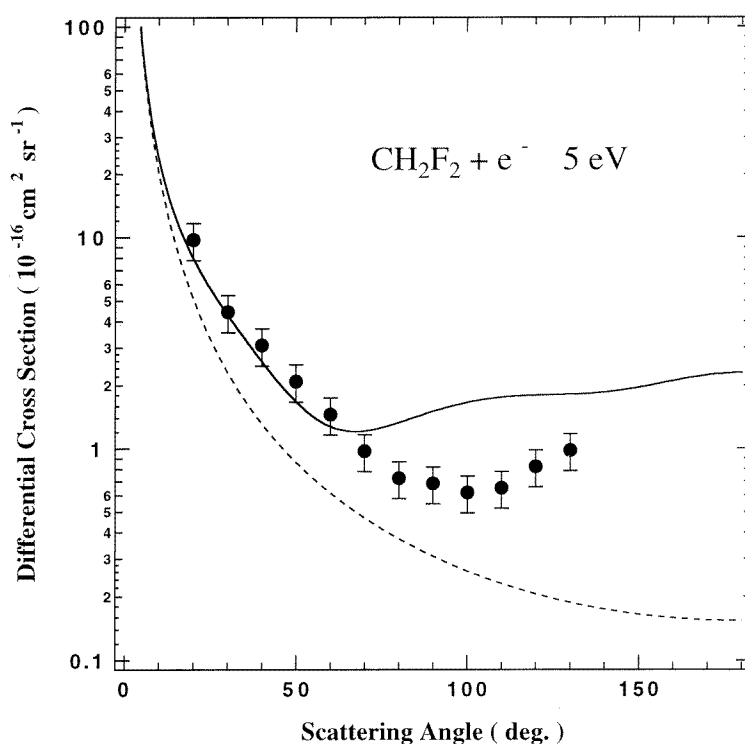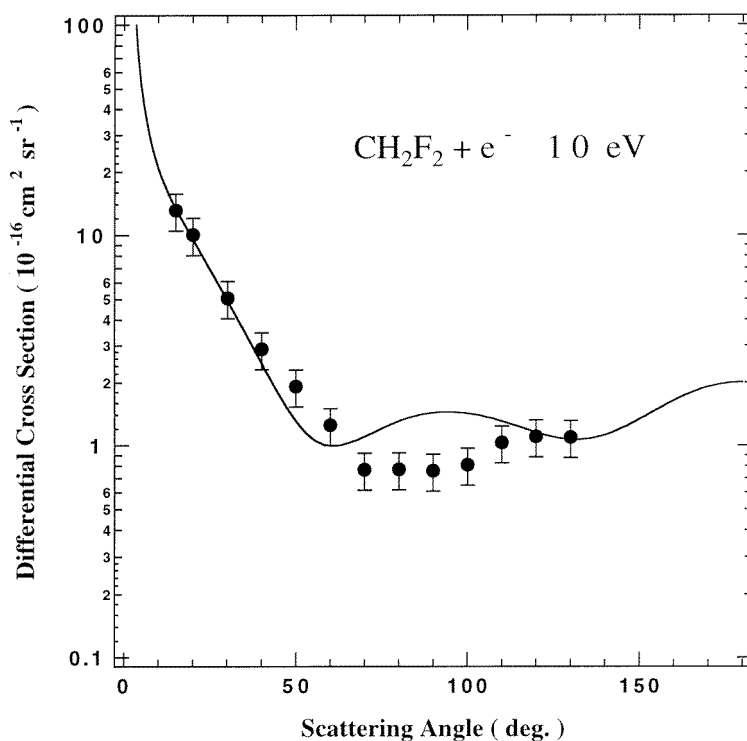

Figure 1. Differential cross section (in 10^{-16} cm² sr⁻¹) for the vibrationally elastic scattering of electrons from CH₂F₂ at the collision energy of 5 eV. The present calculation by the close-coupling method (full curve) is compared with the experiment by Tanaka's group [10, 11] (full circles with error bars) and the present dipole Born calculation (broken curve).

experimental value of the dipole moment (0.778 au). The coupled equations (3) are solved with inclusion of partial waves up to $l = 20$. The rotational energy and transition dipole matrix which are necessary to obtain converged cross sections are derived from Townes and Schawlow [19].

4. Results and discussion

4.1. Differential cross section

Figures 1–5 show the vibrationally elastic DCSs at the collision energies of 5, 10, 15, 20 and 30 eV, respectively. In practice, these DCSs have been calculated with the initial rotational state of CH_2F_2 fixed as the ground one, i.e. $(j\tau) = (00)$. As shown in a previous paper by our group [6], the DCS for a polar molecule depends on the rotational state only in the vicinity of the forward direction (say, at the scattering angle $\theta \leqslant 1°$). The present values of DCSs, therefore, can safely be compared with the experimental data by Tanaka's group [10, 11]. The agreement between the present DCSs and the experimental ones (with an uncertainty of 20%) is generally good. In particular, the present DCSs at 20 and 30 eV well reproduce the shape of the experimental ones (see figures 4 and 5). It is difficult to extrapolate the measured DCSs into the region of scattering angles $\theta \leqslant 15°$ due to a very

Figure 2. Differential cross section for the elastic scattering of electrons from CH_2F_2 at 10 eV. The present calculation by the close-coupling method (full curve) is compared with the experiment by Tanaka's group (full circles with error bars).
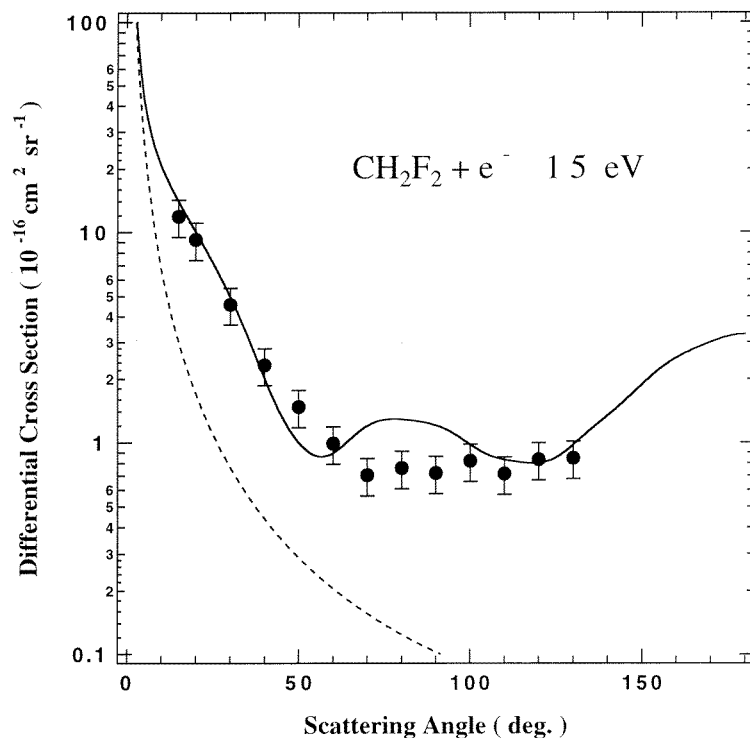
Figure 3. Same as figure 1, but at 15 eV.

Table 1. Integral (Q) and momentum transfer (Q_m) cross sections (in 10^{-16} cm^2) for the vibrationally elastic scattering of electrons from CH_2F_2.

E (eV)	Q(343 K)[a]	Q(00)[b]	Q_m
3	60.51	67.25	25.59
5	48.29	52.36	22.09
7	40.16	43.06	18.74
10	36.65	38.71	16.87
15	32.58	33.96	16.52
20	28.15	29.18	14.74
30	23.63	24.32	11.69

[a] Theoretical cross section averaged over the rotational-state population at the gas temperature of 343 K.
[b] Theoretical cross section fixed the initial rotational state as $(j\tau) = (00)$.

sharp peak caused by the dipole interaction. It should be noted that the present DCSs play a significant role in compensating the experimental data not only in the range of scattering angles $\theta \leqslant 15°$ (but at around 0°) but also $\theta \geqslant 130°$.

Figures 1, 3 and 5 also show the dipole Born DCSs to see the domination of the dipole interaction at the forward direction. At the collision energy of 5 eV, even the dipole Born calculation gives almost the same values of DCS as those by the close-coupling calculation in the range of scattering angles $\theta \leqslant 10°$. As the collision energy increases, the validity of the dipole Born calculation becomes limited to be the forward direction.
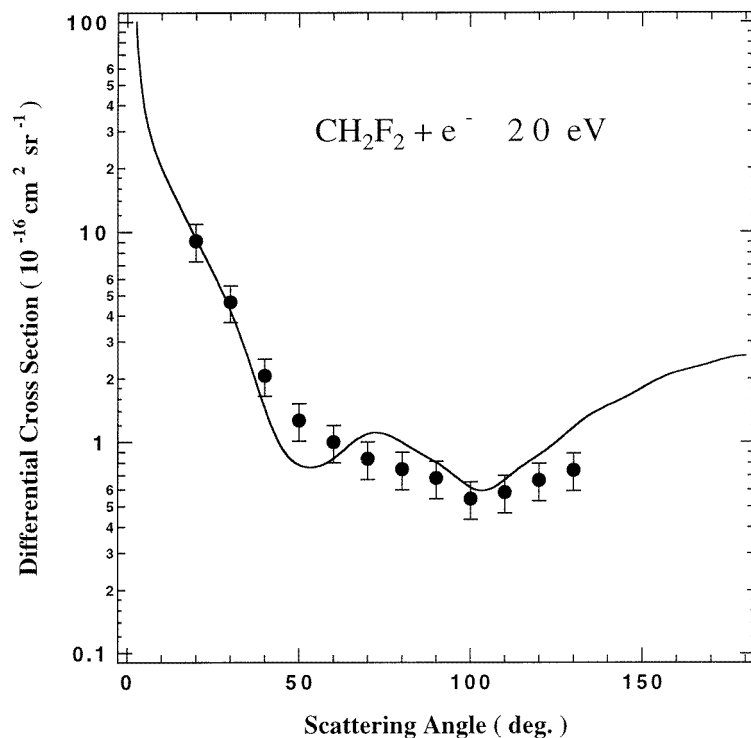
Figure 4. Same as figure 2, but at 20 eV.

4.2. Integral and momentum-transfer cross sections

Table 1 shows the vibrationally elastic ICS(Q) and MTCS(Q_m) at the collision energies (E) of 3–30 eV. Neither experimental nor other theoretical cross sections have been reported so far for both ICSs and MTCSs. The present ICS Q(343 K) (second column) is obtained by being averaged over the distribution of initial rotational states at the gas temperature of 343 K (at which the experiment is carried out). It is noted that at the energy of 3 eV the present ICS Q(00) (third column) with the initial rotational state as $(j\tau) = (00)$ is larger by 6.7×10^{-16} cm^2 than Q(343 K). The difference comes mainly from the DCS in the vicinity of forward direction and becomes smaller as the energy increases (0.7×10^{-16} cm^2 at 30 eV). This trend is similar to that seen in the case of the dipole Born DCS, as is discussed above. The values of Q(343 K) are more reliable than those of Q(00) from the discussion of the previous paper for H$_2$O [6]. In the present calculation, no peak or structure is recognized for both ICSs and MTCSs at the collision energies of 3–30 eV, although a few small peaks are suggested experimentally at around 8 eV [10]. These peaks implied in both ICS and MTCS, however, may be detected in future by means of a more elaborate calculation which, for instance, takes the effects of electron exchange and target polarization into account in a more rigorous manner.
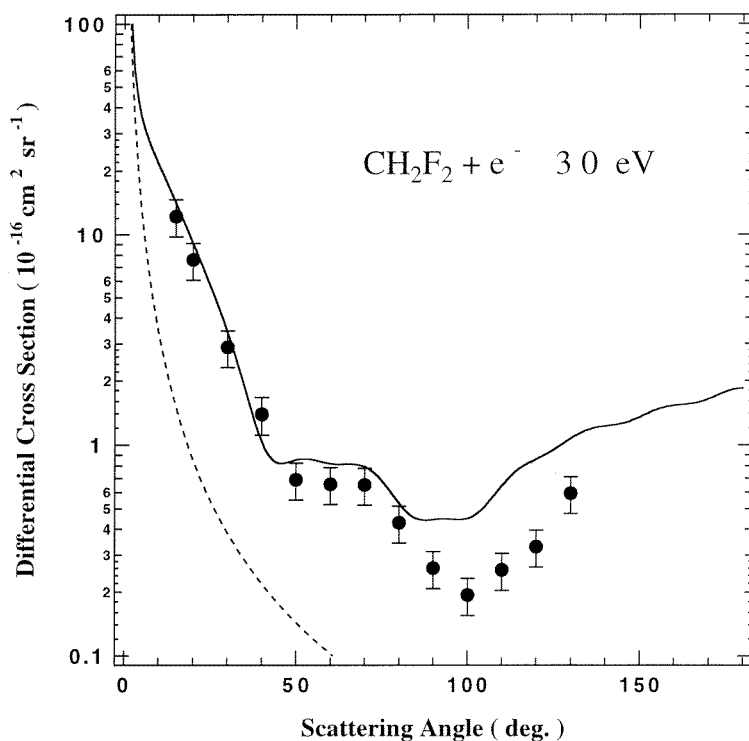
Figure 5. Same as figure 1, but at 30 eV.

5. Conclusions

Vibrationally elastic cross sections for electron scattering from CH$_2$F$_2$ are calculated at collision energies of 3–30 eV. The present calculation is based on the fixed-nuclei approximation. Effects of an *ab initio* electrostatic, electron exchange and target polarization are taken into account. The agreement between the present DCSs and the experimental ones is generally good. The ICSs and MTCSs are estimated theoretically for the first time. It is hoped that the present study will help to develop both experimental and theoretical research of this collision system in the future.

Acknowledgments

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