Elastic scattering of electrons by methane molecules

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Abstract. Vibrationally elastic cross sections for electron collisions with CH_4 are calculated with an *ab initio* electrostatic potential. Effects of electron exchange and target polarization are taken into account approximately. Differential cross sections (DCS) are calculated for the electron energies 10–50 eV and compared with recent measurements. Comparing with the result of a spherical potential model, effects of anisotropy of the molecule are made clear. Integral and momentum-transfer cross sections are also calculated to see the validity of the extrapolation procedure taken in deriving those cross sections from experimental DCS.

1. Introduction

Electron collisions with CH_4 have been studied by many people for the following reasons. Methane is an important constituent of the atmospheres of the outer planets (Atreya 1986). It is one of the key trace elements which could change the upper atmosphere of the earth (Roble and Dickinson 1989). Recently methane has been of interest for plasma processing, particularly for deposition processes (Morgan 1992). It also plays a role in edge plasmas of fusion devices (Tawara *et al* 1992). Theoretically methane is interesting because it is a simple but typical hydrocarbon molecule.

Elastic cross sections for $e + CH_4$ collisions have been calculated by a number of authors (see McNaughten *et al* 1990, Lengsfield *et al* 1991 and references therein). Most of the calculations, however, are concentrated in the region of electron energy below 10 eV, particularly in the region of the Ramsauer–Townsend minimum at around 0.3 eV. It has been generally believed that, *for collision energy above 10 eV, the scattering is determined by a simple model of spherical interaction potential.*

Electron elastic cross section has been measured several times for CH_4 (e.g. Shyn and Cravens 1990, Boesten and Tanaka 1991). Agreement among the differential cross sections (DCS) obtained by different authors is fairly good. The integral elastic cross sections (Q) and the momentum-transfer cross sections (Q_m) derived from different experimental DCS are not necessarily in agreement with each other. Furthermore those values of Q and Q_m are sometimes inconsistent with the total scattering cross sections (Q_T) obtained with an attenuation measurement and the Q_m deduced from a swarm analysis, respectively. This inconsistency is mainly due to the difficulty in extrapolating the measured DCS to the forward and back directions. In this respect, it is very helpful to produce reliable DCS theoretically.

In the present paper, cross sections for elastic scattering (more strictly, vibrationally elastic scattering, because it is difficult to experimentally resolve rotational transitions)

of electrons from CH_4 are calculated in the energy region 10–50 eV. The target molecule is described by an *ab initio* multicentred wavefunction and account is taken of the effect of electron exchange and target polarization. The resulting DCS, and the Q and Q_m calculated therefrom, are compared with measurements. By comparing with the spherical potential model, the effect of the anisotropy of the target is made clear.

2. Theory

Scattering of electrons from methane molecules is considered in the fixed-nuclei approximation. The present method of calculation is the same as that used previously for water molecules (Okamoto *et al* 1993). A general description of the theory is given in the previous paper.

In brief, the interaction between an electron and the methane molecule is represented by a local potential $V(r)$. It consists of three terms, i.e., the electrostatic (V^{st}), electron exchange (V^{ex}) and target polarization (V^{pol}) potentials. V^{st} is obtained from the target charge density in a standard manner. V^{ex} is taken to be the Hara version of the free-electron gas model (Hara 1967). For V^{pol}, we adopt the correlation-polarization potential proposed by Padial and Norcross (1984), which has an asymptotic part in the form $-\alpha_0/(2r^4)$ with α_0 being the static polarizability of methane. To properly consider the molecular symmetry, the potential is expanded in terms of the symmetry-adapted angular basis functions (SAFs)

$$V(r) = \sum_{\lambda v} V_{\lambda v}(r) X_\lambda^v(\hat{r}).$$ (1)

Here $X_\lambda^v(\hat{r})$ is the SAF and the index v denotes collectively the indices specifying the irreducible representation and distinguishing the degenerated members (Burke *et al* 1972).

Similar to expansion (1), the scattering wavefunction $F(r)$ is written as

$$F(r) = \sum_{lv} r^{-1} f_{lv}(r) X_l^v(\hat{r}).$$ (2)

The radial part $f_{lv}(r)$ in equation (2) then satisfies the coupled differential equations (atomic units being used in the present paper unless otherwise stated)

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

where

$$\langle lv | V | l'v' \rangle = \int d\hat{r} X_l^v(\hat{r})^* V X_{l'}^{v'}(\hat{r}).$$ (4)

Solving equation (3) with an appropriate boundary condition, we obtain the S matrix, from which the relevant cross sections are determined (for details, see Okamoto *et al* 1993).

3. Numerical calculation

The electronic structure of methane molecule in its ground state has A_1 symmetry. To generate the target wavefunction, an *ab initio* molecular orbital code GAMESS (the

North Dakota State University version, see Schmidt *et al* 1990) is employed in the SCF approximation. The origin of the coordinates is placed at the carbon atom and the z-axis is taken along one of the C_2 symmetry axes. The hydrogen atoms are located at the corners of a cube and their coordinates are $(L, -L, -L)$, $(-L, L, -L)$, $(-L, -L, L)$, and (L, L, L) with $L = R/\sqrt{3}$, R being the equilibrium C–H distance. Here R is taken to be 2.0541 au (Hirota 1979).

After testing a number of basis sets, we have chosen the one proposed by Lie and Clementi (1974) for the present calculation. It is comprised of 105 primitive Gaussians contracted to 75 basis functions. For carbon, the primitive set (13s8p2d) is contracted to [7s4p2d] and for hydrogen, (8s2p) to [5s2p]. The total energy given by this wavefunction is −40.2155 au. The octupole and the hexadecapole moments obtained are, respectively, 2.40 au and −7.58 au. From the target wavefunction, the electron density is calculated for the evaluation of the interaction potential. For the asymptotic part of the polarization potential, the experimental value of the static polarizability ($\alpha_0 = 17.97$ au; Buckingham and Orr 1969) is adopted.

In the expansion of the potential (equation (1)), we retain the terms up to $\lambda = 8$. To obtain the SAFs for the T_d symmetry, use is made of an algorithm proposed by Fox and his colleagues (Fox and Ozier 1970, Fox and Krohn 1977). The coupled equations (3) are solved with inclusion of partial waves up to $l = 8$ for 10–20 eV and $l = 9$ for 30 and 50 eV. For partial waves higher than this, the polarized Born approximation is used to obtain the relevant elements of the T matrix.

4. Results and discussion

4.1. Differential cross section

Figures 1–5 show the differential cross sections (DCS) calculated at 10, 15, 20, 30 and 50 eV and compare them with the results of the two recent experiments (Shyn and Cravens 1990, Boesten and Tanaka 1991). The agreement between the theory and
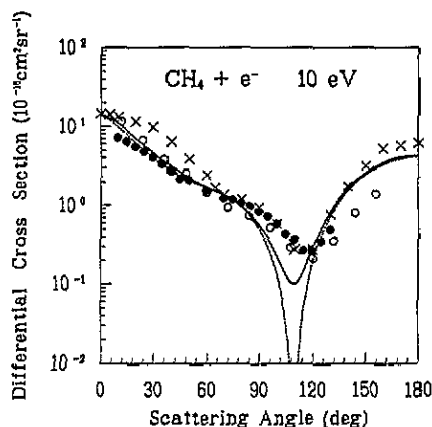

Figure 1. Differential cross sections (in 10^{-16} cm^2 sr^{-1}) at electron energy 10 eV. The calculation with all the potential terms (full curve) is compared to that with only the spherical term retained (dotted curve). Also a comparison is made with the calculation by McNaughten *et al* (1990) (crosses) and the experiments of Boesten and Tanaka (1991) (full circles) and Shyn and Cravens (1990) (open circles).
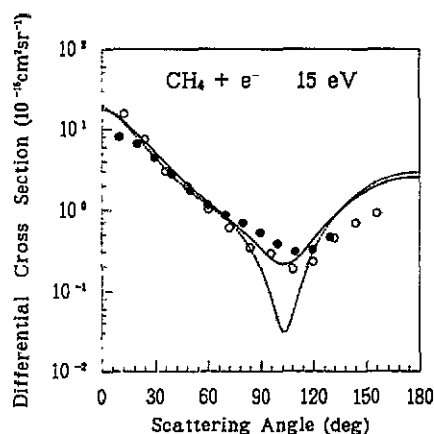
Figure 2. Differential cross sections (in 10^{-16} cm^2 sr^{-1}) calculated at 15 eV with the full potentials (full curve) and the spherical one (dotted curve). They are compared with experimental data obtained by Boesten and Tanaka (1991) (full circles) and Shyn and Cravens (1990) (open circles).
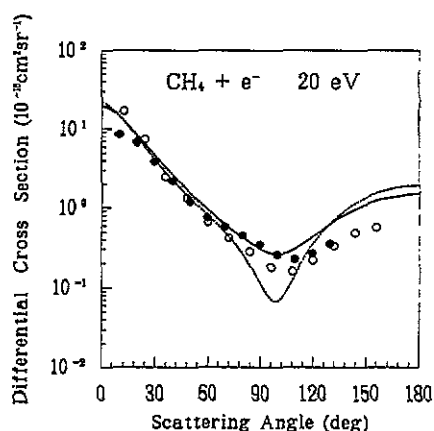

Figure 3. As figure 2, but at 20 eV.

experiment is generally good. In the region of large angles (i.e. $>130°$), the present DCS is larger than the experimental value of Shyn and Cravens. From the comparison of the resulting momentum-transfer cross section (Q_m) with the swarm data (see section 4.2), however, the DCS of Shyn and Cravens in the large angle region might be too small. (Note that a considerable fraction of Q_m comes from the DCS at angles larger than $130°$.)

As mentioned in the introduction, a spherical-potential model is often used to calculate the elastic cross section for CH$_4$, especially in the region of energy above 10 eV. To test the model, we retain only the term with $\lambda = 0$ in equation (1) and calculate DCS. The resulting DCS are also shown in the figures. The DCS of the spherical model are not much different from those obtained with the real anisotropic potential, except in the region of the minimum at around $100°$. At the minimum of the DCS, however, the anisotropy of the potential is indispensable to reproduce the experimental data. At
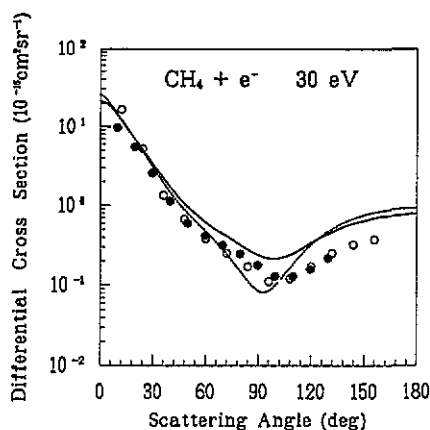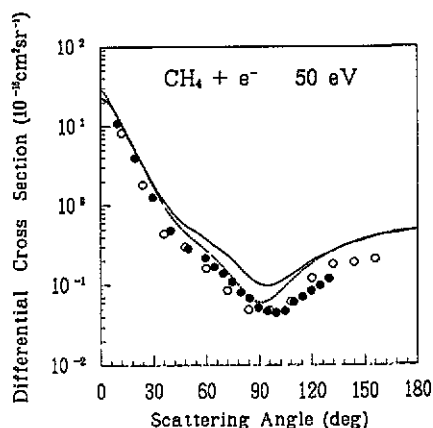
Figure 4. As figure 2, but at 30 eV.

Figure 5. As figure 2, but at 50 eV.

50 eV, the calculation with the spherical potential seems in better accord with the experiment than the calculation taking anisotropy into account. In this case, however, electronically inelastic processes would have a significant effect on the calculation of the elastic cross section. That effect could reduce the cross section with the anisotropic potential to result in agreement with the experiment (Jain 1986).

Recently two elaborate calculations (McNaughten *et al* 1990, Lengsfield *et al* 1991) have been reported on elastic scattering in the $e + CH_4$ system. Lengsfield *et al* applied the complex Kohn variational method to the process. They reported DCS only for collision energy up to 7.5 eV. McNaughten *et al* used a method similar to the present calculation, but they treated electron exchange in a more rigorous manner. They calculated cross sections for 0.1–20 eV. Only the DCS at 10 eV can be compared with the present calculation. Figure 1 shows the comparison. In the region 60–120° the calculation of McNaughten *et al* agrees better with the experiment than ours, but at smaller angles (<60°), the present result is better. As is shown later, the integral cross section of McNaughten *et al* is too large to be consistent with the measured value of Q_T.

Table 1. Integral (Q) and total scattering (Q_T) cross sections for electron collisions with methane. All cross sections are in 10^{-16} cm^2.

	Electron energy (eV)				
	10	15	20	30	50
Q (present)	22.19	20.47	17.61	13.30	8.91
Q (expt)[a]	19.8	17.6	15.3	11.3	5.0
Q (expt)[b]	23.02	18.27	14.41	9.49	6.57
Q (calc)[c]	27.58	23.28	19.85		
Q_T[d]	24.80	21.10	18.60	15.40	12.00

[a] Experimental data obtained by Shyn and Cravens (1990).
[b] Experimental data obtained by Boesten and Tanaka (1991).
[c] Theoretical cross sections obtained by McNaughten *et al* (1990).
[d] Recommended values by Kanik *et al* (1993).

4.2. Integral and momentum-transfer cross sections

Table 1 shows the integral cross sections (Q) obtained in the present calculation. In the table, the present values are compared with the results of the two measurements (Shyn and Cravens 1990, Boesten and Tanaka 1991) and the recent calculation by McNaughten *et al* (1990). When an integral cross section is derived experimentally, an extrapolation of the measured DCS is needed into regions where measurements are not possible. This gives rise to some ambiguity in the resulting Q. To avoid this ambiguity, we also compare the present value of Q with the experimental data on the total scattering cross section (Q_T). The latter quantity includes the contribution from inelastic processes so that Q must be less than Q_T. There are a large number of papers reporting measurement of Q_T. Recently Kanik *et al* (1993) surveyed those papers and determined the best values of Q_T. In table 1 their Q_T are presented to compare with the present Q.

It should be noted first that the present Q is consistent with the best data on Q_T, while the calculation by McNaughten *et al* gives Q larger than Q_T. This reflects the difference in the DCS of the two calculations mentioned in the previous subsection. In this case, the two sets of experimental values of Q are in fair agreement with each other. Our values of Q do not much differ from the experimental data.

The present result of the momentum-transfer cross section (Q_m) is compared in table 2 with the results of the two beam experiments and the calculation by McNaughten

Table 2. Momentum-transfer cross sections (in 10^{-16} cm^2) for electron collisions with methane.

	Electron energy (eV)				
	10	15	20	30	50
Q_m (present)	15.83	11.97	9.05	6.02	3.42
Q_m (expt)[a]	10.5	7.5	5.4	3.5	1.8
Q_m (expt)[b]	20.21	11.78	6.95	3.87	2.22
Q_m (calc)[c]	19.53	13.10	9.56		
Q_m[d]	15.5	12.6	8.80	4.76	

[a] Experimental data obtained by Shyn and Cravens (1990).
[b] Experimental data obtained by Boesten and Tanaka (1991).
[c] Theoretical cross sections obtained by McNaughten *et al* (1990).
[d] Cross sections obtained from a swarm analysis (Davies *et al* (1989).

et al (1990). The momentum-transfer cross section has the same ambiguity as for Q, if obtained from experimental DCS. The cross section Q_m can be derived directly from a swarm experiment. The Q_m obtained in a recent swarm analysis (Davies *et al* 1989) is shown in table 2 for comparison. The present Q_m is in good agreement with the swarm data. The results of the two beam experiments differ very much from each other and, at 10 eV, one is much larger and the other is much smaller than the swarm value. Boesten and Tanaka (1991) fitted their DCS with an analytical form based on a spherical potential. As is shown in the previous subsection, a spherical model is fairly good except in the region of a minimum DCS at around 100°. Boesten and Tanaka fitted their DCS even in the minimum region with a spherical model. There may have arisen an increase in the DCS extrapolated in the large angle region, resulting in too large a Q_m at 10 eV. (Though not shown here, their Q_m is too large at 5–10 eV.)

The calculation by McNaughten *et al* gives Q_m in agreement with the present value at 15 and 20 eV. At 10 eV, however, their Q_m is much larger than ours and the swarm data.

Finally it is worth comparing the present calculation with that of Gianturco and his colleagues (Gianturco *et al* 1987, Gianturco and Scialla 1987). In their calculation, they followed a procedure very similar to ours, but they concentrated mainly on the lower energy region (i.e. <20 eV). They calculated integral elastic cross sections, Q, with using several different models of exchange potential. Their values of Q calculated with the model exchange potential of Hara are read from their figure to be 21.2×10^{-16} cm^2 and 17.7×10^{-16} cm^2 at 10 and 20 eV, respectively. These values can be compared with the present calculation (table 1) and the agreement is good. The only difference in the two calculations is the target wavefunction employed. Gianturco's group used a one-centre SCF wavefunction, while the present calculation is based on a multicentred one. From the above comparison, we can conclude that the two functions give almost the same (integral) cross section, at least at energies 10–20 eV. It should be mentioned, however, that the wavefunction of Gianturco *et al* produces quite a large octupole moment (3.46 au; Gianturco and Thompson 1976), compared with the present (2.40 au) or other SCF-type wavefunctions (see, for example, Diercksen and Sadlej 1985). This may affect the angular distribution of the scattered electrons. It is not possible, however, to compare DCS, because no corresponding DCS was reported by Gianturco. (Gianturco *et al* (1987) shows DCS at 10 eV, but based on another model of exchange potential.) No momentum-transfer cross sections are available either for comparison.

After testing several different models of the exchange potential, Gianturco and Scialla (1987) concluded to recommend the modified semiclassical exchange approximation (MSCE) for use. Their cross section with the MSCE is somewhat larger than the present or their cross section obtained with the Hara model. When compared with the total scattering cross section Q_T (table 1), their cross section with MSCE (23.74×10^{-16} cm^2 at 10 eV and 18.99×10^{-16} cm^2 at 20 eV) is rather too large, particularly at 20 eV. Any comparison of DCS would be interesting.

5. Conclusion

In the present paper, differential cross sections (DCS) have been calculated for the elastic scattering of electrons from CH$_4$. The calculation is based on an *ab initio* electrostatic

potential taking account of electron exchange and target polarization. The DCS calculated at 10–50 eV of the collision energy are in generally good agreement with the results of recent measurements. Comparing with the DCS obtained in a spherical-potential model, the validity of the latter model was tested. The model was found to give a cross section not much different from that obtained taking anisotropy into account. The only exception is the minimum of DCS at around 100°. The spherical model gives too deep a minimum.

From the present DCS, a calculation was made of integral (Q) and momentum-transfer (Q_m) cross sections. The integral cross section obtained is consistent with the total scattering cross section recommended by Kanik *et al* (1993). The present Q_m is very close to the value determined from a recent swarm analysis. The cross sections Q and Q_m obtained from experimental DCS often have some uncertainty due to the necessary extrapolation to the forward and backward directions. The present calculation would be helpful in delineating the uncertainty inherent in the experimental data of Q and Q_m.

Acknowledgments

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