

## Calculation of integral cross sections for vibrationally inelastic electron–methane scattering

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**Abstract.** Integral cross sections are presented for vibrationally inelastic electron–methane scattering. They were calculated by a method which is an extension of the single-centre expansion approach previously applied by us to elastic electron–molecule scattering. The scattering wavefunction is first calculated within the adiabatic nuclei approximation, and is then substituted once into the Lippmann–Schwinger equation in order to correct for non-adiabaticity. This yields inelastic cross sections in good overall agreement with experiment. Threshold peaks are found in the cross sections for excitation of the infrared active modes. The results show that our method is a promising approach with which to investigate the inelastic scattering of electrons from polyatomic molecules.

### 1. Introduction

Cross sections for the scattering of electrons from methane were measured as early as the 1920s, in the pioneering experiments of Brode (1925), Brüche (1927, 1930) and Ramsauer and Kollath (1930). Since then, electron–methane has been one of the most studied examples of electron scattering from polyatomic molecules, and has come to be regarded as a test system by which to compare theory with experiment. There are also practical reasons for studying electron–methane scattering, as it is known to play an important role in the physics of plasmas, atmospheres and the interstellar medium.

The total integral cross sections for electron–methane scattering have been measured recently in several experiments, which include those of Kanik *et al* (1992), Zecca *et al* (1991), Dababneh *et al* (1988), Lohmann and Buckman (1986), Sueoka and Mori (1986), Jones (1985), Ferch *et al* (1985) and Floeder *et al* (1985). The results of these experiments are generally in good agreement, showing a Ramsauer minimum below 1 eV, and a broad shape resonance (caused mostly by the  $T_2$  contribution to the total cross section) centred at about 8 eV. Differential cross sections have been measured for elastic scattering (see references cited in Mapstone and Newell 1992) and for vibrationally inelastic scattering (Lunt *et al* 1994, Boesten and Tanaka 1991, Shyn 1991, Sohn *et al* 1983, Tanaka *et al* 1983 and Rohr 1980). Momentum-transfer cross sections have been measured using swarm experiments (Davies *et al* 1989, Duncan and Walker 1972).

Most of the theoretical studies of electron–methane scattering have been predictions of the elastic cross sections at energies from about 0 to 15 eV. These calculations have employed a variety of methods, such as use of a single-centre expansion (SCE) method

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(Gianturco *et al* 1995), the complex Kohn method (Lengsfeld *et al* (1991)), the Schwinger multichannel method (Lima *et al* 1989), and the *R*-matrix method (Nestmann *et al* 1994).

In treating only vibrationally elastic scattering, the above calculations were able to employ simple descriptions of the nuclear dynamics, and hence concentrate on modelling the electron-CH<sub>4</sub> interaction potential. This approach has proved very successful, since some of the more recent calculations (for example those of Gianturco *et al* (1995) and Lengsfeld *et al* (1991)) have managed to predict cross sections close to the experimental values, using models of the interaction potential that are wholly *ab initio*. A limitation of these calculations, however, is that they do not permit accurate comparisons to be made of the integral cross sections, since (as mentioned above) the experimental integral cross sections are measured for total scattering, and hence include vibrationally inelastic contributions. Better comparisons of these cross sections with experiment could be made if the *ab initio* methods which have been developed for elastic scattering were extended to vibrationally inelastic scattering.

Such calculations would also be useful in interpreting the vibrationally inelastic differential cross sections which have been measured by Rohr (1980), Sohn *et al* (1983) and Lunt *et al* (1994) at energies below 5 eV. These cross sections rise sharply at the thresholds for vibrational excitation, and, in the results of Rohr and Sohn *et al*, develop into quite sharp threshold peaks. These results are consistent with the Born calculations of Davis and Schmidt (1972), who calculated large cross sections near threshold, under the assumption that they resulted from direct excitation of the infrared active vibrations. This direct excitation mechanism was also assumed by Duncan and Walker (1972), who derived inelastic cross sections from the results of their swarm experiments, and found peaks at the thresholds for excitation of the infrared active modes. Whether this mechanism is indeed responsible for the threshold peaks, however, is still open to debate, since attempts to interpret similar peaks in the scattering of electrons from polar molecules have shown that threshold scattering can probably be explained by a variety of mechanisms (Morrison 1988). *Ab initio* calculations would help to resolve this debate, since they make no assumptions about the mechanism for threshold scattering, and would show whether the sharp rises in cross section occur only at the thresholds for excitation of the infrared active vibrations. The differential cross section experiments were not well enough resolved to make this distinction.

Many of the calculations for elastic scattering referred to above were carried out with the nuclear geometry of CH<sub>4</sub> fixed at its equilibrium value. Probably the simplest way to extend them to vibrationally inelastic scattering, therefore, is to work within the adiabatic nuclei (AN) approximation, which assumes that the motion of the nuclei and of the scattering electron are adiabatically separable (Chase 1956). The elastic calculations have then to be repeated at a set of nuclear geometries, and the results used to construct the AN wavefunction. Such calculations are relatively inexpensive, and can usually be expected to give good overall results. If they are to be applied to electron-CH<sub>4</sub> scattering, however, corrections must be made for non-adiabaticity, since the AN approximation is known to fail at low energies (see, for example, Morrison 1986), and hence to give bad descriptions of threshold scattering.

One way to introduce non-adiabatic corrections into the AN wavefunction is to substitute it into the right-hand side of the (exact) Lippmann-Schwinger equation. This yields the 'off-shell' scattering amplitude, a formulation of the scattering amplitude which was first proposed by Shugard and Hazi (1975), and later applied successfully to inelastic electron-H<sub>2</sub> scattering by Morrison and co-workers (Morrison 1986, Morrison *et al* 1991). Off-shell scattering amplitudes for inelastic electron-H<sub>2</sub> scattering have also been calculated

by Rescigno *et al* (1993), using a method based on the Kohn variational principle. This method has recently (Rescigno *et al* 1994) been applied to vibrationally inelastic electron-CH<sub>4</sub> scattering, in calculations of the integral cross sections for excitation of the CH<sub>4</sub> stretching modes at scattering energies between 0–2 eV.

In this paper we present integral cross sections for excitation of all the vibrational modes of CH<sub>4</sub> at scattering energies between 0–12 eV. They were calculated from the off-shell scattering amplitudes, using an extension of the single-centre expansion approach previously applied by us to the elastic scattering of electrons from polyatomic molecules (Gianturco *et al* 1994). Details of this method are given in section 2, where we show that calculation of the off-shell scattering amplitudes from our AN wavefunctions is particularly straightforward. The results are presented and compared with experiment in section 3.

## 2. Theory

### 2.1. The off-shell transition amplitude

To a good approximation, the electron-molecule scattering equations may be formulated in the body-frame (BF), in which the coordinates of all particles are specified with respect to the equilibrium geometry of the molecule, and the effects of molecular rotation are neglected. The wavefunctions must then satisfy

$$[\hat{H}_m(Q) + \hat{T}_e(r) + V(r, Q) - E] \Psi(r, Q) + \int W(r, r', Q) \Psi(r', Q) dr' = 0 \quad (1)$$

where  $\hat{H}_m$  is the vibrational Hamiltonian of the molecule,  $\hat{T}_e$  is the electronic kinetic energy operator and  $Q$  and  $r$  are the BF coordinates of the molecular vibrations and of the electron. The electron-molecule interaction potential is represented by a local term  $V(r, Q)$ , and a non-local term  $W(r, r', Q)$ .

The solutions of equation (1) can be expanded as

$$\psi^{\gamma_0 v_0}(r, Q) = \sum_{lmv} Y_{lm}(\hat{r}) \chi_v(Q) u_{\gamma v}^{\gamma_0 v_0}(r). \quad (2)$$

Here,  $\chi_v(Q)$  are the molecular vibrational wavefunctions, each of which has an energy of  $\epsilon_v$  with respect to the vibrational ground state of the molecule.  $u_{\gamma v}^{\gamma_0 v_0}(r)$  are the solutions of the body-fixed vibrationally close coupled (BFVCC) equations (Chandra and Temkin 1976) and may be defined to satisfy the boundary conditions

$$u_{\gamma v}^{\gamma_0 v_0}(r) \longrightarrow \sqrt{k_v} [r j_l(k_v r) \delta_{vv_0} \delta_{ll_0} \delta_{mm_0} - r \eta_l(k_v r) K_{\gamma v}^{\gamma_0 v_0}] \quad (3)$$

where  $k_v = \sqrt{2E_v}$  and  $E_v (= E - \epsilon_v)$  is the vibrational channel energy in atomic units. Throughout this section the label  $\gamma$  is used to refer to  $(l, m)$ , and the functions  $j_l(kr)$  and  $\eta_l(kr)$  are defined after the usual convention.

The (rotationally summed) integral cross sections for vibrationally inelastic scattering can be calculated directly from the elements of the  $K$ -matrix in (3) by using the formula,

$$\sigma(v_0 \rightarrow v) = \frac{\pi}{k_0^2} \sum_{lm} \sum_{l_0 m_0} |T_{\gamma v}^{\gamma_0 v_0}|^2 \quad (4a)$$

where

$$T = \frac{2iK}{1 - iK}. \quad (4b)$$

An exact calculation of the  $K$ -matrix, however, is feasible for only a very limited range of systems (typically diatomics), since the number of BFVCC equations to be solved is usually unmanageable. The  $K$ -matrix is therefore often calculated using an approximate method, one of the most common of which is the AN approximation (Chase 1956). This approximation assumes that the electron-molecule collision time is much smaller than the period of vibration of the molecule, and that the scattering wavefunctions can therefore be described within the Born-Oppenheimer approximation. The AN scattering wavefunctions are given by

$$\psi_{AN}^{v_0 v_0}(\mathbf{r}, Q) = \chi_{v_0}(Q) \sum_{lm} Y_{lm}(\hat{\mathbf{r}}) u_{\gamma}^{v_0}(r; Q) \quad (5)$$

where  $u_{\gamma}^{v_0}(r; Q)$  are the channel functions obtained from a set of fixed nuclei (FN) calculations at different values of  $Q$ . The FN calculations are performed at  $E_0$  (the ground-state vibrational channel energy), so that  $u_{\gamma}^{v_0}(r; Q)$  may be defined to satisfy the boundary conditions

$$u_{\gamma}^{v_0}(r; Q) \longrightarrow \sqrt{k_0} [r j_l(k_0 r) \delta_{ll_0} \delta_{mm_0} - r \eta_l(k_0 r) K_{\gamma\gamma_0}^{FN}(Q)]. \quad (6)$$

The AN  $K$ -matrix for vibrationally inelastic (and elastic) scattering is given by

$$K_{\gamma v}^{v_0 v_0} = \int \chi_v(Q) K_{\gamma\gamma_0}^{FN}(Q) \chi_{v_0}(Q) dQ. \quad (7)$$

Since the AN approximation assumes the nuclear and electronic motion to be adiabatically separable, its success can only be guaranteed at energies well above threshold. The question as to how much the AN cross sections are in error at lower energies has therefore received much attention. Studies (for example by Morrison 1986) have shown that the AN cross sections do not tend to zero at the threshold for vibrational excitation, and hence that the AN approximation is unsuitable for investigating such phenomena as the threshold peaks in  $\text{CH}_4$ . As a result, alternative formulae have been proposed which attempt to reproduce the correct behaviour at threshold. In one such formula (Morrison 1986), the matrix  $K_{\gamma\gamma_0}^{FN}(Q)$  in equation (6) is replaced by the matrix  $K_{\gamma\gamma_0}^{\text{OFF}}(Q)$ , given by

$$K_{\gamma\gamma_0}^{\text{OFF}}(Q) = -2\sqrt{k_v} \int_0^a j_l(k_v r) U_{\gamma\gamma_0}(r; Q) r dr. \quad (7a)$$

Here,

$$U_{\gamma\gamma_0}(r; Q) = \sum_{l'm'} V_{\gamma\gamma'}(r; Q) u_{\gamma'}^{v_0}(r; Q) + \sum_{l'm'} \int_0^a W_{\gamma\gamma'}(r', r; Q) u_{\gamma'}^{v_0}(r'; Q) r' dr' \quad (7b)$$

and  $a$  refers to any value of  $r$  beyond which the potential can be neglected. This yields the 'off-shell'  $K$ -matrix, a formalism of the  $K$ -matrix which corresponds to the off-shell scattering amplitude that was first proposed by Shugard and Hazi (1975). The off-shell  $K$ -matrix has been tested by Morrison and co-workers (Morrison 1986, Morrison *et al* 1991)

in calculations of inelastic cross sections for electron-H<sub>2</sub> scattering. These calculations showed that the off-shell treatment reproduced the BFVCC cross sections accurately at all energies down to and at threshold, whereas the AN results diverged from the BFVCC values near threshold.

The superiority of the off-shell  $K$ -matrix can be explained by recognizing that it describes the asymptotic behaviour of the functions

$$u_{\gamma v_0 v_0}^{\text{OFF}}(r) = \sqrt{k_v} r j_l(k_v r) \delta_{ll_0} \delta_{mm_0} \delta_{vv_0} + 2 \int_0^a G_{lv}(r, r') \int \chi_v(Q) U_{\gamma v_0}(r'; Q) \chi_{v_0}(Q) dQ dr' \quad (8a)$$

in which

$$G_{lv}(r, r') = k_v r r' j_l(k_v r_<) \eta_l(k_v r_>) \quad (8b)$$

and  $r_<$  and  $r_>$  refer to the lesser and greater of  $r$  and  $r'$ . Equation (8a) is obtained by substituting the AN wavefunction of (5) into the right-hand side of the partial-wave Lippmann-Schwinger equations (LSE), the exact solutions of which are the BFVCC functions,  $u_{\gamma v_0}^{\text{BFVCC}}(r)$ . The off-shell  $K$ -matrix therefore includes non-adiabatic corrections, and corresponds to a wavefunction which is a first-order approximation to the exact BFVCC wavefunction. Higher-order approximations to the BFVCC wavefunction could be obtained by substituting the  $u_{\gamma v_0 v_0}^{\text{OFF}}(r)$  functions back into the LSE, and continuing in an iterative solution of the exact wavefunction. For a sufficiently weak potential, such an iterative calculation would be equivalent to calculating the Born series.

We note that the formula for  $K_{\gamma v_0}^{\text{OFF}}$  given in (7a) is unnecessarily general, since it gives the  $K$ -matrix elements that are obtained when *any* wavefunction with the form of (5) is substituted into the LSE. For the particular case of the AN wavefunction, a simpler formula, containing only a one-dimensional integral (instead of the six-dimensional integral in (7a) and (7b)) can be derived by combining the expression

$$2U_{\gamma v_0}(r; Q) = \left[ \frac{d^2}{dr^2} + k_0^2 - \frac{l(l+1)}{r^2} \right] u_{\gamma}^{v_0}(r; Q) \quad (9)$$

with equation (7a). This yields

$$K_{\gamma v_0}^{\text{OFF}}(Q) = -\sqrt{k_v} \left\{ f_{\gamma}^{v_0}(r; Q) + (k_0^2 - k_v^2) \int_0^a j_l(k_v r) u_{\gamma}^{v_0}(r; Q) r dr \right\} \quad (10a)$$

where

$$f_{\gamma}^{v_0}(r; Q) = [j_l(k_v a) a] u_{\gamma}^{v_0}(a; Q)' - [j_l(k_v r) r] u_{\gamma}^{v_0}(r; Q)' \quad (10b)$$

and a primed function denotes its first derivative with respect to  $r$ . Having calculated the AN wavefunction, therefore, equation (10a) can be used to calculate the off-shell  $K$ -matrix at very little extra expense. With the use of our SCE method (see section 2.2) the integral in equation (10a) is particularly straightforward to evaluate, since the fixed nuclei calculations generate  $u_{\gamma}^{v_0}(r; Q)$  along a set of quadrature points from  $r = 0$  to  $r = a$ .

## 2.2. The SCE method

The results to be presented in section 3 were obtained by calculating the off-shell  $K$ -matrices as described above. The fixed nuclei wavefunctions  $u_{\gamma}^{i0}(r; Q)$ , and  $K$ -matrices  $K_{\gamma\gamma}^{\text{FN}}(Q)$ , were calculated using our SCE method, which has previously been applied to the elastic scattering of electrons from a variety of polyatomic molecules (Gianturco *et al* 1994). The SCE method may briefly be described as follows.

The electronic ground-state wavefunction of the target molecule is represented by a single determinant of SCF-HF molecular orbitals. This is generated using a standard quantum chemistry package, and is then used to calculate the local and non-local parts of the electron-molecule interaction potential in terms of a SCE about the molecular centre of mass. The neglect of excited electronic states is compensated for by including a polarization potential  $V_{\text{pol}}(r)$  in the local potential. At long range  $V_{\text{pol}}(r)$  is given as a function of the molecular polarizability; at short range it is given by a suitable (energy independent) model potential.

The coupled channel equations to be solved contain integrals over  $u_{\gamma}^{i0}(r; Q)$ , which result from inclusion of the non-local potential. This difficulty is overcome by using an iterative procedure based on the use of Padé approximants (Nuttall 1967). In each iteration cycle the coupled channel equations are converted to a set of inhomogeneous differential equations which are solved by propagation using the De Vogelaere algorithm (Lester 1968). This procedure yields a final wavefunction which is calculated along a set of quadrature points in the radial coordinate, and which can therefore conveniently be used to calculate the off-shell  $K$ -matrices. Details of the iterative procedure may be found in Gianturco *et al* (1994) and Lucchese and McKoy (1983).

In solving the coupled channel equations full use is made of the molecular symmetry. The  $Y_{lm}(\hat{r})$  functions in (5) are replaced by the functions  $\chi_{p\mu}^{ih}(\hat{r})$ , each of which transforms as the  $\mu$ th component of the  $p$ th irreducible representation of the molecular point group, with  $h$  distinguishing between different bases with the same  $(p, \mu, l)$ .

## 3. The vibrationally inelastic cross sections

### 3.1. Details of the calculation

Methane has four vibrational modes which have the characteristics shown in table 1. In the calculations, it was assumed that the vibrations could be adequately described within the normal-mode approximation. The vibrational wavefunctions were thus represented by products of Hermite polynomials and used the harmonic frequencies,  $\omega_h$ , of table 1, together with the associated normal coordinates (taken from Gray and Robiette 1979). It was further assumed that coupling between different normal modes could be neglected throughout the whole collision. The validity of this assumption will be discussed below in section 3.2.

**Table 1.** Characteristics of the vibrational modes of methane.  $\omega_h$  and  $\omega_{\text{exp}}$  are the harmonic and experimentally observed vibrational frequencies (in eV), taken from the work of Gray and Robiette (1979).  $\Gamma$  labels the symmetries of the modes under the  $T_d$  point group.

	$\omega_h$	$\omega_{\text{exp}}$	$\Gamma$	Activity
$\nu_1$	0.375	0.362	$A_1$	Raman
$\nu_2$	0.196	0.190	$E$	Raman
$\nu_3$	0.391	0.374	$T_2$	IR
$\nu_4$	0.170	0.163	$T_2$	IR

The calculations were therefore performed independently for each vibrational mode, allowing only one normal coordinate to vary, and fixing the other eight at their equilibrium values. Fixed nuclei calculations were performed at a set of Gauss-Hermite quadrature points along the varied normal coordinate, using the SCE method as described in section 2.2. Rotationally summed integral cross sections were then calculated from the off-shell  $K$ -matrices. In the SCE calculations, the short-range polarization potential was taken to be the free electron gas (FEG) model, as introduced by O'Connell and Lane (1983), and subsequently used by Gianturco *et al* (1995).

Table 2 shows inelastic cross sections for excitation of each vibrational mode from the ground to the first excited state (i.e. for  $\nu_i = 0 \rightarrow 1$ , with  $i = 1, 4$ ). They were calculated from the off-shell  $K$ -matrices as described above. The HF-SCF molecular orbitals were calculated using Gaussian 92 with a 6-31G\*\* basis. The close-coupled equations were truncated at  $l = 15$  in the  $\nu_1$  calculations,  $l = 9$  in the  $\nu_3$  calculations, and  $l = 7$  in the  $\nu_2$  and  $\nu_4$  calculations. Five Gauss-Hermite quadrature points were used along the varied normal coordinate. The iterative procedure was continued until the results of successive iterations differed by less than 0.1%. Under these conditions, the total convergence error in the cross sections was estimated to be less than 5%.

Table 2. Vibrationally inelastic integral cross sections, calculated as described in the text, for excitation of (a)  $\nu_1 = 0 \rightarrow 1$ ,  $\nu_3 = 0 \rightarrow 1$ , and (b)  $\nu_2 = 0 \rightarrow 1$ ,  $\nu_4 = 0 \rightarrow 1$ . The scattering energies ( $E$ ) are given in eV; the integral cross sections (ICS) are given in units of  $0.1 \text{ \AA}^2$ .

	$E$	ICS	$E$	ICS	$E$	ICS	$E$	ICS
(a)								
$\nu_1$	0.3752	0.0038	0.60	0.12	1.75	0.15	8.0	1.93
	0.38	0.028	0.65	0.13	2.0	0.16	9.0	1.77
	0.39	0.047	0.70	0.13	3.0	0.26	10.0	1.54
	0.40	0.060	0.75	0.13	4.0	0.54	11.0	1.34
	0.45	0.093	1.00	0.14	5.0	1.04	12.0	1.17
	0.50	0.11	1.25	0.14	6.0	1.60		
	0.55	0.12	1.50	0.15	7.0	1.91		
$\nu_3$	0.3915	0.06	0.50	1.67	1.2	1.69	6.0	4.19
	0.392	0.15	0.55	1.81	1.4	1.60	7.0	5.14
	0.396	0.44	0.60	1.90	1.8	1.42	8.0	5.40
	0.40	0.59	0.65	1.94	2.0	1.37	9.0	5.21
	0.42	1.03	0.70	1.95	3.0	1.38	10.0	4.70
	0.44	1.27	0.75	1.96	4.0	1.89	11.0	4.20
	0.46	1.45	1.00	1.83	5.0	2.95	12.0	3.74
(b)								
$\nu_2$	0.198	0.077	0.40	0.67	1.4	0.79	6.0	3.43
	0.22	0.29	0.45	0.70	1.6	0.79	7.0	3.95
	0.24	0.39	0.50	0.72	1.8	0.80	8.0	4.02
	0.26	0.47	0.60	0.75	2.0	0.82	9.0	3.79
	0.28	0.52	0.80	0.78	3.0	1.06	10.0	3.45
	0.30	0.56	1.0	0.79	4.0	1.64	11.0	3.10
	0.35	0.63	1.2	0.79	5.0	2.53	12.0	2.79
$\nu_4$	0.171	0.96	0.40	4.90	1.4	2.63	6.0	2.78
	0.174	1.65	0.45	4.73	1.6	2.44	7.0	3.32
	0.18	2.43	0.50	4.56	1.8	2.28	8.0	3.66
	0.20	3.71	0.60	4.21	2.0	2.16	9.0	3.77
	0.25	4.78	0.80	3.63	3.0	1.84	10.0	3.73
	0.30	5.03	1.0	3.20	4.0	1.88	11.0	3.60
	0.35	5.02	1.2	2.88	5.0	2.22	12.0	3.44

Table 3 shows total cross sections that were obtained by adding the inelastic cross sections in table 2 to a set of elastic cross sections. The elastic cross sections were calculated using the SCE method (as in the inelastic calculations) with the CH<sub>4</sub> geometry fixed at the equilibrium value.

**Table 3.** Integral cross sections calculated as described in the text for purely elastic scattering,  $\sigma_{\text{elastic}}$ , and for elastic plus inelastic scattering,  $\sigma_{\text{tot}}$ . The scattering energies ( $E$ ) are given in eV; the cross sections are given in Å<sup>2</sup>.

$E$	$\sigma_{\text{elastic}}$	$\sigma_{\text{tot}}$
0.05	4.94	4.94
0.10	2.59	2.59
0.22	1.00	1.45
0.41	0.95	1.59
0.60	1.42	2.11
0.79	1.97	2.62
1.0	2.62	3.21
2.0	5.67	6.12
3.0	9.14	9.59
4.0	13.01	13.60
5.0	17.23	18.11
6.0	21.08	22.29
7.0	23.80	25.23
8.0	25.29	26.79
9.0	25.72	27.17
10.0	25.48	26.82
11.0	24.86	26.09
12.0	24.09	25.21

### 3.2. Discussion

The cross sections presented in table 2 are plotted in figures 1 and 2. In discussing the figures, we will refer to the cross sections for excitation of the  $\nu_i$  vibration from the ground to the first excited state as the ' $\nu_i$  cross sections'. Figures 1 and 2 also show the  $\nu_{13}$  and  $\nu_{24}$  cross sections, defined as the sums of the  $\nu_1$  and  $\nu_3$ , and of the  $\nu_2$  and  $\nu_4$  cross sections. These are plotted to facilitate comparison with the differential cross section measurements (Lunt *et al* 1994, Boesten and Tanaka 1991, Shyn 1991, Sohn *et al* 1983, Tanaka *et al* 1983, Rohr 1980), which give results for the  $\nu_{13}$  and the  $\nu_{24}$  cross sections only.

The results in figures 1 and 2 agree with the measurements of Rohr and Sohn *et al* in predicting threshold peaks in both the  $\nu_{13}$  and  $\nu_{24}$  cross sections, with the height of the  $\nu_{24}$  peak being about twice that of the  $\nu_{13}$  peak. The threshold peaks in figures 1 and 2 are evidently caused by excitation of the infrared active modes ( $\nu_3$  and  $\nu_4$ ), suggesting that they are a result of direct (as opposed to resonance) excitation, brought about by coupling of the scattering electron with the geometry dependence of the molecular dipole moment. This direct mechanism was assumed in the Born calculations of Davis and Schmidt (1972) and was found to give large cross sections near threshold. Unlike the Born calculations, however, our calculations make no prior assumption about the excitation mechanism, and can hence be considered strong evidence in favour of the direct mechanism.

Calculations of the  $\nu_1$  and  $\nu_3$  cross sections from the off-shell scattering amplitudes have also been performed by Rescigno *et al* (1994), at energies from 0–2 eV. These calculations found a peak in the  $\nu_{13}$  cross section with approximately the same height and width as



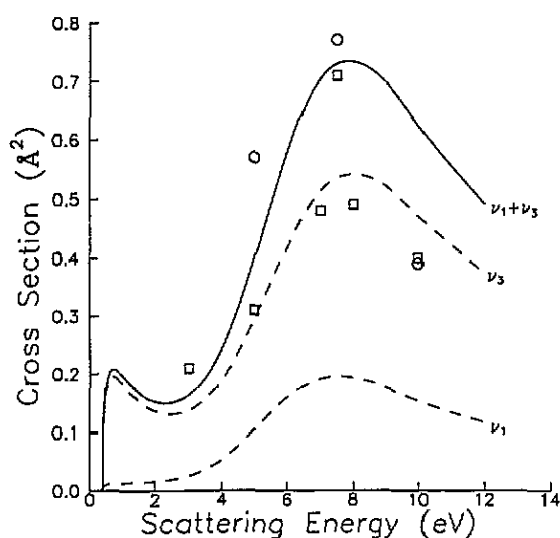


Figure 1. Vibrationally inelastic integral cross sections, calculated as described in the text, for excitation of the  $\nu_1$  and  $\nu_3$  modes (broken curves). The full curve is the sum of the calculated  $\nu_1$  and  $\nu_3$  cross sections. Also shown are the experimental results of Tanaka *et al* (1983) ( $\square$ ) and Shyn (1991) ( $\circ$ ).

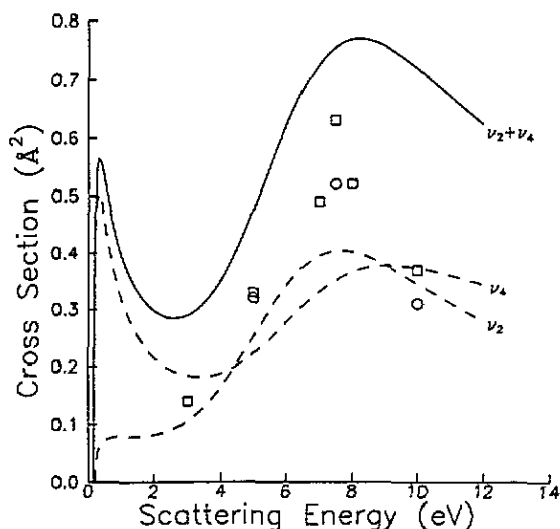


Figure 2. Vibrationally inelastic integral cross sections, calculated as described in the text, for excitation of the  $\nu_2$  and  $\nu_4$  modes (broken curves). The full curve is the sum of the calculated  $\nu_2$  and  $\nu_4$  cross sections. Also shown are the experimental results of Tanaka *et al* (1983) ( $\square$ ) and Shyn (1991) ( $\circ$ ).

the threshold peak shown in figure 1. The threshold peaks of Rescigno *et al*, however, contained almost equal contributions from the  $\nu_1$  and  $\nu_3$  cross sections.

Figures 1 and 2 show that our calculations predict broad peaks in each of the inelastic cross sections at about 7.5 eV. These peaks almost certainly result from the  $T_2$  shape resonance, which causes similar peaks at 7.5 eV in the elastic cross sections. Our predictions are in good agreement with the experimental results of Shyn (1991) and Tanaka *et al* (1983) (shown as squares and circles in figures 1 and 2), yielding cross sections which lie within the 30–40% error bars of the experimental results. The results in figures 1 and 2 show that contributions from the infrared inactive modes are comparable to those from the infrared active modes in the region of the shape resonance.

The cross sections of table 3 are plotted in figures 3 and 4, where they are compared with the experimental measurements of Jones (1985), Lohmann and Buckman (1986) and Dababneh *et al* (1988). The calculated total integral cross sections are clearly in very

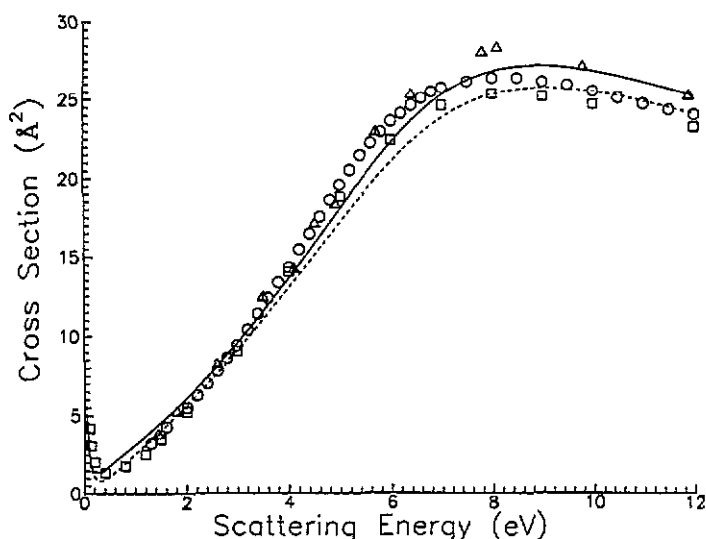


Figure 3. Calculated elastic (broken curve) and total (full curve) integral cross sections. Also shown are the experimental measurements of Lohmann and Buckman (1986) ( $\square$ ), Jones (1985) ( $\circ$ ) and Dababneh *et al* (1988) ( $\Delta$ ).

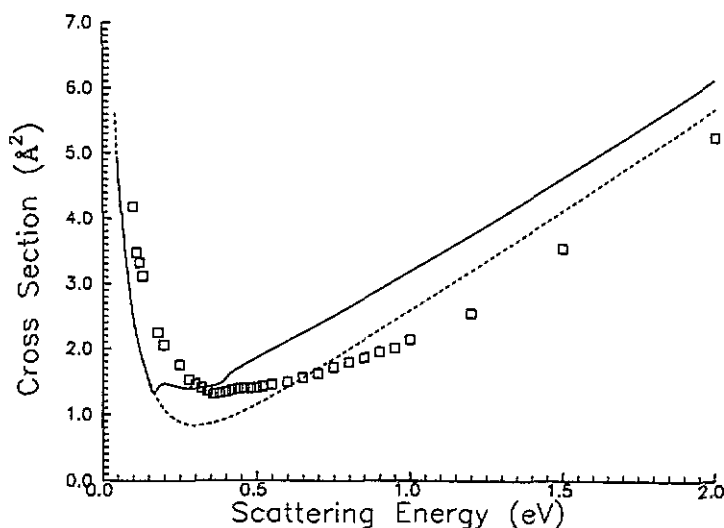


Figure 4. Calculated elastic (broken curve) and total (full curve) integral cross sections in the region of the Ramsauer minimum. Also shown are the experimental measurements of Lohmann and Buckman (1986) ( $\square$ ).

good overall agreement with experiment. Contributions from the inelastic cross section near threshold result in a Ramsauer minimum which has a well depth very close to the experimental value, but which has an anomalous shape, with humps at the thresholds for vibrational excitation. The first hump can probably be discounted as an artifact of our calculations, which locate the Ramsauer minimum at too low an energy: in the experimental cross sections, any threshold features in the  $\nu_{24}$  cross sections would be hidden by the sharp

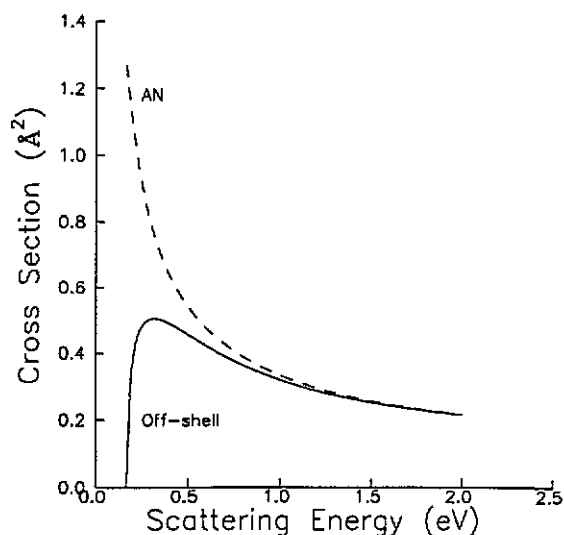


Figure 5. Comparison of the cross sections for  $\nu_4$  excitation, calculated from the AN and the off-shell  $K$ -matrices in the region of the shape resonance.

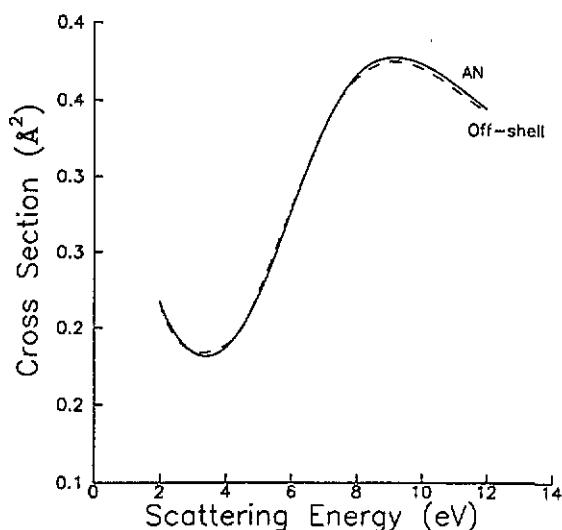


Figure 6. Comparison of the cross sections for  $\nu_4$  excitation, calculated from the AN and the off-shell  $K$ -matrices in the region of the threshold peak.

increase in the elastic cross section which occurs to the left of the Ramsauer minimum. A less pronounced feature corresponding to the second hump is present in the total cross sections of Lohmann and Buckman (see figure 4), but has not been observed by the other experiments. This suggests that our calculations probably overpredict the heights of the threshold peaks.

In addition to the off-shell results discussed so far, the calculations also gave the corresponding AN cross sections (see section 2.1). These may be compared with the off-shell results in order to estimate how much non-adiabatic coupling is present at a given energy. Figures 5 and 6 illustrate the results of this comparison for the  $\nu_4$  cross sections; comparisons for the other cross sections gave similar results. The figures show that, as expected, the AN results fail to describe the scattering near threshold but are adequate at higher energies.

As was mentioned above, the calculations were performed separately for each normal

mode, under the assumption that coupling between different modes could be neglected. The validity of this assumption depends on how much time the scattering electron spends close to the molecule. Model calculations (Gauyacq 1990, Kazansky and Sergeeva 1994) have demonstrated that trapping of the scattering electron by a resonance can lead to significant coupling between different vibrational modes. Such coupling could be present in the electron-CH<sub>4</sub> cross sections in the region of the shape resonance, but would probably be small because the resonance is broader than the period of vibration.

We mentioned in section 2.1 that higher-order non-adiabatic corrections could be added to the off-shell results by substituting the wavefunction corresponding to the off-shell *K*-matrix back into the Lippmann-Schwinger equation. Such a calculation would be useful in assessing how well the off-shell cross sections describe scattering near threshold, and will be reported in a forthcoming publication (Althorpe and Gianturco 1995).

#### 4. Conclusions

We have extended our SCE method to calculate the vibrationally inelastic cross sections for the scattering of low-energy electrons from polyatomic molecules. The method has been applied to electron-methane scattering, in calculations of the integral cross sections for excitation of each of the vibrational modes. The results show threshold peaks in the cross sections for excitation of the infrared active modes, and can hence be considered evidence for the direct excitation mechanism which has been proposed to account for threshold scattering in electron-methane. Total cross sections obtained by adding the inelastic to a set of elastic cross sections are in very good overall agreement with experiment.

Most of the computational effort in the method is taken up by a set of FN calculations along the normal coordinate. The FN results are then used to construct the AN wavefunction, which is substituted once into the Lippmann-Schwinger equation, to yield a scattering amplitude (the off-shell scattering amplitude introduced by Shugard and Hazi (1975)) which includes corrections for non-adiabaticity. In our method, evaluation of the off-shell scattering amplitude is particularly simple, requiring only the evaluation of a one-dimensional integral over the FN wavefunctions.

The calculations have assumed that coupling between motion in different normal coordinates could be neglected throughout the whole collision. The method could, however, be extended to systems in which there is coupling between motion in two normal coordinates, (as for example between the symmetric stretching and bending modes in electron-CO<sub>2</sub> scattering). It could also be extended to include higher-order non-adiabatic corrections. The results for electron-CH<sub>4</sub> scattering calculated in this paper suggest that our method is a promising approach with which to investigate the vibrationally inelastic scattering of electrons from polyatomic molecules.

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