Vibrational excitation of CH_4 by electron impact: 3–20 eV

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Abstract. Differential cross sections (DCS) for the vibrational excitations ($\nu_{2,4}$, 170 meV; $\nu_{1,3}$, 360 meV) of CH_4 by electron impact have been investigated for incident energies of 3 to 20 eV in the range of 30 to 140° using a crossed-beam apparatus. Integral and momentum transfer cross sections are calculated from the DCS. At about 7.5 eV, the angular distribution shows d-wave behaviour, and the integral cross sections are enhanced to about 10^{-16} cm². The parameters of angular correlation theory with the irreducible tensor method for the T_2 molecular symmetry of CH_4 were obtained by fitting. It was found that the d wave alone suffices to explain the angular distributions due to the presence of a broad resonant excitation process in the $\nu_{2,4}$ and $\nu_{1,3}$ channels. At incident energies of 10 to 20 eV, the angular distributions are isotropic within the experimental error. At lower energies of 3 to 5 eV, the distributions are practically constant within the angular range of 40 to 140°, but the cross sections continuously increase towards smaller angles.

1. Introduction

Strong IR absorption bands of methane have been found in the spectra of the atmospheres of Jupiter, Saturn, Uranus and Neptune. Methane has also been the leading choice for use in backward Raman pulse compression of excimer lasers such as the KrF laser which is used in laser fusion, because the 2916 cm^{-1} (361.5 meV) Q branch of the ν_1 symmetric-stretch vibration of methane has a very high Raman cross section and dominates the spectrum (Murray *et al* 1979). Therefore, the lineshape of the Q branch of methane has been extensively studied by several methods, but as far as we are aware, vibrational excitation by electron impact has not been investigated in sufficient detail.

Vibrational excitation of methane as well as other hydrocarbon molecules by slow electrons of 0.1–1 eV, in general, seems to be quite efficient (about 10^{-16} cm²), as can be deduced from an analysis of swarm experiments. However, no direct evaluation of the cross section is possible and usually some experimentally unverified assumptions are made. Moreover, physical mechanisms leading to the large vibrational cross sections in methane have not been established. The relationship between the Ramsauer minimum and vibrational excitation has been discussed in recent reports of measurements of total cross sections by Barbarito *et al* (1979), as well as in articles on differential cross section measurements by Rohr (1980) (2 to 5 eV, 10 to 120°) and by Sohn *et al* (1983) (0.1 to 1.8 eV, 35 to 110°). In a previous report (Tanaka *et al* 1982), we showed that in vibrationally elastic e + CH_4 scattering, the angular distribution near 7.5 eV is characteristic of a d-wave-dominated weak resonance as was theoretically predicted (Gianturco and Thompson 1976) and experimentally

established at 5 eV by Rohr (1980). Also, resonant enhancement has been observed at 7.5 eV in the vibrational excitations of the $\nu_{2,4}$ and $\nu_{1,3}$ channels for a scattering angle of 80° (Okada *et al* 1980). These features are usually difficult to detect in elastic and electronic excitation cross sections, but emerge in vibrational excitation. In order to gain further understanding of the resonance behaviour, we have extended the previous study to measure differential cross sections of resonant vibrational excitation in CH_4.

In this report, we present normalised, absolute differential cross sections for the vibrationally inelastic $\nu_{2,4}$ and $\nu_{1,3}$ excitation of CH_4 in the energy range of 3 to 20 eV, over the angular range of 20 to 140°. For each impact energy, the DCS were also integrated to obtain integral and momentum transfer cross sections. In § 2 we briefly describe the methods employed in the measurements and in § 3 we give the results.

2. Apparatus and method

The apparatus of the present measurements has been described previously (Tanaka *et al* 1981). A monochromator with a 127° cylindrical electrostatic field produces an energy-selected electron beam of the required impact energy with a typical current of a few nA. The primary electron beam is collected by a Faraday cup and focused onto a methane beam at right angles by adjusting the exit optics of the monochromator. The methane beam is generated by effusion from a nozzle, its pressure is typically about 10^{-3} Torr in the scattering centre. Electrons that are scattered through an angle of θ are detected in an analyser system in which another 127° electrostatic cylindrical field is used as a dispersive element, and are counted by a channeltron detector. A scattering angle from 30 to 140° is covered by rotating the analyser.

The overall resolution during these measurements was 30 meV. Methane has four vibrational normal modes; with the present resolution, the peaks corresponding to the ν_2, ν_4 modes and ν_1, ν_3 modes overlap and are given as composite measurements indicated by $\nu_{2,4}$ and $\nu_{1,3}$. This is sufficient to separate clearly the $\nu_{2,4}$ from elastic and $\nu_{1,3}$ excitation, but insufficient to resolve any rotational structures. The electron energy scale was calibrated by measurement of the 19.3 eV resonance in He.

Figure 1 shows a typical energy-loss spectrum of CH_4 at 5 eV at a scattering angle of 90°. From the measured energy-loss spectra, the ratio $R(E_0, \theta) = I_\nu/I_0$ of the peak heights of the vibrational and the elastic scattering excitations was determined. These ratios are equal (to a good approximation) to the ratio of the respective DCS ($I_\nu/I_0 = \sigma_\nu/\sigma_0$). The elastic DCS ($\sigma_0$) measured by Tanaka *et al* (1982) are utilised together with the intensity ratios to obtain the absolute DCS (σ_ν) for the vibrational excitations.

3. Results and discussion

Values of $R(E_0, \theta)$ were obtained at incident energies of 3, 5, 7, 7.5, 8, 10, 15 and 20 eV in the angular range from 30 to 140° in steps of 10° for all energies. As mentioned above, the energy resolution is not high enough to resolve the pure rotational transitions in CH_4. Cross sections obtained from the present measurements are given in table 1. The ratios are given in parentheses. Values of the elastic DCS of CH_4 at 7 and 8 eV were obtained by interpolating their results between 6 and 7.5 eV, and between 7.5 and 9 eV, respectively.
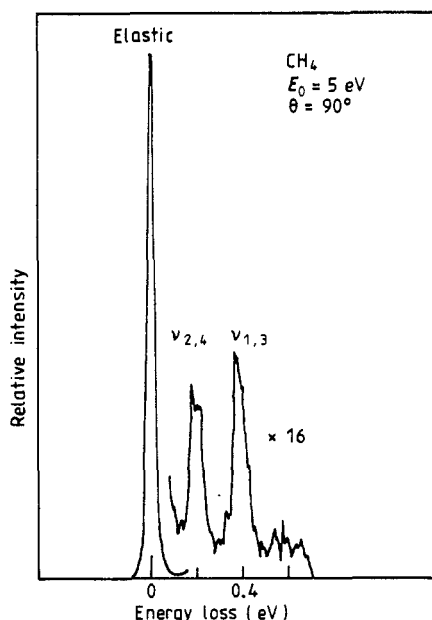
Figure 1. Energy-loss spectrum of CH_4 at 7.5 eV impact energy and a scattering angle of 90°. The features corresponding to vibrationally inelastic scattering to the composite vibrational modes are labelled $\nu_{2,4}$ and $\nu_{1,3}$.

The errors associated with the present DCS were estimated from the statistical spread in the intensity ratio measurements and from the errors of the elastic DCS. The estimated errors in the measured ratios are from 16 to 38%, and the elastic DCS have an error of 17 to 30%. The overall errors calculated as the square root of the sum of the squares of the corresponding errors, amount to 26 to 48% for the present DCS as shown in table 1.

Figure 2 shows $\sigma_{2,4}$ and $\sigma_{1,3}$ as functions of the scattering angles and incident energies. There are no experiments or theoretical calculations to compare with the present measurements. The angular dependence for the DCS of $\nu_{2,4}$ and $\nu_{1,3}$ are similar over the whole energy range investigated: both deviate from an isotropic distribution in the energy range of 7 to 8 eV and are characteristic of d-wave scattering. The angular distributions for incident energies of 10 to 20 eV are approximately constant. At lower energies of 3 to 5 eV, the distributions are practically constant within the angular range of 40 to 140° but the cross sections increase continuously towards smaller angles. As discussed in detail in the earlier paper on the elastic DCS, a broad resonant maximum in the integral and momentum transfer cross sections is located at 7.5 eV. The angular distributions at energies up to about 7.5 eV are characteristic of a d-wave-resonant scattering and agreed quite well with the broad T_2 symmetry (mainly d-wave) resonance predicted theoretically by Gianturco and Thompson (1976, 1980). In general, weak resonances are barely detectable in an elastic channel, but should stand out prominently in the vibrational excitation channels.

Methane belongs to the symmetry group T_d. There are in all five symmetry species, in three of which a normal vibration is possible, A_1, E and T_2, although higher vibrational levels may also be found in A_2 and T_1. A_1 consists of one degenerate (ν_1, 362 meV), E of one doubly degenerate (ν_2, 190 meV), and T_2 of two triply

degenerate species (ν_3, 374 meV; ν_4, 162 meV), respectively. The ν_3 and ν_4 are IR active, but all four are Raman active. As mentioned above, however, the ν_2, ν_4 modes and the ν_1, ν_3 modes overlap in the composite $\nu_{2,4}$ and $\nu_{1,3}$ due to the present resolution of the spectrometer. Its ground state has a configuration $(1a_1)^2(2a_1)^2(1t_2)^6(3a_1)^0(2t_2)^0\ldots$, yielding an a $^1A_1$ ground state. The lowest unoccupied orbital is $3a_1$. The next unoccupied orbital is expected to be $2t_2$ and was experimentally observed at 10.4 eV. The excited state was assigned to $2\,^1T_2$ (Caldwell and Gordon 1978). Thus, we could interpret the resonance, most probably as the $^2T_2$ compound state comprising the target molecule plus an electron in the $2t_2$ orbital.

In addition, we have calculated the angular distributions $W(\theta)$ using the angular correlation theory with irreducible tensors for the T_2 molecular symmetry group of the compound state. The general expressions including the vibronic symmetry of the final state for the resonant electron–molecule reactions are given by Andrick and

Table 1. Differential $\sigma_{2,4}$, $\sigma_{1,3}$, integral σ_I and momentum transfer σ_M cross sections for $\nu_{2,4}$ and $\nu_{1,3}$ vibrational excitations in CH_4. Units are $10^{-18}\,cm^2\,srr^{-1}$ for DCS, and $10^{-18}\,cm^2$ for σ_I and σ_M. In parentheses are the ratios $R(E_0, \theta)$ in units of 10^{-2}. The errors are the averages of the corresponding column.

θ (deg) E_0 (eV)	DCS ($\nu_{1,3}$)							
	3	5	7	7.5	8	10	15	20
30	3.7	2.8	3.9	7.3	3.9	3.1	2.7	1.6
	(4.6)	(1.8)	(1.6)	(2.4)	(1.4)	(0.99)	(0.96)	(0.47)
40	1.9	2.5	3.0	6.4	3.3	2.8	2.1	1.1
	(3.5)	(2.4)	(1.3)	(2.6)	(1.3)	(0.91)	(0.85)	(0.64)
50	0.71	2.1	3.0	4.4	3.6	3.0	1.7	1.3
	(1.4)	(1.8)	(1.7)	(2.2)	(1.9)	(1.4)	(1.1)	(1.3)
60	0.94	1.7	3.1	4.0	3.3	3.2	1.9	1.4
	(1.1)	(1.4)	(2.2)	(2.8)	(2.3)	(2.4)	(2.0)	(1.9)
70	0.66	1.5	3.1	5.0	3.1	2.8	1.6	0.89
	(0.81)	(1.0)	(2.0)	(3.2)	(2.2)	(2.4)	(2.3)	(1.8)
80	0.77	1.7	3.5	5.1	3.6	3.0	1.5	0.77
	(0.82)	(1.2)	(2.3)	(3.6)	(2.7)	(2.8)	(2.8)	(1.7)
90	0.89	1.9	3.9	5.7	3.7	2.5	1.7	1.6
	(1.3)	(1.7)	(3.4)	(4.7)	(3.3)	(3.1)	(4.1)	(4.5)
100	0.97	1.9	3.7	5.0	4.4	2.8	2.1	1.9
	(1.7)	(2.3)	(4.3)	(7.4)	(6.7)	(5.7)	(7.9)	(6.5)
110	1.0	2.0	4.0	4.4	4.8	3.4	2.3	1.6
	(2.4)	(4.3)	(10)	(14)	(15)	(13)	(8.7)	(6.4)
120	1.2	3.2	4.3	5.0	4.3	4.3	2.5	2.1
	(4.6)	(12)	(20)	(23)	(22)	(17)	(8.5)	(6.6)
130	2.0	3.5	4.5	5.9	4.2	3.1	1.6	1.4
	(8.2)	(12)	(10)	(12)	(8.7)	(6.0)	(3.5)	(3.4)
140	2.2	3.0	4.4	6.3	4.0	3.1	1.7	1.7
	(7.8)	(3.8)	(4.0)	(5.4)	(3.6)	(3.0)	(3.9)	(3.4)
Error (%)	45	32	31	38	29	34	29	34
σ_I	21	31	48	71	49	40	24	19
σ_M	21	33	50	72	51	41	23	20
Error (%)	47	35	34	41	33	37	33	37

Table 1. (continued)

θ (deg) E_0 (eV)	DCS ($\nu_{2,4}$)							
	3	5	7	7.5	8	10	15	20
30	1.9	4.3	5.1	6.6	5.1	3.1	1.2	0.66
	(2.3)	(2.8)	(2.2)	(2.2)	(1.8)	(0.99)	(0.31)	(0.2)
40	1.6	2.9	4.4	5.2	4.2	3.3	1.4	0.70
	(3.1)	(2.7)	(1.9)	(2.1)	(1.2)	(1.1)	(0.59)	(0.40)
50	0.51	2.7	3.8	4.6	3.4	3.2	1.3	1.3
	(1.0)	(2.4)	(2.1)	(2.3)	(1.8)	(1.6)	(0.82)	(1.3)
60	0.73	2.2	3.4	4.4	3.8	3.3	1.4	0.70
	(0.85)	(1.8)	(2.5)	(3.0)	(2.7)	(2.4)	(1.5)	(0.97)
70	0.48	2.2	3.7	4.4	3.9	3.1	1.1	0.60
	(0.59)	(1.5)	(2.5)	(2.8)	(2.7)	(2.7)	(1.7)	(1.2)
80	0.70	2.3	3.9	4.6	3.8	2.7	0.73	0.50
	(0.74)	(1.6)	(2.6)	(3.4)	(2.8)	(2.6)	(1.4)	(1.1)
90	0.67	2.6	4.6	5.1	4.3	2.5	0.85	0.64
	(0.99)	(2.4)	(4.0)	(4.3)	(3.9)	(3.2)	(2.1)	(1.8)
100	0.73	2.3	3.8	5.1	4.1	2.5	1.2	0.75
	(1.3)	(2.7)	(4.5)	(7.5)	(6.4)	(5.1)	(4.1)	(2.6)
110	0.78	2.3	3.6	4.1	4.2	3.0	1.4	0.71
	(1.9)	(4.9)	(9.5)	(13)	(13)	(11)	(5.3)	(2.8)
120	1.2	2.7	3.3	3.8	3.9	3.0	1.3	1.7
	(4.5)	(10)	(16)	(18)	(20)	(12)	(4.6)	(5.2)
130	1.2	2.3	3.6	3.9	4.9	2.7	1.2	1.1
	(5.0)	(8.0)	(8.1)	(7.8)	(10)	(5.3)	(2.5)	(2.7)
140	1.3	1.9	3.2	4.6	3.3	3.0	1.3	1.3
	(4.2)	(2.5)	(2.9)	(4.0)	(3.0)	(3.0)	(2.4)	(2.6)
Error (%)	48	31	32	36	26	31	33	43
σ_I	14	33	49	63	52	37	15	11
σ_M	13	29	46	61	50	36	15	13
Error (%)	50	34	35	39	30	34	36	45

Read (1971). Assuming the resonance to be of symmetry T_2 as mentioned above, the values of (l_1, m_1) for the electron waves in the incident channel are restricted to $(1, 0)$, $(1, \pm 1)$, $(2, \pm 1)$ and $(2, \pm 2)$, as T_2 is given by the direct product $A_1 \times T_2$ in the resonance of $A_1 \to T_2 \to A_1$. From a consideration of the large centrifugal barrier, higher partial waves have been excluded. In the vibrational excitations the resonance decays into the following modes of vibrations: (a) a totally symmetric stretching mode ν_1 of symmetry A_1; the exit channel (l_2, m_2) contains the same partial waves as the entrance channel; (b) a doubly-degenerate bending mode ν_2 of symmetry E; since the exit electron wave can have the symmetries T_2 and T_1 (from the $T_2 \times E$), the same partial waves as the entrance channel would be allowed for symmetry T_2. The leading term of the waves is $l = 3$ for symmetry T_1, but here it can be excluded because of its small importance for low-energy scattering; (c) a triply degenerate stretching mode ν_3 and a triply degenerate bending mode ν_4, both of them belonging to symmetry T_2; since the direct product $T_2 \times T_2$ gives the symmetries T_2, T_1, E and A_1 for outgoing waves, the waves $(2, 0)$ and $(2, 2)$ would be allowed for symmetry E, and the wave
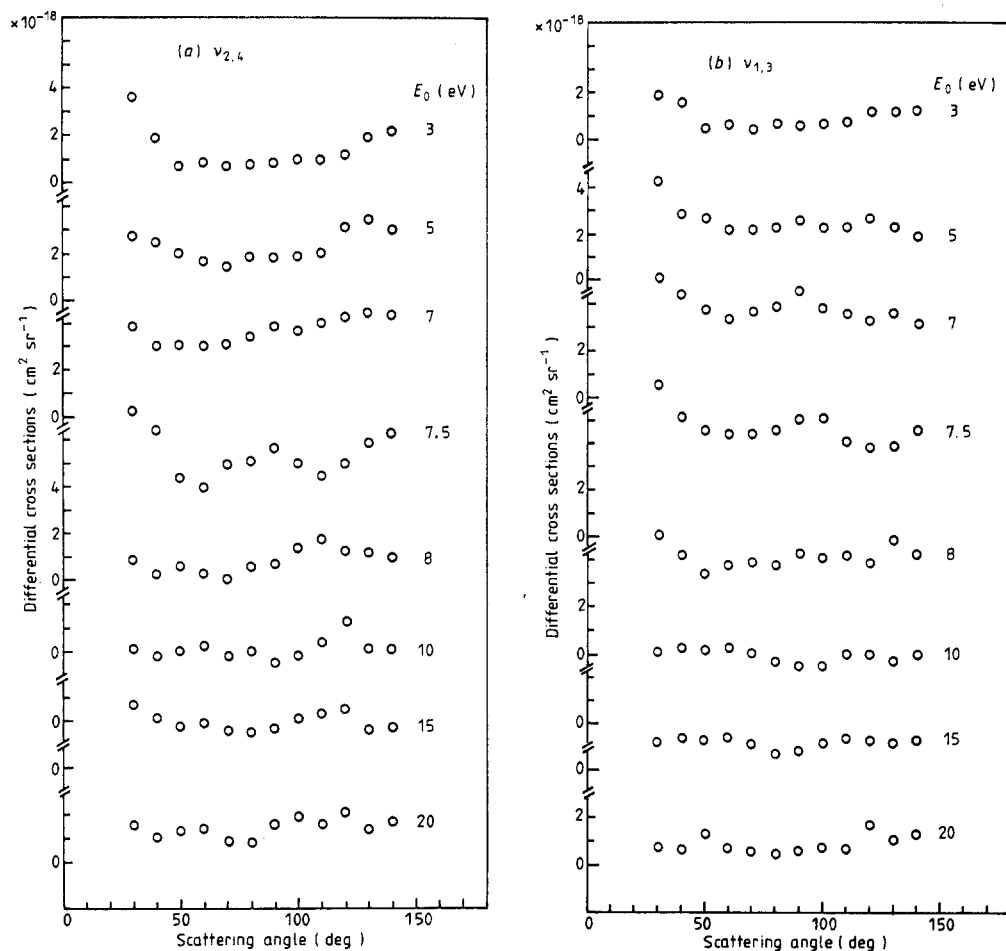
Figure 2. Differential cross sections for the $\nu_{2,4}$ and $\nu_{1,3}$ vibrational excitation in CH_4 between 3 to 20 eV.

(0, 0) for A_1. With the present resolution, the decaying processes $\nu_{2,4}$, $\nu_{1,3}$ have to be combined namely A_1 and T_2, as well as E and T_2. We have fitted the observed angular distribution by assuming a mixture of s, p and d waves, and obtained the following differential cross sections: for $\nu_{2,4}$

$$W(\theta) = 5.247 - 0.274 \cos\theta - 5.201 \cos^2\theta$$
$$- 0.328 \cos^3\theta + 11.708 \cos^4\theta \qquad (10^{-18}\,cm^2) \qquad (1)$$

for $\nu_{1,3}$

$$W(\theta) = 4.990 + 0.530 \cos\theta - 7.876 \cos^2\theta$$
$$- 0.155 \cos^3\theta + 13.672 \cos^4\theta \qquad (10^{-18}\,cm^2). \qquad (2)$$

These curves are plotted in figure 3. In the case of nonlinear molecules, the derivation of $W(\theta)$ is more complicated and the number of parameters was increased to 11 for $\nu_{2,4}$ and 10 for $\nu_{1,3}$. The fits are quite reasonable. The ratio of the amplitudes
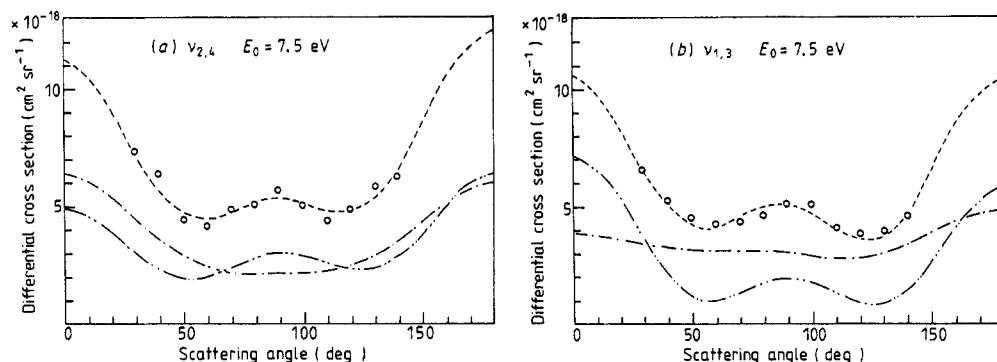
Figure 3. Angular distributions for vibrational excitation of (a) the $\nu_{2,4}$ and (b) the $\nu_{1,3}$ in CH_4 by electron impact at 7.5 eV. The points represent the measured angular distribution. Calculated angular distributions: in (a), $\nu_2(— \cdot \cdot —)$, $\nu_4(— \cdot —)$ and their sum $\nu_{2,4}(----)$; in (b), $\nu_1(— \cdot \cdot —)$, $\nu_3(— \cdot —)$, and thir sum $\nu_{1,3}(- - - -)$.

of the p wave to the d wave is about 1 : 100. Also in figure 3 we present the partial contributions of the vibronic symmetries A_1, T_2 and E to each composite mode. The agreement between the present measurements and the theoretical prediction is a further indication of a broad resonance near 7.5 eV in CH_4. The shape resonance shows clearly $l = 2$ behaviour.

Also shown in table 1 are the integral (σ_I) and momentum transfer (σ_M) cross sections. Since the range of θ covered in the data was $30° \leqslant \theta \leqslant 140°$ the DCS curves had to be extrapolated from 30 to 0° and 140 to 180°. For this purpose two methods of extrapolation were used. (i) For 3–5 eV and 10–20 eV; the DCS were extrapolated to 0° by extending the curves with the shape determined manually from the three
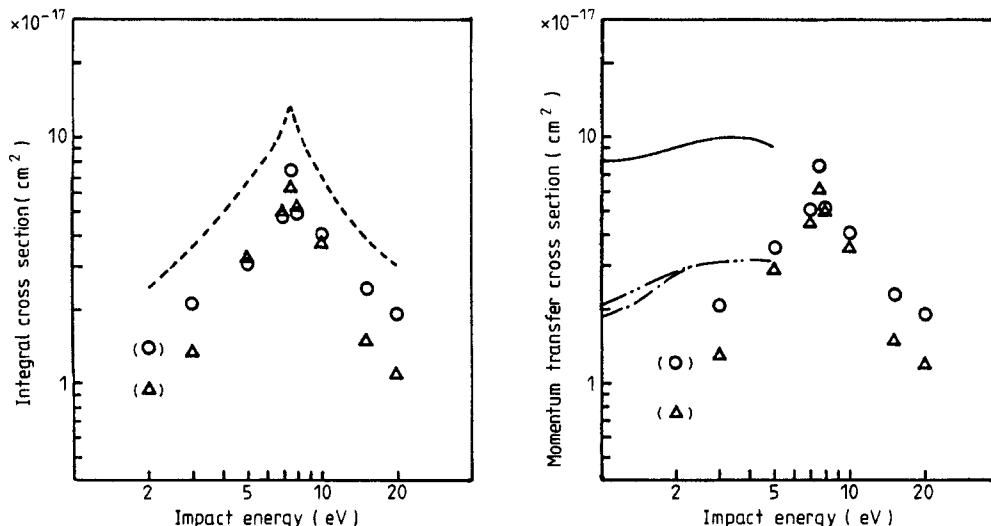

Figure 4. Integral (σ_I) and momentum transfer (σ_M) cross sections for vibrationally inelastic scattering in CH_4: O, $\nu_{2,4}$, $\triangle$, $\nu_{1,3}$; (O) ($\triangle$), the corresponding values of Rohr (calculated extrapolating by method (i)); - - - - -, cross section sums for excitation sof $\nu_{2,4}$ and $\nu_{1,3}$; ——, Pollack (1968); — $\cdot$ — (ν_2) and — $\cdot \cdot$ — (ν_4), Duncan and Walker (1972).

lowest experimentally measured data points. Between 140° and 180°, the DCS were taken as constant. (ii) For 7–8 eV; in the 7.5 eV short-lived shape resonance region, the present fittings were used for the low and high-angle extrapolations. The curves were integrated to obtain integral and momentum transfer cross sections. The estimated errors in σ_I and σ_M are 30 to 50%. These errors are based on the error of the DCS itself, and on an estimate of the extrapolation error.

Present integral and momentum transfer cross sections (see figure 4) are also compared with total vibrational cross sections from transport coefficients in swarm experiments of Pollack (1968) and Duncan and Walker (1972), and with integrated vibrational cross sections from the crossed-beam experiments of Rohr (extrapolated by method (i)). They confirm a resonance-enhanced vibrational excitation which is centred at 7.5 eV, arising from a broad shape resonance in the T_2 symmetry. The general trends of the energy dependence of the both modes are similar, but $\nu_{1,3}$ is slightly sharper than $\nu_{2,4}$. As mentioned by Rohr, the values derived from the swarm data of Pollack seem to be too large by a factor of more than 3 at 3 eV. However the agreement with the data of Duncan and Walker is reasonable at 5 eV. The sum of the cross sections of both composite modes, that is, the total vibrational cross sections are indicated in figure 4. This shows experimentally that vibrational excitation of methane by slow electrons, in general, is efficient (in the order of 10^{-16} cm^2).

4. Conclusion

The work presented here provides a broad range of quantitative data for the vibrational excitation of the $\nu_{2,4}$ and $\nu_{1,3}$ modes in methane over an angular range of 30 to 140° and an energy range of 3 to 20 eV, and its corresponding integral and momentum transfer cross sections. We find that the vibrational excitation by electron impact at about 7.5 eV is dominated by a broad T_2 symmetry resonance. The angular distributions show clearly the characteristics of d-wave scattering, which also have been deduced theoretically using the angular correlations.

Acknowledgments

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