Vibrational excitation of methane by 15 and 30 eV intermediate-energy electron impact

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(Received 9 October 1996; accepted 31 December 1996)

Absolute measurements of differential electron-collision cross sections have been performed for the vibrational excitation of methane in its electronic ground state at impact energies of 15 eV and, for the first time, at 30 eV, in the 8°–95° angular range. The normalization to the absolute scale has been carried out using the inelastic/elastic ratios and the absolute elastic differential cross section obtained from a relative flow technique recently developed in our laboratory, in which the elastic differential cross section of methane was compared to that of nitrogen at each impact energy and at each scattering angle. Special attention has been given to the small scattering angular range ($\leqslant 40°$) where minima have been observed in the vibrational cross sections and where simultaneous independent measurements have been made on two different electron spectrometers. © *1997 American Institute of Physics.* [S0021-9606(97)01813-8]

I. INTRODUCTION

Electron-impact vibrational excitation processes are important in the atmospheres of both the earth and other planets. Other applications are also found in gaseous laser media, in gaseous discharges, and in electron-impact induced chemical reactions on surfaces. Absolute measurements of vibrational differential cross sections are also very important if the dynamics of the electron-molecule interactions are to be better understood. Moreover, with the development of the computational methods, absolute values for the vibrational scattering should also allow a good test for the validity of the theoretical models.[1]

The present work reports a new experimental determination of the absolute differential cross sections for the vibrational excitation of the bending and stretching fundamental modes of methane in its ground electronic state. This molecule is particularly interesting since it has been identified as a source of strong infrared absorption in the upper atmospheres of outer planets, such as Jupiter, Saturn, Uranus, or Neptune.[2,3] Moreover, methane plays a role in the terrestrial atmosphere as a ''greenhouse'' molecule, and it is involved in the ozone depletion problem as a scavenger of chlorine atoms.

Differential cross sections for the bending and stretching fundamental modes of methane have been measured in the electron impact energy range between 3 and 20 eV, where the vibrational cross sections are quite high and enhanced by the 7.5 eV shape resonance.[4–7] A summary of the previous studies reported in the literature on the vibrational differential electron-collision cross sections of methane is presented in Table I. The angular range explored by earlier authors was set in most cases between 30 and 140°. Vibrational excitation of methane has been also investigated at very low impact energies to characterize threshold structures in the vibrational cross sections.[8,9]

We have measured the absolute vibrational differential cross sections of methane at impact energies of 15 eV and, for the first time, at 30 eV, in the 8°–95° angular range. Most of the measurements have been performed at Liège (Laboratoire de Spectroscopie d'Electrons diffusés, University of Liège); however, in order to confirm the observation of minima in the vibrational angular cross sections at the small scattering angles ($\leqslant 40°$), simultaneous measurements have also been carried out in the Molecular Physics Laboratory of the University College London.

II. EXPERIMENT

A. The electron energy loss spectrometers

1. The electron spectrometer at Liège

The apparatus used at Liège is a Vacuum Generator SEELS 400 spectrometer, adapted for the investigation of gaseous targets, a detailed description of which has been reported earlier.[10,11] A 150° hemispherical-sector energy filter fitted with a three-element lens produces an electron beam of the required impact energy. Its intensity, as monitored by a Faraday cup mounted on the spectrometer, is typically $(5–10)\times10^{-10}$ A. This electron beam intersects the molecular beam at 90°, the molecular beam being produced by flowing the gas through a needle with a 1 mm internal diameter and a 136.5 mm length. The analyzer is of the same type as the monochromator and can rotate perpendicularly around the molecular beam between 0° and +120°. The signal is detected by an electron multiplier of the continuous dynode type, amplified and stored using a data acquisition system

 0021-9606/97/106(14)/5990/11/$10.00

TABLE I. Summary of the previous works on the vibrational differential electron-collision cross sections for the bending and stretching fundamental modes of methane in its ground electronic state.

Author	Energy range (eV)	Angular range (°)
Tanaka *et al.* (Ref. 4)	3–20	30–140
Curry *et al.* (Ref. 5)	7.5–20	32–142
Shyn (Ref. 6)	5–15	12–168
Mapstone and Newell (Ref. 7)	3–15	30–140

under the control of a Macintosh IIfx computer. The same computer is also used for the treatment and the analysis of the data.

All measurements have been made at a constant pass energy with a resolution between 30 and 45 meV, according to the experimental conditions. This resolution is obviously insufficient to resolve any rotational structure.

The vacuum in the vessel is maintained by a cryogenic pumping which allows to reach a residual pressure of about 5×10^{-9} Torr.

The methane was obtained from UCAR (purity $\geqslant$99.95%) while the Ar and N_2 gaseous samples were the commercial ones from l'Air Liquide, with an announced purity better than 99.999%.

The spectrometer is coupled with a relative flow introduction system allowing the normalization of the cross sections to the absolute scale.

2. The electron spectrometer at London

The electron spectrometer used in London has been described in detail elsewhere.[12] Briefly, it consists of two sections, a monochromator and an analyzer. In the monochromator, electrons emitted from a thoriated tungsten filament are focused into a collimated monoenergetic electron beam which is crossed at 90° with the gas beam. Electrons scattered from the gas beam are detected by an analyzer, of the same type as the monochromator and rotatable from $-10°$ to $+120°$ relative to the direction of the primary electron beam. The apparatus has been operated at the constant pass energy mode, with an overall energy resolution of 50–60 meV.

B. The relative flow technique

1. Principle

The relative flow normalization method is based on the measurement of the ratio of the elastic differential cross section of the gas under study (X) to the known absolute elastic differential cross section of a reference gas (ref) at a given impact energy E_0 and scattering angle θ.[13] The method requires the measurement of the ratio of the elastically scattered intensity $\dot{N}_e(E_0,\theta)_X/\dot{N}_e(E_0,\theta)_{\mathrm{ref}}$ of the unknown gas to that of the reference gas. In a beam–beam scattering experiment, this ratio can be expressed by the following relation:[14–16]

$$\frac{\dot{N}_e(E_0,\theta)_X}{\dot{N}_e(E_0,\theta)_{\mathrm{ref}}}=\frac{\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)_X}{\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)_{\mathrm{ref}}}\times\frac{C(E_r)}{C(E_r)}\times\frac{[V_{\mathrm{eff}}(\theta)]_X}{[V_{\mathrm{eff}}(\theta)]_{\mathrm{ref}}}, \tag{1}$$

where $\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)$ is the elastic differential cross section at the impact energy E_0, and a scattering angle θ, $C(E_r)$ is the transmission function of the analyzer as a function of the residual energy of the electrons, and $V_{\mathrm{eff}}(\theta)$ is the effective collision volume (the overlap between the incident electron beam and the molecular beam inside the view cone of the analyzer). When the ratio of the elastically scattered electron intensities is determined at constant impact electron current, transmission function of the analyzer, and scattering angle, Eq. (1) simplifies to

$$\frac{\dot{N}_e(E_0,\theta)_X}{\dot{N}_e(E_0,\theta)_{\mathrm{ref}}}=\frac{\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)_X}{\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)_{\mathrm{ref}}}\times\frac{\int_r[\rho(r)]_X}{\int_r[\rho(r)]_{\mathrm{ref}}}, \tag{2}$$

where $\rho(r)$ represents the spatial distribution of the molecular beam density.

The latter relation shows that in order to determine the unknown $\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)_X$ in terms of the known $\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)_{\mathrm{ref}}$, one must evaluate the ratio of the density distribution of the gas under study to that of the reference gas. If the Knudsen numbers, i.e., the mean free paths of the two gases are equal, and if the intermolecular collisions do not affect significantly the density distributions, the flux distributions from the needle are identical for both gases inside the collision volume.[16,17] The ratio of the density spatial distributions is then given by

$$\frac{[\rho(r)]_X}{[\rho(r)]_{\mathrm{ref}}}=\frac{\dot{N}_X}{\dot{N}_{\mathrm{ref}}}\times\sqrt{\frac{m_X}{m_{\mathrm{ref}}}}, \tag{3}$$

where $\dot{N}$ is the mass flow rate and m the gas molecular (atomic) mass.

Nickel *et al.*[16,18] have shown that by appropriately adjusting the ratio of flow rate of the two gases such that:

$$\frac{\dot{N}_{\mathrm{ref}}}{\dot{N}_X}=\frac{\delta_X^2}{\delta_{\mathrm{ref}}^2}\times\sqrt{\frac{m_X}{m_{\mathrm{ref}}}}, \tag{4}$$

where δ is the kinetic molecular (atomic) diameter, and the Knudsen numbers of the two gases and the gas radiation patterns are identical. Combining Eqs. (2) and (3), the ratio of the cross sections will be given by

$$\frac{\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)_X}{\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)_{\mathrm{ref}}}=\frac{\dot{N}_e(E_0,\theta)_X}{\dot{N}_e(E_0,\theta)_{\mathrm{ref}}}\times\frac{\dot{N}_{\mathrm{ref}}}{\dot{N}_X}\times\sqrt{\frac{m_{\mathrm{ref}}}{m_X}}, \tag{5}$$

which is usually called the relative flow relation.

2. The gas flow experimental setup

The gas flow system used in Liège is based on that developed by Register *et al.*[19] and is shown in Fig. 1. To avoid contamination problems, it consists of two gas lines, one for the gas of interest and one for the reference gas. Each gas line is composed of a MKS mass flow meter coupled with a precision gas flow valve; this allows not only the measurement of the gas mass flow rate but also controls the flow into the vacuum chamber. The system is pumped by a turbomo-

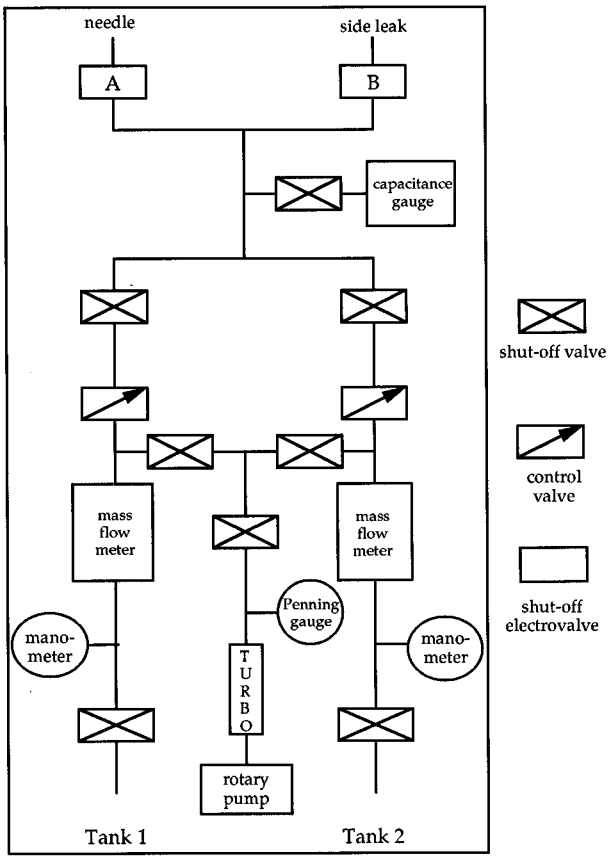

FIG. 1. The relative flow experimental setup.

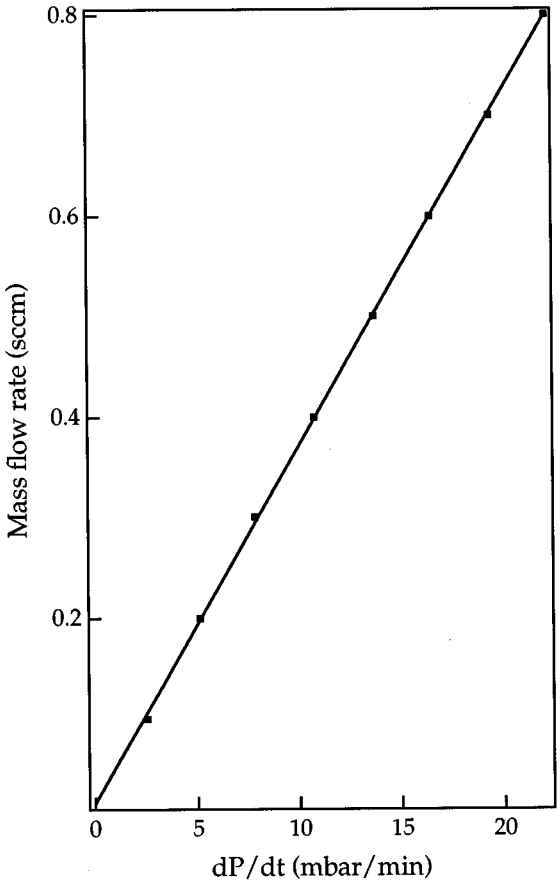

FIG. 2. Linearity test of the mass flow meters in the 0–0.8 sccm flow rate range.

lecular pump. The residual pressure read at the Penning gauge (Fig. 1) is 5×10^{-6} Torr and allows a good determination of the zero of the flow meters.

Two electrovalves, A and B, direct the gas flow to either the needle (molecular beam) or a side leak which allows to estimate the contribution of the background scattering (both the direct electron beam contribution and scattering by the background gas) to the scattering from the molecular beam. A capacitance gauge is mounted on the introduction line just after the control valves and allows the measurement of the absolute pressure before the needle (''head pressure'').

To check the linearity of the mass flow meters, a given mass flow rate was first established in the vacuum chamber through the side leak. Then, after measuring the absolute pressure and the mass flow rate, the leak valve was closed. The time required for the capacitance manometer to reach 10 mbar was measured and this procedure was repeated for different mass flow rates. Since the gas flow occurs into a fixed volume (when leak valve B is closed), the mass flow rate should be directly proportional to the variation of the pressure versus the time (dP/dt). The proportionality relation, obtained by deriving the ideal gas law is the following:

$$\dot{N}=\left(\frac{V}{kT}\right)\times\frac{dP}{dt}, \tag{6}$$

where V is the volume, k is the Boltzmann constant, and T is the temperature.

Figure 2 shows that this relation is obeyed over our operating range of 0–0.8 sccm and that the flow meters are linear over this region.

C. Test of the relative flow experimental setup: Measurement of the absolute elastic cross section of argon

As a test of our relative flow experimental set-up, the absolute elastic differential cross section of argon has been determined in the 15–30 eV impact energy range and has been compared to the absolute data available in the literature.

Since helium cannot be evacuated by the cryogenic pump, the relative flow method has been applied using nitrogen as a reference gas. In that context, the relative flow relation becomes

$$\frac{\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)_{\mathrm{Ar}}}{\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)_{\mathrm{N_2}}}=\frac{\dot{N}_e(E_0,\theta)_{\mathrm{Ar}}}{\dot{N}_e(E_0,\theta)_{\mathrm{N_2}}}\times\frac{\dot{N}_{\mathrm{N_2}}}{\dot{N}_{\mathrm{Ar}}}\times\sqrt{\frac{m_{\mathrm{N_2}}}{m_{\mathrm{Ar}}}}. \tag{7}$$

To reproduce as closely as possible the same flux distribution from the needle of both gases, we have adjusted the mass flow rates and the head pressures such that[16,18]

$$\frac{\dot{N}_{\mathrm{N_2}}}{\dot{N}_{\mathrm{Ar}}}=\frac{\delta^2_{\mathrm{Ar}}}{\delta^2_{\mathrm{N_2}}}\times\sqrt{\frac{m_{\mathrm{Ar}}}{m_{\mathrm{N_2}}}}, \tag{8}$$

where δ_{Ar} is the kinetic atomic diameter of argon and δ_{N_2} is the kinetic molecular diameter of nitrogen.[20]

In the present measurements, head pressures of 1.6 Torr (0.2 sccm) N_2 and 1.44 Torr (0.18 sccm) Ar have been chosen. These backpressure values have kept the vacuum chamber in the 10^{-6} Torr range throughout the experiment. These working conditions are correct if the gas density distribution profiles are only slightly affected by the intermolecular collisions. The condition for this has been recently studied by Buckman *et al.*,[17] who examined the spatial profiles of molecular beams (of He, Ar, N_2) exiting from a 1 mm internal diameter needle and measured their width in function of the mean free path (pressure range: 0.021–3.33 Torr). They found that at a given mean free path the width of the helium beam was in all cases smaller or equal to those of either Ar or N_2, while the argon and nitrogen widths were quite similar. Thus, it may be concluded that using nitrogen in this work as a secondary standard should minimize any errors that may arise from the use of a needle in the application of the relative flow method.

The quantities required for the determination of the cross section ratio have been measured in following way. First, a beam of argon is formed by flowing the gas through the needle and the elastically scattered electron intensity $\dot{N}_e(E_0,\theta)_{Ar}$ is measured. At the same time, the corresponding mass flow rate $\dot{N}_{Ar}$ is recorded. Then, the argon flow is stopped and the vacuum chamber is evacuated to obtain a pressure of about 1×10^{-8} Torr. Nitrogen is then introduced in the spectrometer under the same experimental gun and detector conditions to measure the elastically scattered intensity $\dot{N}_e(E_0,\theta)_{N_2}$ and the mass flow rate $\dot{N}_{N_2}$. To avoid some of the possible sources of errors during the measurement of the elastic cross section ratio, we have taken the following precautions:

(i) The shapes of the Ar and N_2 elastic peaks being slightly different at a same scattering angle, the scattered electron intensities have been obtained by integrating on the area of the elastic peak.

(ii) The contribution of the background scattering to the scattering from the molecular gas beam has been estimated by flowing the gas through the side leak and establishing the proper background pressure. In the 15–30 eV impact energy range of interest, this contribution has been evaluated to be about 2% for scattering angles $\geqslant 20°$.

(iii) The direct beam intensity has been monitored, before and after each measurement of the elastically scattered electron intensity and of the mass flow rate, using a Faraday cup.

(iv) The calibration of the incident electron energy scale has been achieved by observing the $v'=0$ and $v'=1$ levels of the nitrogen $^2\Sigma_g^+$ Feshbach resonance in the $v''=0$ and $v''=1$ exit channels of the electronic ground state which are located at 11.48 and 11.75 eV, respectively.[21] The accuracy is about 10 meV. The true zero scattering angle has been determined from the symmetry of the elastic scattering in helium.

The elastic differential cross section ratios have been obtained at 15, 20, and 30 eV impact energies in the angular range of 20°–115°. Measurements have been made every 10°, except in the 60°–80° angular region where the elastic differential cross section of argon exhibits a minimum and therefore smaller angular steps have been used. The differential cross section ratios have been multiplied by the absolute vibrationally elastic differential cross section of nitrogen[22,23] to obtain the absolute values of the elastic differential cross section of argon.

TABLE II. Estimation of the various sources of errors that contribute to the total error in the measurement of the $DCS_{elas}(E_0,\theta)_{Ar}/DCS_{elas}(E_0,\theta)_{N_2}$ ratio.

1. Error in the ratio of flow rates $\frac{\dot{N}_{N_2}}{\dot{N}_{Ar}}$.	±5%
2. Statistical error in the ratio $\frac{\dot{N}_e(E_0,\theta)_{Ar}}{\dot{N}_e(E_0,\theta)_{N_2}}$.	$\leqslant$±5%
3. Estimated error due to the change in the direct electron beam current.	±3%
Total error	$\leqslant$±13%

Table II summarizes our estimation for the various sources of errors that contribute to the total error in the measurement of the differential cross section ratio

$$\frac{DCS_{elas}(E_0,\theta)_{Ar}}{DCS_{elas}(E_0,\theta)_{N_2}}.$$

This overall error has been estimated to about ±13%, which is well supported by our several independent sets of measurements. The value of this latter error may increase in the angular region of the deep minima where a small error in the calibration of the scattering angle scale can give rise to large variations in the cross section values. To obtain the absolute elastic cross section of argon, the ratios have been multiplied by the previously measured absolute elastic cross section of N_2.[22,23] Then, the error in the value of the elastic differential cross section of argon has been estimated to ±18% which is the square root of the sum of squares in the error of the cross section ratio (±13%) and of the N_2 elastic differential cross section (±13%).

1. The elastic differential cross section of argon at 15 eV

The absolute values of the elastic differential cross section experimentally determined at 15 eV are presented in tabular form in Table III. We have compared in Fig. 3 our measurements with those previously obtained by Srivastava *et al.*[24] with the relative flow normalization method, as also by Williams[25] and Furst *et al.*[26] from a phase-shift analysis. The various sets of data very well agree with each other in the angular range covered.

TABLE III. Absolute elastic differential cross sections of argon at 15, 20, and 30 eV in function of the scattering angle θ. The units are 10^{-16} cm^2/sr. The relative uncertainty of the DCS is estimated to be $\pm 18\%$.

θ (deg)	15 eV	20 eV	30 eV
20	8.9	7.0	5.1
30	6.0	5.0	3.1
40	3.6	3.0	1.8
50	1.8	1.4	0.75
60	0.75	0.49	0.22
65	0.50	0.22	0.059
69	⋯	⋯	0.017
70	0.34	0.097	0.0090
71	0.32	⋯	0.0065
72	⋯	0.071	0.0058
73	0.33	0.062	0.0060
75	0.32	0.056	0.021
78	⋯	0.076	⋯
80	0.41	0.10	0.10
90	0.52	0.33	0.34
100	0.64	0.54	0.43
115	0.24	0.42	0.38

2. The elastic differential cross section of argon at 20 eV

At 20 eV impact energy, four experimental sets of data can be found in the literature. First the values of Srivastava *et al.*[24] obtained by the relative flow method, the absolute values of Williams and Willis[27] and of Furst *et al.*[26] normalized by a phase-shift analysis, and the data set of DuBois and Rudd.[28]

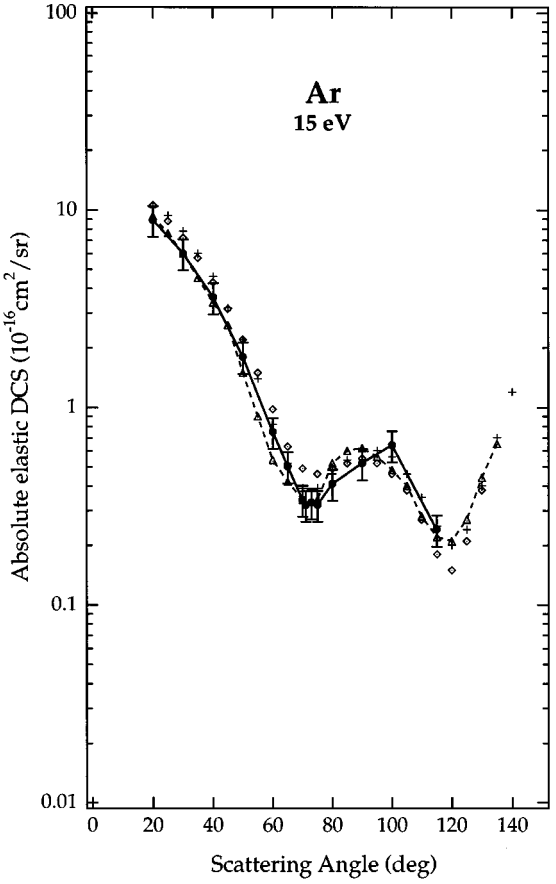

FIG. 3. Absolute elastic differential cross section of argon versus the scattering angle θ at 15 eV impact energy. △(---) Srivastava *et al.* (1981); + Williams (1979); ◇ Furst *et al.* (1989); ●(—) Present results.

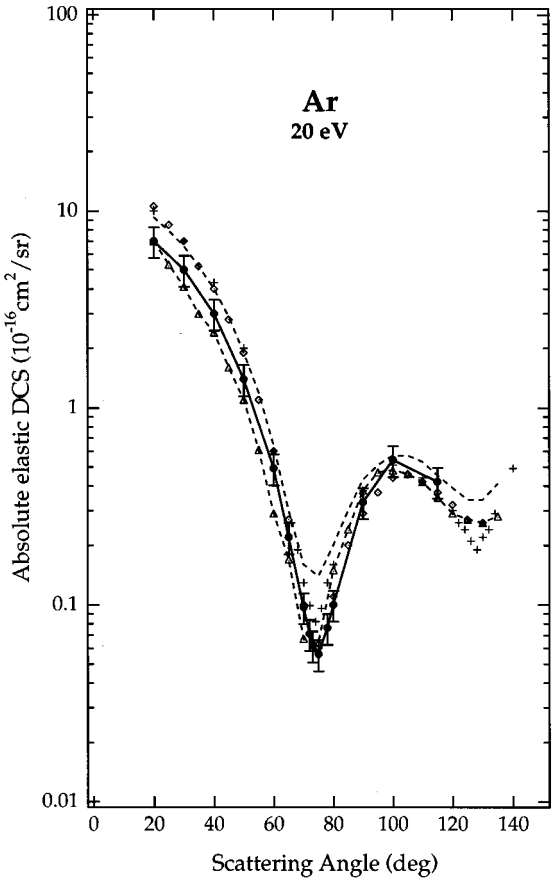

FIG. 4. Absolute elastic differential cross section of argon versus the scattering angle at 20 eV impact energy. △(---) Srivastava *et al.* (1981); --- DuBois and Rudd (1976); + Williams and Willis (1975); ◇ Furst *et al.* (1989); ●(—) Present results.

The elastic differential cross section of argon determined at 20 eV in the 20°–115° angular range is presented in Fig. 4 where it is compared to the other sets of data. At the small scattering angles ($\leqslant$70°), our absolute values are in good agreement with the other sets of data and are intermediate between those of Srivastava *et al.*[24] and those of Furst *et al.*,[26] Williams and Willis,[27] and DuBois and Rudd.[28] In the region of the minimum of the cross section, a discrepancy occurs between our results and those of DuBois and Rudd.[28] This disagreement may be due to a difference between the angular resolutions of the two spectrometers. At high scattering angles (90°–115°), all the sets of data well agree with each other.

3. The elastic differential cross section of argon at 30 eV

The absolute values of the elastic differential cross section of argon obtained at 30 eV in the 20°–115° angular range are presented in Table III and are shown in Fig. 5 where they are compared to the experimental results ob-

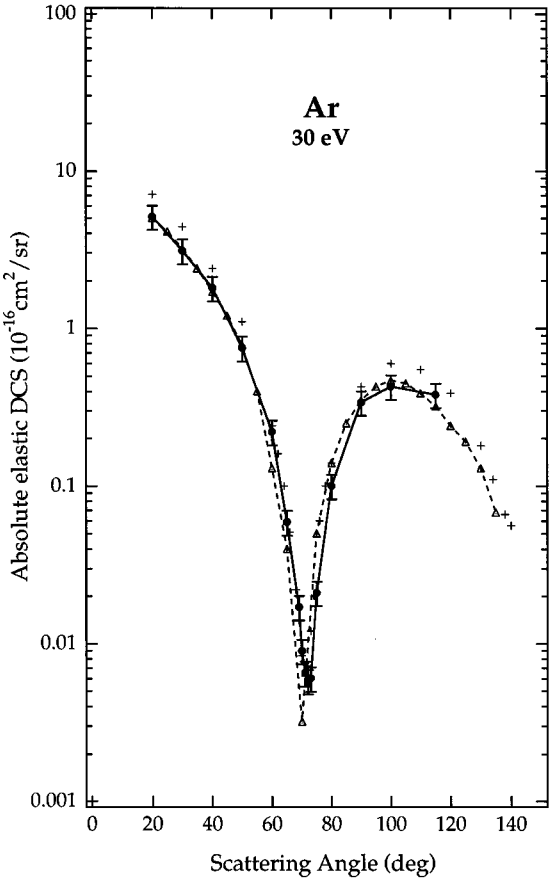

FIG. 5. Absolute elastic differential cross section of argon versus the scattering angle at 30 eV impact energy. △(---) Srivastava *et al.* (1981); + Williams and Willis (1975); ●(—) Present results.

tained by Srivastava *et al.*[24] and by Williams and Willis.[27] The agreement between our measurements and those of Srivastava *et al.*[24] is very good, except in the region of the deep minimum where a very small difference in the calibration of the scattering angle scale can involve large variations in the cross section values (Fig. 5). The agreement between our measurements and those of Williams and Willis[27] is quite good, except in the small scattering angular range (20°–50°) where our results are smaller of about 30%.

4. Conclusion

The elastic collision cross sections of argon have been obtained using a relative flow technique at 15, 20, and 30 eV impact energies in the 20°–115° scattering angular range. The good agreement with the experimental results of other workers suggests that the present instrument is well characterized.

III. RESULTS AND DISCUSSION

To put the vibrational angular cross sections of methane on an absolute scale, the following procedure has been followed. First, the absolute elastic differential cross sections have been determined from a relative flow technique at 15 and 30 eV impact energies in the 8°–95° angular range. Second, the vibrational electron energy loss spectra have been recorded at those energies for the angular range of interest, in order to evaluate the vibrational/elastic intensity ratios. Finally, using the intensity ratios and the absolute elastic angular cross sections, the vibrational differential cross sections have been derived.

We will first present the absolute elastic differential cross sections of methane recorded at 15 and 30 eV impact energies between 8° and 95°. Then a typical vibrational electron energy loss spectrum of methane will be shown and analyzed. Finally, absolute vibrational angular cross sections will be displayed and compared, where possible, with previous experimental works.

A. The absolute elastic cross sections

The absolute elastic collision cross sections of methane have been obtained at 15 and 30 eV impact energies for scattering angles ranging from 8° to 95°. Normalization upon an absolute scale has been carried out by means of a relative flow technique with nitrogen as calibration standard (Sec. II). Briefly, the intensity of electrons elastically scattered from N_2 has been measured and immediately followed by the measurements of the scattered electron intensity from CH_4 under the same experimental conditions. This procedure has been repeated for each scattering angle of interest. The mass flow rates and the head pressures have been adjusted to reproduce as closely as possible the same density distribution from the needle of both gases.[16,18] In the present work, 1.5 Torr N_2 head pressure (0.20 sccm) and 1.2 Torr CH_4 head pressure (0.22 sccm) have been chosen. These backpressure values have kept the vacuum chamber pressure on the 10^{-6} Torr range throughout the experiment. The absolute elastic differential cross sections have been derived from the use of the relative flow formula:

$$\frac{\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)_{\mathrm{CH_4}}}{\mathrm{DCS}_{\mathrm{elas}}(E_0,\theta)_{\mathrm{N_2}}}=\frac{\dot{N}_e(E_0,\theta)_{\mathrm{CH_4}}}{\dot{N}_e(E_0,\theta)_{\mathrm{N_2}}}\times\frac{\dot{N}_{\mathrm{N_2}}}{\dot{N}_{\mathrm{CH_4}}}\times\sqrt{\frac{m_{\mathrm{N_2}}}{m_{\mathrm{CH_4}}}}. \tag{9}$$

The elastic cross sections are displayed in Figs. 6 and 7 and presented in tabular form in Table IV. The errors on the absolute values have been determined in the same way as those for the Ar elastic cross section (Sec. II) and have been estimated to be ±18%. Comparison with the other sets of absolute data available in the literature, i.e., the absolute measurements of Shyn and Cravens[29] and of Boesten and Tanaka,[30] is also shown in Figs. 6 and 7.

At 15 eV electron impact energy, our absolute values are in very good agreement with those of Boesten and Tanaka[30] across the whole angular range of interest in this work. In contrast, some discrepancies with the data set of Shyn and Cravens[29] appear at small angles (≤20°) where our values are lower by as much as 80% and in the 80°–95° angular region where differences of 40% between the two series of measurements are observed.

The elastic differential cross section of methane measured for 30 eV impact energy electrons agrees well with the two earlier sets of data.[29,30]

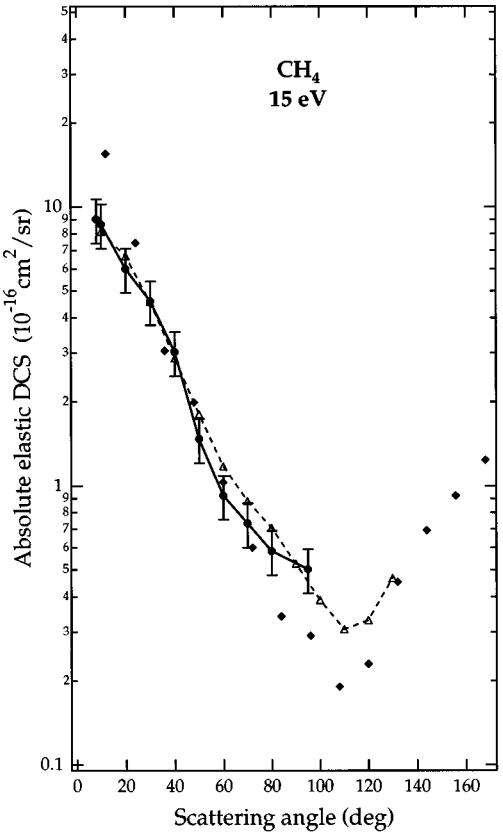

FIG. 6. Absolute elastic differential cross section of methane versus the scattering angle at 15 eV impact energy. △(---) Boesten and Tanaka (1991); ♦ Shyn and Cravens (1990); ●(—) Present results.

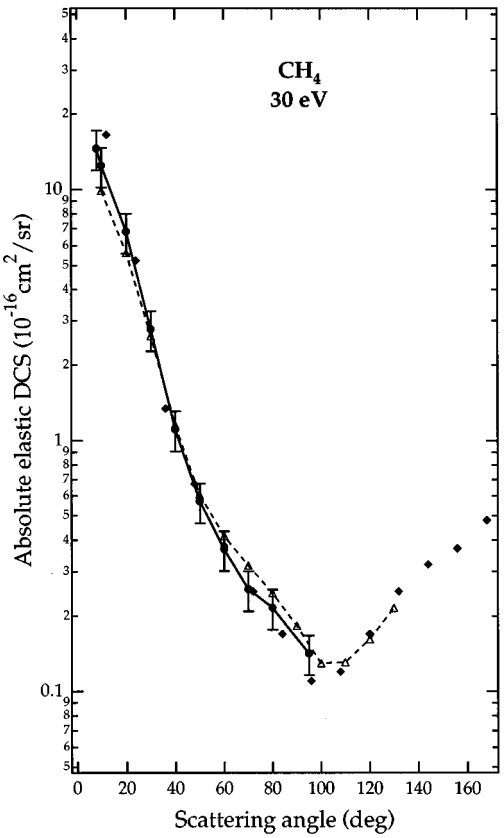

FIG. 7. Absolute elastic differential cross section of methane versus the scattering angle at 30 eV impact energy. △(---) Boesten and Tanaka (1991); ♦ Shyn and Cravens (1990); ●(—) Present results.

B. The electron energy loss spectra

In order to obtain the inelastic/elastic ratios, vibrational excitation spectra have been recorded at 15 and 30 eV incident energies in the angular range of interest.

The methane molecule has a tetrahedral geometry and belongs to the T_d symmetry point group. There are nine vibrational normal modes distributed among three irreducible representations and degenerated into four vibrational energies. The ν_1 stretching mode belongs to the A_1 symmetry. The bending mode ν_2 is of the E type and is doubly degenerate, while the ν_3 stretching and ν_4 bending vibrational modes have the T_2 symmetry and are triply degenerate. The associated frequencies have been determined by infrared and Raman spectroscopies and are 362 meV (ν_1), 192 meV (ν_2), 374 meV (ν_3), and 162 meV (ν_4).[31] All four vibrational normal modes are Raman active, but the ν_3 and ν_4 modes are additionally infrared active. A typical vibrational excitation spectrum recorded at 15 eV and 10° scattering angle is shown in Fig. 8. In addition to the elastic peak, it exhibits two bands. The first band is located around 175 meV and corresponds to the excitation of the ν_2 and ν_4 bending modes (not resolved within our experimental resolution of 30–45 meV), while the second peak is centered around 370 meV and is related to the excitation of the stretching vibrational modes ν_1 and ν_3 (once again unresolved). These two bands will be labeled $\nu_{2,4}$ and $\nu_{1,3}$, respectively. A combination of the $\nu_{2,4}$ bending modes and of the $\nu_{1,3}$ stretching modes is also observed around 540 meV.

The intensity ratios of the vibrational scattering to the elastic scattering has been determined by measuring the ratios of the areas of the vibrational and elastic features. The contribution of the elastic scattering peak and of the background signal to the vibrational excitation has been estimated by fitting a smooth curve, as shown in Fig. 8 by the dashed line. This procedure has been also applied to derive the inelastic/elastic scattering intensity ratios in London.

TABLE IV. Absolute elastic differential cross sections of methane at 15 and 30 eV in function of the scattering angle θ. The units are 10^{-16} cm^2/sr. The relative uncertainty of the DCS is estimated to be ±18%.

θ (deg)	15 eV	30 eV
8	9.01	14.5
10	8.6	12.4
15	7.3	9.6
20	6.0	6.8
30	4.6	2.8
40	3.0	1.1
50	1.5	0.57
60	0.92	0.37
70	0.73	0.26
80	0.58	0.22
95	0.50	0.14

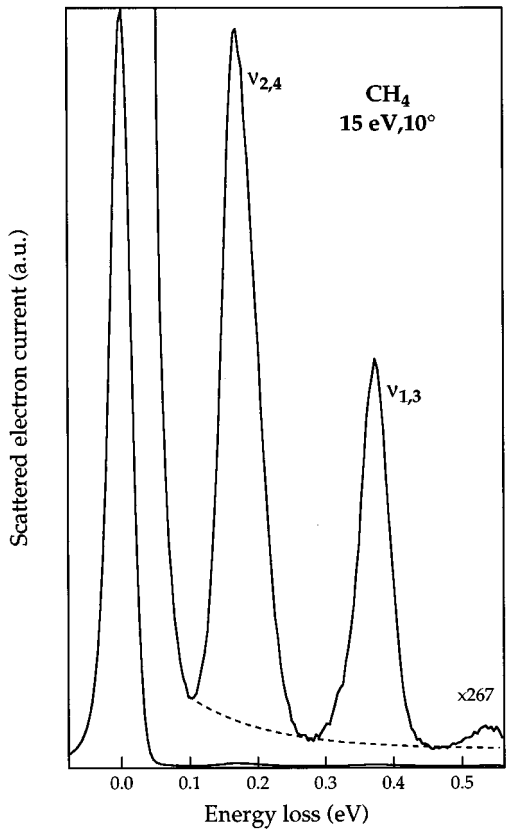

FIG. 8. Vibrational electron energy loss spectrum of methane recorded at 15 eV impact energy for a 10° scattering angle with an energy resolution of 30 meV.

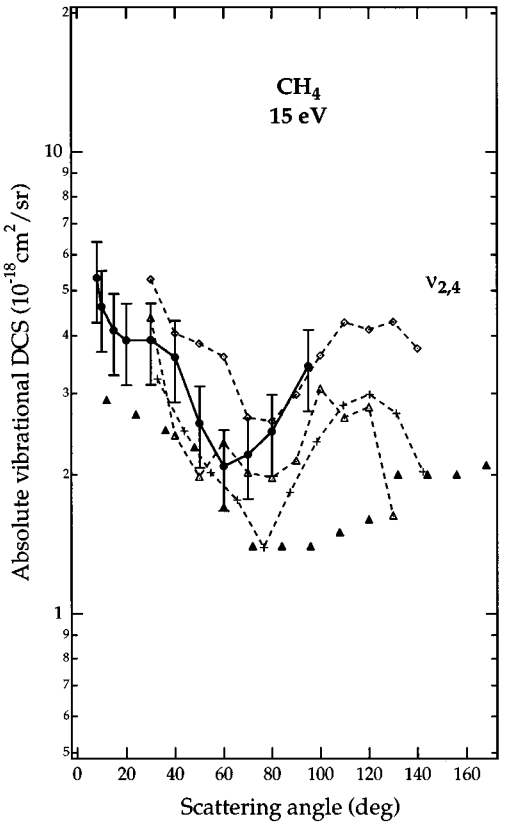

FIG. 9. Absolute differential cross section for the excitation of the $\nu_{2,4}$ bending group of modes of methane versus the scattering angle at 15 eV impact energy. △(---) Tanaka *et al.* (1983); +(---) Curry *et al.* (1985); ▲ Shyn (1991); ◇(---) Mapstone and Newell (1994); ●(—) Present results.

C. The absolute vibrational cross sections

As the vibrational/elastic intensity ratios are approximately equal to the ratio of the respective differential cross sections, absolute vibrational differential cross sections may be directly found by multiplication with the absolute elastic differential cross section. The overall error on the vibrational cross sections has been estimated on basis of the statistical uncertainty on the ratio measurement combined with the error on the elastic cross section and is estimated to be ±20%. The vibrational cross sections are shown in Figs. 9–12 and are compared, where possible, to other previous works.

1. The absolute vibrational cross sections at 15 eV

The absolute differential cross sections of the $\nu_{2,4}$ and $\nu_{1,3}$ groups of modes are displayed in Figs. 9 and 10 where they are compared to other existing sets of data. They are also tabulated in Table V.

Our measurements of the $\nu_{2,4}$ differential cross section between 8° and 95° exhibit a smooth plateau at about 20° followed by a much more pronounced minimum located around 70° (Fig. 9). For comparison, four sets of measurements were available in the literature (Table I): The absolute measurements of Tanaka *et al.*[4] [normalized to the absolute elastic cross section of Tanaka *et al.*[32]]; the absolute values of Shyn[6] [normalized to the absolute elastic cross section of Shyn and Cravens[29]]; the set of data of Curry *et al.*[5] [normalized to the relative elastic cross section of Curry *et al.*[5] itself normalized to the absolute measurements of Tanaka *et al.*[32]]; finally the recent values of Mapstone and Newell[7] [normalized to the relative elastic cross section of Mapstone and Newell,[33] itself normalized to the absolute values of Tanaka *et al.*[32]]. To allow a better comparison, all the vibrational measurements involving a normalization to the absolute elastic cross section of Tanaka *et al.*[32] have been renormalized to the more recent measurements of the Tanaka's group.[30] This has been made for the measurements of Tanaka *et al.*[4] and of Mapstone and Newell[7] but has not been realized for the values of Curry *et al.*[5] for which the elastic and inelastic measurements were not performed at the same scattering angles, leading to a difficult evaluation of the vibrational/elastic intensity ratios. Our absolute values agree quite well with the values of Tanaka *et al.*[4] for the angular range studied (8°–95°), while a strong discrepancy of as much as 60% appears at small and large angles with the measurements of Shyn.[6] Since the $\nu_{2,4}$ peak is close to the elastic peak, this difference may be due to the difference of the resolutions between the two experiments (30–45 meV for the present work and 80 meV for the work of Shyn). The agreement between the shape of our $\nu_{2,4}$ bending mode cross section and the shapes of the Mapstone and Newell[7] and of Curry *et al.*[5] is quite good in the 30°–95° angular range. However the present data are lower than those of Mapstone and Newell[7] in the 30°–

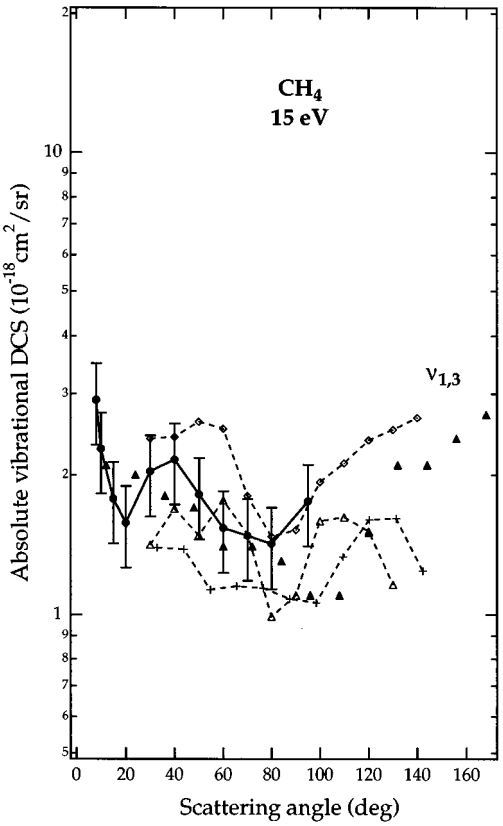

FIG. 10. Absolute differential cross section for the excitation of the $\nu_{1,3}$ stretching group of modes of methane versus the scattering angle at 15 eV impact energy. △(---) Tanaka *et al.* (1983); +(---) Curry *et al.* (1985); ▲ Shyn (1991); ◇(---) Mapstone and Newell (1994); ●(—) Present results.

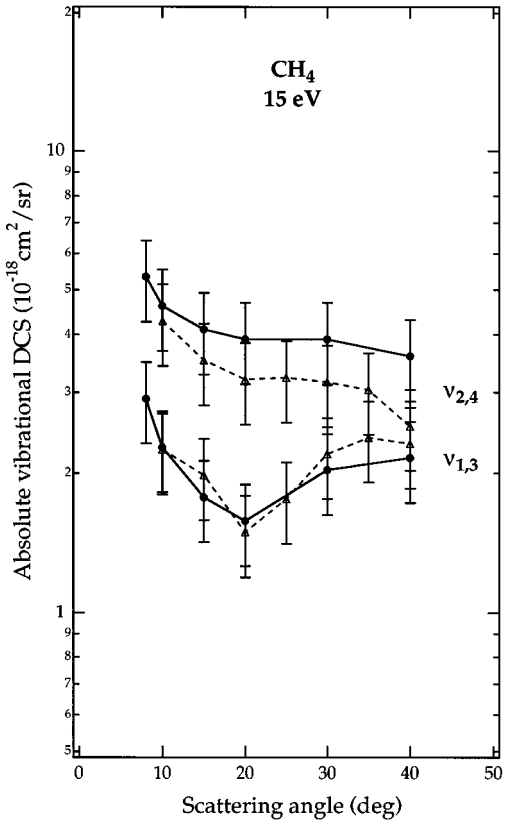

FIG. 11. Comparison of the $\nu_{2,4}$ and $\nu_{1,3}$ differential cross sections of methane measured at 15 eV impact energy at Liège with that recorded in London in the small angular range (≤40°). △(---) London; ●(—) Present results.

70° angular range while they are higher than those of Curry *et al.*[5] between 30° and 95°. This latter difference may be due to the fact that the data of Curry *et al.*[5] have not been renormalized to the recent absolute elastic cross section of Boesten and Tanaka.[30]

The absolute differential cross section for the excitation of the $\nu_{1,3}$ group of modes recorded at 15 eV between 8° and 95° is shown in Fig. 10. A quite sharp minimum is observed at 20° and another broader one, around 70°. Comparison with the values of Mapstone and Newell[7] and of Curry *et al.*[5] in the 30°–95° angular range again agrees in shape but not in magnitude. Agreement between the present data and those of Tanaka *et al.*[4] is reasonable between 30° and 70° but is poorer in the region of the minimum where the values of Tanaka *et al.*[4] are lower by about 30%. In contrast to the $\nu_{2,4}$ values, the present $\nu_{1,3}$ values agree reasonably well with Shyn.[6] However, it should be noted that in the 12°–40° small angular range, no minimum is present in the Shyn's $\nu_{1,3}$ cross section (Fig. 10).

To confirm the shapes of the vibrational cross sections in the small angular range 8°–40° and in particular to confirm the presence of a sharp minimum at 20° in the cross section of the $\nu_{1,3}$ stretching group of modes, an independent series of measurements of the vibrational/elastic intensity ratios have been carried out in London. These ratios have been normalized to the absolute elastic cross section measured at Liège in order to deduce the absolute $\nu_{2,4}$ and $\nu_{1,3}$ cross section values. The results are displayed in tabular form (Table VI) and shown in Fig. 11 where they are compared to the measurements of Liège. There is a good agreement between the two sets of data and the minimum in the $\nu_{1,3}$ cross section is well reproduced. A small discrepancy should be noted in the case of the $\nu_{2,4}$ cross section where the London values are slightly lower, although within the error bars. This may be due to a difference between the energy resolutions of the two spectrometers (30–45 meV and 50–60 meV).

2. The absolute vibrational cross sections at 30 eV

Differential cross sections recorded for the $\nu_{2,4}$ and $\nu_{1,3}$ group of modes at 30 eV impact energy between 8° and 95° are presented in Fig. 12 with a comparison to the values obtained from the London electron spectrometer. Both vibrational cross sections show a minimum around 70°–80° (Fig. 12; Tables V and VI), while the cross section of the $\nu_{1,3}$ stretching modes exhibits a second minimum at a scattering angle of 20°, as observed at 15 eV impact energy. The independent series of measurements carried out in London at scattering angles ranging from 15° to 40° are in good agreement with the Liège data, although again within the error bars, the cross section of the $\nu_{2,4}$ bending modes is slightly smaller than that obtained at Liège.

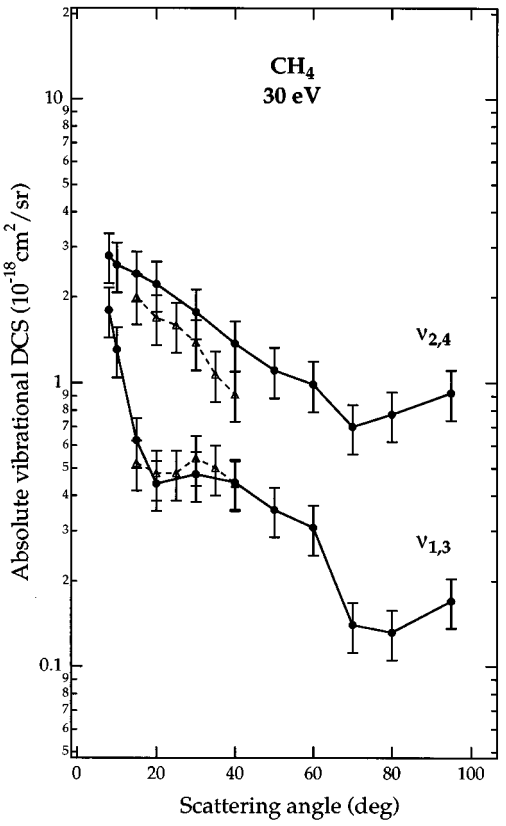

FIG. 12. Absolute differential cross section for the excitation of the $\nu_{2,4}$ bending and of the $\nu_{1,3}$ stretching groups of modes of methane versus the scattering angle at 30 eV impact energy. △(---) London; ●(—) Present results.

IV. CONCLUSION

Absolute differential electron-collision cross sections have been measured for the excitation of the $\nu_{2,4}$ bending and of the $\nu_{1,3}$ stretching groups of modes of methane in its electronic ground state, at impact energies of 15 eV and, for the first time, 30 eV, and over an angular range between 8° and 95°. Normalization to the absolute values has been performed using the absolute elastic differential cross section determined from a relative flow technique and the inelastic/elastic intensity ratios derived from the vibrational electron energy loss spectra. The $\nu_{2,4}$ cross sections measured at 15 and 30 eV impact energies are larger than the $\nu_{1,3}$ ones over the whole angular range studied. It can be explained by the dependence of the electron-molecule interaction potential with the nature of the vibrational mode which is excited.[11] Hence, some theoretical calculations are needed in order to quantify the different electron-molecule interaction terms (dipole, quadrupole, polarization,⋯) involved in the excitation of the vibrational mode.

At the impact energy of 15 eV, the $\nu_{2,4}$ and $\nu_{1,3}$ vibrational differential cross sections both present a minimum around the 70°–80° scattering angle. An additional minimum is also evidenced, for the first time, at 20° in the differential cross section of the stretching $\nu_{1,3}$ group of modes, while a smooth plateau is observed around 20° in the $\nu_{2,4}$ bending differential cross section. Comparison between the present differential cross sections and the previous work has established the shapes of the various vibrational cross sections. The agreement in absolute magnitude of the cross sections is, however, poorer and some discrepancies have been evidenced.

The differential cross section of the $\nu_{2,4}$ bending group of modes recorded at 30 eV impact energy in the 8°–95° scattering angular range decreases smoothly up to 70° where it reaches a minimum before increasing up to 95°. As observed at 15 eV impact energy, the $\nu_{1,3}$ differential cross section exhibits minima around 70°–80° and at 20°.

The simultaneous independent series of measurements carried out in the Molecular Physics Laboratory of the University College London at the small scattering angles (⩽40°) agree very well with the results obtained from the Laboratoire de Spectroscopie d'Electrons diffusés of the University of Liège. This has confirmed the occurrence of minima at 20° scattering angle in both the 15 and 30 eV $\nu_{1,3}$ differential cross sections.

TABLE V. Absolute vibrational differential cross sections of methane (Liège) at 15 and 30 eV in function of the scattering angle θ. The units are 10^{-18} cm^2/sr. The relative uncertainty of the DCS is estimated to be ±20%.

	15 eV		30 eV	
θ	$\nu_{2,4}$	$\nu_{1,3}$	$\nu_{2,4}$	$\nu_{1,3}$
8	5.3	2.9	2.8	1.8
10	4.6	2.3	2.6	1.3
15	4.1	1.8	2.4	0.63
20	3.9	1.6	2.2	0.44
30	3.9	2.0	1.8	0.48
40	3.6	2.2	1.4	0.45
50	2.6	1.8	1.1	0.36
60	2.1	1.5	0.99	0.31
70	2.2	1.5	0.70	0.14
80	2.5	1.4	0.77	0.13
95	3.4	1.8	0.92	0.17

TABLE VI. Absolute vibrational differential cross sections of methane (London) at 15 and 30 eV in function of the scattering angle θ. The units are 10^{-18} cm^2/sr. The relative uncertainty of the DCS is estimated to be ±20%.

	15 eV		30 eV	
θ	$\nu_{2,4}$	$\nu_{1,3}$	$\nu_{2,4}$	$\nu_{1,3}$
10	4.3	2.3	⋯	⋯
15	3.5	2.0	2.0	0.52
20	3.2	1.5	1.7	0.48
25	3.2	1.8	1.6	0.48
30	3.2	2.2	1.4	0.54
35	3.0	2.4	1.1	0.50
40	2.5	2.3	0.90	0.44

ACKNOWLEDGMENTS

F. Motte-Tollet and J. Heinesch are grateful to the Patrimoine of the University of Liège, to the Fonds National de la Recherche Scientifique, and to the Fonds de la Recherche Fondamentale Collective of Belgium for financial support.

One of us (F. Motte-Tollet) wishes to acknowledge M.-J. Hubin-Franskin and M. Furlan for assistance and fruitful discussions. We wish also to express our gratitude to G. Quoilin and H. Balbeur for their highly valuable technical assistance to the building of the relative flow experimental set-up. J. M. Gingell acknowledges support of the EPSRC for the financial support of a postgraduate studentship. N. J. Mason acknowledges support of a Royal Society University Research Fellowship. The authors are also pleased to acknowledge support of the British Council to allow collaboration between the two research laboratories.

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