Excitation of the four fundamental vibrations of CH_4 by electron impact near threshold

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Abstract. Absolute differential elastic and vibrational excitation cross sections have been measured for CH_4 at 90° and from 0.1 to 1.5 eV, with resolution of all four vibrational modes. Threshold peaks were observed in the excitation of the ν_1, ν_3 and ν_4 modes, but not in the ν_2 mode. These results are in good agreement with the recent calculation of Nishimura and Gianturco [*J. Phys. B: At. Mol. Opt. Phys.* **35** (2002) 2873]. No near threshold structures were observed.

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1. Introduction

Electron collisions in methane play a role in various planetary atmospheres and in technological plasmas. A scientifically interesting feature are the threshold peaks in the vibrational excitation cross sections, reported by Rohr [1]. Threshold peaks and sharp near-threshold structures in the vibrational excitation cross sections are of considerable interest [2]. They have been discovered initially in molecules having a permanent dipole moment, in particular in the hydrogen halides. They are ascribed to vibrational Feshbach resonances where an extra electron is bound (in the fixed nuclei view) for a certain range of internuclear distances, or certain range of molecular geometries in the polyatomic case, by the combination of dipole, quadrupole and polarization potentials. The threshold peaks [3] and later also near threshold structures [4] have been found also in CO_2, an initially surprising finding because CO_2 does not have a permanent dipole moment to bind an extra electron. CO_2 does, however, have polar C=O bonds, a consequence of the very different electronegativities of the C and O atoms, giving it a substantial quadrupole moment and a transition dipole moment when it is bent. The situation in CO_2 is now theoretically understood, the observations have recently been successfully reproduced by Vanroose *et al* using a virtual state model [5].

The observation of the threshold peaks by Rohr [1] and later also of near threshold structures by Sohn *et al* [6] for CH_4 is even more surprising in this respect because the electronegativities of the C and H atoms are similar and the bonds are not very polar. This circumstance motivates a more detailed study of the near threshold behavior of the vibrational excitation cross sections in methane.

The present work employs the improved resolution and low energy capacity of the electron spectrometer in Fribourg [7] to achieve this goal. In particular the improved resolution is used to record the cross sections for all four vibrational modes separately, whereas nearly all previous experiments were limited to recording the sums of the cross sections for the close-lying (ν_2, ν_4) and (ν_1, ν_3) pairs of modes (usually denoted as $\nu_{2,4}$ and $\nu_{1,3}$). The work concentrates on the threshold region and covers the energy range up to 1.5 eV.

A number of important studies of electron collisions with methane have been carried out in the past, but only work below 2 eV will be reviewed here. Work at higher energies has been reviewed by Bundschu *et al* [8]. Müller *et al* [9] achieved a very high resolution of $13-15$ meV and resolved the ν_2 and ν_4 vibrations in energy-loss spectra recorded at $E_0 = 0.5$ and 7.5 eV. They deconvoluted the rotational structure of the vibrationally elastic and the ν_2 and ν_4 inelastic energy-loss peaks, using the partial sum-rules of Shimamura [10], at 0.5 and 7.5 eV and derived the rotational-vibrational excitation cross sections as a function of scattering angle in the range 15° - 140°. Distinct cross sections for the ν_2 and ν_4 vibrations were obtained also by Tanaka *et al* [11], albeit at 7.5 eV, above the energy range studied here. Sohn *et al* [6] measured the elastic and vibrational excitation cross sections as a function of electron energy at the scattering angles of 35°, 55°, 90° and 110°. They confirmed the threshold peaks at certain scattering angles and report deep structures near threshold in the $\nu_{2,4}$ cross section. Sohn *et al* [12] measured the absolute differential elastic cross sections from 0.2 to 5 eV and in the $15° - 140°$ angular range. Schmidt [13] derived the integral and momentum transfer elastic and vibrational excitation cross sections from transport coefficients, from very low energies up to 2 eV. Bundschu *et al* [8] measured the elastic and vibrational excitation cross sections at incident energies between 0.6 and 5.4 eV and 12 to 130°. They also calculated elastic differential cross

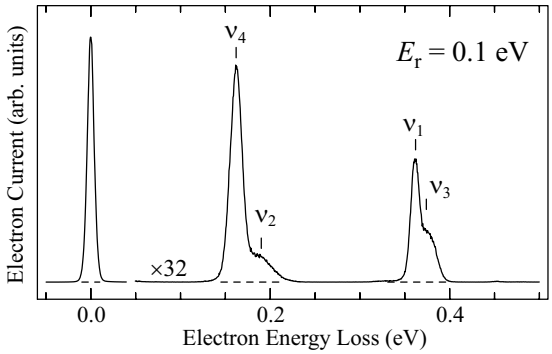

Figure 1. Electron energy loss spectrum of CH_4.

sections using a single-center expansion and closed-coupled equations.

Lengsfield *et al* [14] presented an *ab initio* calculation of integral and differential elastic cross sections using the complex Kohn method. Gianturco *et al* [15] calculated the elastic integral and differential cross sections around the Ramsauer-Townsend minimum with *ab initio* static + exchange interactions. Cascella *et al* [16] calculated the integral vibrational excitation cross sections at energies below 15 eV using the adiabatic approximation for the nuclear motion. An improved calculation with the exact vibrational coupled equations was presented by Nishimura and Gianturco [17].

2. Experiment

The measurements were performed using a spectrometer with hemispherical analyzers [7, 18]. The energy resolution was about 10 meV in the energy-loss mode, at a beam current of around 40 pA. The energy of the incident beam was calibrated on the 19.365 eV [19] ^{2}S resonance in helium and is accurate within ±10 meV. The analyzer response function was determined on the elastic scattering in helium. CH_4 was introduced through a 0.25 mm diameter effusive nozzle kept at ∼30°C. Absolute values of the elastic cross sections were determined by comparison with the theoretical helium elastic cross section [20], using the relative flow method, and are accurate within about ±25%. The inelastic cross sections are accurate within about ±35%.

3. Results and Discussion

Figure 1 shows an energy loss spectrum of CH_4 with the four fundamental vibrations listed in table 1. The width of the elastic peak is about 9 meV. As pointed out by Müller *et al* [9], pure rotational excitation is very weak at low energies, and the peak width is essentially due to the instrumental resolution. The vibrationally inelastic peaks, with the exception of ν_1, are substantially broader. The ν_4 peak, for example, is 16 meV wide, indicating substantial rotational excitation even at this low energy. The ν_2 and ν_3 peaks appear as shoulders on the more intense ν_4 and ν_1 peaks, similarly to the spectra of Müller *et al* [9]. A better separation is not possible at room temperature, even with a better resolution, because of rotational broadening.

A number of overtone and combination vibrations are also excited, as indicated by the wider range energy loss spectrum shown in figure 2, but only weakly. The

Table 1. Vibrational modes of methane (symmetry T_d) [21].

mode	sym species	type	frequency (meV)	activity
ν_1	a_1	sym stretch	361.7	Raman
ν_2	e	twisting	190.2	Raman
ν_3	t_2	antisym stretch	374.3	IR
ν_4	t_2	scissoring	161.9	IR

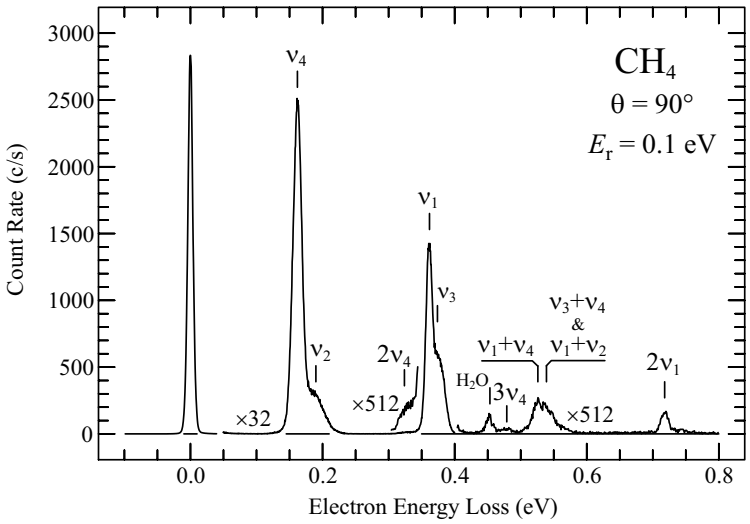

Figure 2. A wider range of the electron energy loss spectrum.

present work will therefore be limited to the study of the excitation of the fundamental vibrations. Rotationally integrated cross sections are measured as a function of electron energy. These cross sections are obtained by first fitting the observed energy-loss bands into Gaussian profiles at several discrete energies as shown in figure 3. The widths of the Gaussians are 15 meV and 30 meV for the ν_4 and ν_2 peaks at 0.61 eV, respectively, the excitation of ν_2 is accompanied with much more rotational excitation than that of ν_4. This observation agrees with the conclusion of Müller *et al* [9]. The widths at 1.2 eV in figure 3 are 16 meV and 33 meV, that is, the widths vary only slowly with electron energy. The cross section as a function of energy can thus be obtained by recording the excitation functions at the centers of the vibrational energy losses and adjusting them for the widths of the Gaussian profiles obtained at few discrete energies. The resulting curves (also corrected for the instrumental response function) then reflect the areas under the deconvoluted profiles, that is, the rotationally integrated cross sections.

The cross sections obtained in this way are shown in figure 4. A deep Ramsauer-Townsend minimum is seen in the elastic cross section, in agreement with earlier work. The present elastic cross section agrees very well with the data of Sohn *et al* [12] and of Bundschu *et al* [8].

Threshold peaks are observed in the excitation of the ν_1, ν_3 and ν_4 modes, but not in the ν_2 mode. Cross sections very near threshold have been measured by Rohr [1],

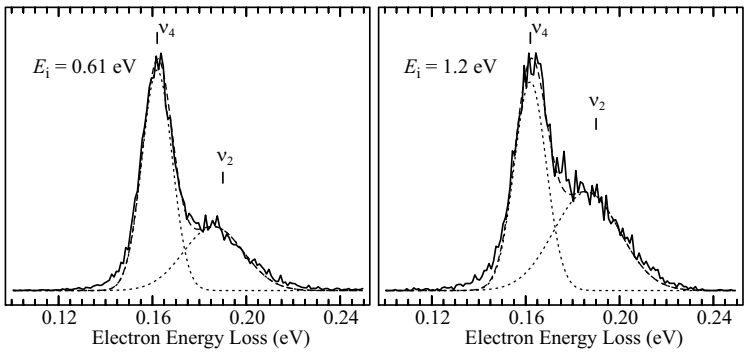

Figure 3. Gaussian fits of the electron energy loss spectra.

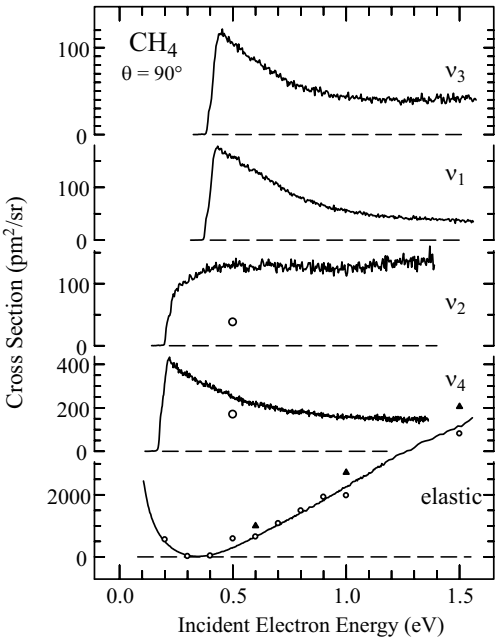

Figure 4. The low energy range of the cross sections for elastic scattering and for the excitation of the fundamental vibrations. Shown for comparison is also the elastic data of Sohn *et al* [12] (small open circles) and of Bundschu *et al* [8] (filled triangles), as well as the ν_2 and ν_4 inelastic data at 0.5 eV of Müller *et al* [9] (large open circles).

albeit at 60°, so that his curves can not be compared directly with the present data. His 60° and the present 90° data agree qualitatively on the presence of a threshold peak in the $\nu_{2,4}$ cross section but differ in shape otherwise. This may indicate that the shapes of at least some of the cross sections depend substantially on scattering angle.

A more direct comparison is possible with the later data of Sohn *et al* [6], who measured the $\nu_{2,4}$ and the $\nu_{1,3}$ cross sections as a function of energy from threshold to 1 eV above at 35°, 75°, 90° and 105°. Their results indicate that the cross section depends fairly strongly on scattering angle. At 90° they observe a pronounced

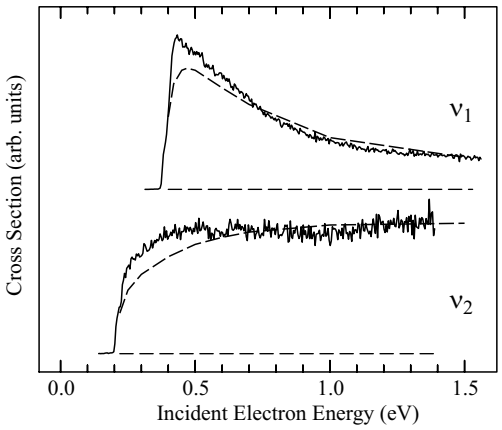

Figure 5. Comparison of the shapes of the present experimental cross sections with the integral cross sections of Nishimura and Gianturco [17] (dashed) for the two Raman active modes.

threshold peak in the $\nu_{2,4}$ cross section, in agreement with the present data. They observe only a weak threshold peak in the $\nu_{1,3}$ cross section at 90°, however, in contrast to the present results. In addition, they observed a narrow dip in the $\nu_{2,4}$ cross section, particularly at 90° and at 105°. No such structure could be observed in the present work, neither at 90° nor at 105°. Figure 4 also shows the absolute, rotationally summed values of the 90° ν_2 and ν_4 cross sections of Müller *et al* [9]. The agreement is not satisfactory, both in terms of the absolute value and in terms of the ν_4/ν_2 ratio, which is 1.7 in the present work (at 0.61 eV, see also figure 3), opposed to 4.5 in the data of Müller *et al* [9] (at 0.5 eV, see their figure 11). The sum of the present ν_2 and ν_4 cross sections can further be compared to the $\nu_{2,4}$ cross section of Bundschu *et al* [8] at 1 eV (with a stated confidence limits of ±21%). The two values agree very well, both the present and their values are 280 pm^2 sr^{-1}.

Nishimura and Gianturco [17] calculated the angle-integrated cross sections in the relevant energy range. An infrared active mode (ν_4) has been shown to be strongly anisotropic (forward peaked) [9], indicating that a comparison of 90° differential and integral cross section is not meaningful. The cross section for the Raman active mode ν_2 has been shown to be more isotropic in the same study and a comparison of integral and differential cross sections, shown in figure 5, appears meaningful in qualitative terms. The shapes are in excellent agreement, in particular a pronounced threshold peak is found for the ν_1 vibration, whereas the ν_2 cross section has the shape of a rounded step at threshold. The dipole moment derivative is zero for these IR inactive modes and, as pointed out by Nishimura and Gianturco [17], the fundamental difference between these two modes is that the derivatives of the polarizability with respect to the normal coordinate is zero for ν_2 but has a sizeable magnitude for ν_1. This is reflected in the Raman intensities which are 230 and 7.0 $Å^4$ amu^{-1} for ν_1 and ν_2, respectively [22]. It appears that, in the absence of a dipole derivative, the polarizability derivative is essential for the presence of a threshold peak.

4. Conclusions

The cross sections for the excitation of the four fundamental vibrations in methane were measured and revealed threshold peaks in all modes except one. The threshold peaks in the cross sections for the IR active vibrations ν_3 and ν_4 appear to be the consequence of the sizeable dipole moment derivatives. The threshold peak in the cross sections for the strongly Raman active vibration ν_1 appears to be linked to the large magnitude of the derivative of the polarizability. The cross section of the IR inactive and Raman very weak vibration ν_2 does not have a threshold peak.

The values of the elastic cross section agree well with earlier measurements. Substantial discrepancies are found between the present data and references [6, 9] for the vibrational excitation cross section. On the other hand the present sum of the ν_2 and ν_4 cross sections at 1 eV agrees very well with the $\nu_{2,4}$ value given by Bundschu *et al* [8]. More measurements of the vibrational excitation cross sections in function of the scattering angle and calculations of differential cross sections would be desirable to resolve the remaining discrepancies and to provide a more detailed comparison of theory and experiment.

Acknowledgments

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