Positron-impact vibrational excitation of CH₄: Comparing calculations with experiments for the symmetric and antisymmetric stretching modes

Tamio Nishimura ¹, Franco A. Gianturco *

Department of Chemistry and INFM, The University of Rome, Città' Universitaria, 00185 Rome, Italy

Abstract

We report the quantum close-coupling dynamical equations which are relevant for describing vibrationally inelastic processes in low-energy collisions between a beam of positrons and the CH₄ molecule. The interaction potential we employ to model the forces at play is described in detail and we report also our numerical technique for solving the scattering equations. The cross sections are obtained for the vibrational excitations of the symmetric and the antisymmetric bond-stretching modes of the CH₄ molecule and are compared both with simpler approximations and with recent experiments observing the energy losses into the two combined modes. Our calculations turn out to reproduce the energy dependence of the experimental findings, but not their absolute values, especially near threshold. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

The theoretical cross sections for vibrationally inelastic scattering of positrons (e⁺) from methane (CH₄) molecules are reported for the first time in this paper. This is a continuation of our work on the vibrational excitation processes for polyatomic molecules in the gas phase, occurring either by positron [1,2] or by electron impact [3,4]. Making use of a positron as a projectile instead of an electron adds some interesting phenomena to the collision system considered. Needless to say, an incident positron is distinguishable from all the bound electrons of the molecular target, so there is therefore no effect from electron exchange which needs instead to be considered in the case of electron–molecule (atom) collisions. Furthermore, a positron has the possibility of picking off one of the electrons of the target thereby forming a positronium (Ps) atom, provided that the collision energy is above the threshold for the Ps formation energy which is 5.8 eV for the e⁺–CH₄ system.

The CH₄ molecule belongs to the T₄ point group and has four types of normal modes which describe its lower-lying vibrations, i.e. the symmetric stretching (ν₁), the twisting (ν₂), the antisymmetric...
stretching ($v_3$) and the scissoring ($v_4$) modes. Thus, the excitation processes in a polyatomic molecule which is considered having a low vibrational energy content, could be treated as occurring separately through its different normal modes of vibration which carry different fundamental frequencies and belong to different symmetries. It is therefore interesting to try to understand, within this somewhat simplified picture, how the separate vibrational excitation cross sections for each vibrational mode depend on the feature of the specific mode involved without further considering the mixing within the modes that are expected to physically occur when ‘hotter’ molecular targets are examined.

While, on the experimental side, total cross sections for many types of atoms and molecules have been reported so far (see [5,6] and references quoted therein), due to the development of better collimated positron beams [7] it has occurred only recently that the relative differential cross sections of elastic processes for CH$_4$ have been reported over a large range of scattering angles (30–135º) [7]. In that case, however, the data still correspond to quasielastic (elastic scattering plus rotational and vibrational excitations) cross sections because of the fairly large energy spread of their positron beams with a full width at half maximum (FWHM) of about 2 eV. Furthermore, the last few years have also witnessed the development of a novel technique involving a magnetized beam of cold positrons [8], which allowed one to carry out measurements of absolute vibrationally inelastic cross sections for CO, CO$_2$ and H$_2$ [8] and also for CH$_4$ [9]. These data, therefore, have been measured for the first time at energies as low as 0.5 and up to several eV with a greatly improved FWHM value of 18 meV. These experiments have thus stimulated the interest of theoreticians and spurred the formulation of computational methods which could provide explanation as to how the phenomenon is occurring at the nanoscopic level. In the case of H$_2$, we have actually calculated vibrational excitation cross sections which reproduce well the experimental findings [10,11], and the same occurs for the case of the CO molecule [8]. In the case of CH$_4$, due to the higher resolution required, the excitation of the $v_1$ and $v_3$ modes, as well as those of the $v_2$ and the $v_4$ modes, cannot be completely resolved by current measurements. Because of these difficulties, therefore, the experimental data need even more to be supplemented by theoretical analysis which could then allow us to better understand the complete picture of the vibrational excitation dynamics triggered by positron projectiles. As a first step, we report in this paper our computed cross sections for the lowest excitations of both the $v_1$ and the $v_3$ modes, and compare them with the experiments which contain such excitations in a combined form.

The details of the present theory are described in next section while the numerical techniques are presented in more detail by Section 3. In Section 4, we report the final cross sections and discuss their behavior with reference to the experiments and to the other available calculations. We give our preliminary conclusions on the present results in the last section of the paper. Atomic units (a.u.) are used throughout the present analysis unless otherwise stated.

2. Theory

The details of the present theory have been already reported in our previous papers [2,12,13]. We therefore provide here only a brief reminder of it to the reader. In order to obtain vibrational excitation cross sections for positron scattering from polyatomic molecules we need to solve the Schrödinger equation of the total system,

$$(H - E)\Psi = 0$$

for the wavefunction $\Psi$ with a fixed value of the total energy $E$. Here $H$ is the total Hamiltonian given by

$$H = H_{\text{mol}} + K + V,$$

where $H_{\text{mol}}, K$ and $V$ represent the operators of the molecular Hamiltonian, of the kinetic energy for the scattered positron, and of the interaction between the incident positron and the target molecule, respectively. The $H_{\text{mol}}$ of this study only consists of the rotational and vibrational parts of the more complicated full molecular electronuclear Hamiltonian. This means that we consider it to be given here only as
\[ H_{\text{mol}} = H_{\text{rot}} + H_{\text{vib}}. \]  

(3)

Hence we include no effect from the possible electronic excitations or from other target’s reactive and break-up processes. In other words, we assume that during the scattering the molecular electronic wavefunction is always that of its electronic neutral ground state \( A_1 \). It should also be noted that no Ps formation channel is considered throughout the present calculations as it seems to be fairly negligible at the energies we are considering.

We can also assume that the orientation of the target molecule is fixed during the collision (i.e., we invoke what goes under the name of the rotationally sudden approximation [14]), since the molecular rotation is usually slower when compared with the velocity of the projectile at the energies we are considering. This is also called the fixed-nuclear orientation (FNO) approximation [14], and corresponds to ignoring the \( H_{\text{rot}} \) term in Eq. (3). Then, the total wavefunction could be generally expanded as follows:

\[
\Psi(r_p| R) = r_p^{-1} \sum_{\ell m} u_{\ell m}(r_p) X_{\ell p}(r_p) \chi_{\ell m}(R).
\]  

(4)

Here, \( \chi_{\ell m} \) is the vibrational wavefunction of the molecule with the vibrational quantum number \( n = (n_1, n_2, \ldots, n_s) \) with \( s \) representing each vibrational mode of the target nuclei. The variables \( R \) and \( r_p \) now denote the molecular nuclear geometry and the position vector of the positron from the center-of-mass (c.o.m.) of the target, respectively. The unknown \( u_{\ell m} \) functions describe the radial coefficients of the wavefunction of the incident particle and the \( X_{\ell p} \) are the symmetry-adapted angular basis function introduced earlier by us [15],

\[
X_{\ell p}^{mn}(r_p) = \sum_m b_{n\ell m}^m Y_{\ell m}(r_p),
\]  

(5)

where the functions \( Y_{\ell m} \) are the usual spherical harmonics. The suffix \( p \) stands for the chosen irreducible representation, \( \mu \) distinguishes the component of the basis if its dimension is greater than one, and \( h \) does that within the same set of \( (p \mu h) \). In this paper, \( v \) in Eq. (4) stands for the indices \( (p \mu h) \) collectively.

After substituting Eq. (4) into Eq. (1) under the FNO approximation, we obtain for \( u_{\ell m}(r_p) \) a set of full close-coupling equations which now also include vibrational channels. These are also called the body-fixed vibrational close-coupling (BFVCC) equations [11],

\[
\begin{align*}
\frac{d^2}{dr_p^2} - \frac{l(l+1)}{r_p^2} + k_n^2 &= u_{\ell m}(r_p) \\
&= 2 \sum_{l'\ell'} \langle lvn|l'v'n' \rangle u_{l'\ell'}(r_p),
\end{align*}
\]  

(6)

where \( k_n \) is written as

\[
k_n^2 = 2(E - E_{\ell m}^{\text{vib}})
\]  

(7)

with \( E_{\ell m}^{\text{vib}} \) being the energy of specific molecular vibration we are considering. Any of the elements of the interaction matrix in Eq. (6) is given by

\[
\langle lvn|l'v'n' \rangle = \sum_{l_0 n_0} \langle n|V_{l_0 n_0}|n' \rangle \int d_r X_{l_0 l}(r_p)^* X_{l_0 l}(r_p) X_{l_1 l'}(r_p) X_{l_1 l'}(r_p),
\]  

(8)

where

\[
\langle n|V_{l_0 n_0}|n' \rangle = \int dR \{ \chi_n(R) \}^* V_{l_0 n_0}(r_p | R) \{ \chi_{n'}(R) \}.
\]  

(9)

This method is essentially a generalization of the method proposed long ago (called the ‘hybrid theory’) for the simple case of a diatomic molecule [16]. When solving Eq. (6) under the boundary conditions that the asymptotic form of \( u_{l'\ell'}^{\text{vib}} \) is represented by a sum containing the incident plane wave of the projectile and the outgoing spherical wave,

\[
\begin{align*}
&\lim_{r_p \to \infty} u_{l'\ell'}^{\text{vib}} R^{-1} \\
&\quad \left\{ \delta_{ll'} \delta_{\ell\ell'} \delta_{mm'} \sin \left(k_{n'} r_p - \frac{l'\pi}{2} \right) \\
&\quad + \left( k_n \right)^{\frac{1}{2}} K_{l'\ell'}^{\text{vib}} \cos \left(k_{n'} r_p - \frac{l'\pi}{2} \right) \right\},
\end{align*}
\]  

(10)

we obtain the \( K \)-matrix elements. Therefore, the integral cross section for the vibrationally inelastic scattering is given by

\[
Q(n \to n') = \frac{\pi}{k_n} \sum_{l_0} \sum_{l_1} |T_{l_0 l_{1\ell'}}^{\text{vib}}|^2,
\]  

(11)

where \( T_{l_0 l_{1\ell'}}^{\text{vib}} \) is the \( T \)-matrix element.
The interaction potential \( V \) between the impinging positron and the molecular target is represented here by us in the form of a local potential. Thus, \( V \) is described by the sum of the repulsive electrostatic \( (V_{\text{el}}) \) and the attractive positron correlation–polarization \( (V_{\text{polar}}) \) terms. Possible cancellation in specific regions of space could be caused between the two potential terms because of the well-known fact that they have opposite signs, a feature specific to positron dynamics which makes the resulting cross section to be very sensitive to the particular form of \( V_{\text{polar}} \) which is being employed in the calculations. To obtain the \( V_{\text{polar}} \) in shorter range of \( r_p \), use is made of a simple parameter-free model potential \( (V_{\text{corr}}) \). The fundamental theory to construct the \( V_{\text{corr}} \) term is based on an electron–positron correlation energy \( (\varepsilon^{e-p}) \) obtained for each electron that is considered to be bound as if in a homogeneous electron gas [17]. The relationship between \( V_{\text{corr}} \) and \( \varepsilon^{e-p} \) consistent with the local density approximation and a variational principle applied to the total collision system yield the following results [18]

\[
V_{\text{corr}}(r_p) = \frac{d}{d\rho} \left\{ \rho(r_p)\varepsilon^{e-p}[\rho(r_p)] \right\},
\]

where \( \rho \) denotes the undistorted electron density of the target correctly obtained from many-body calculations. The quantity \( \varepsilon^{e-p} \) has been originally derived from an expectation value of the ground state of a Hamiltonian which represents an undistorted electron gas and one positron [19]. Based on this work, Boronski and Nieminen [20] have given the interpolation formulae of \( \varepsilon^{e-p} \) over the entire range of the density parameter \( r_s \), which satisfies the relationship of \( \varepsilon^{e-p} \).

In our present formulation of this model (given before in [18]), the short-range \( V_{\text{corr}} \) is connected smoothly with the asymptotic form \( (V_{\text{pol}}) \) of its spherical component,

\[
V_{\text{pol}}(r_p) \sim -\sum_{i=1}^{\infty} \frac{\alpha_i}{2^i r_p^{2i+2}}.
\]

Here, \( \alpha_i \) is the target polarizability with \( i = 1 \) and 2, for instance, denoting the dipole and quadrupole components, respectively. In the present calculation we retained only the dipole term of Eq. (13) for the \( V_{\text{pol}} \) potential for the \( \text{CH}_4 \) target.

3. Numerical details

The target wavefunction of \( \text{CH}_4 \) was calculated at the SCF (self-consistent field) level using the single-center expansion (SCE) applied to a multi-center Gaussian-type orbitals (GTOs) [13], and the basis set employed was given within the atomic and molecular orbital code \text{GAUSSIAN} 98 package [21]. The terms of the multipolar expansion for the interaction potential in Eq. (8) were retained up to \( l_0 = 24 \) and the scattered wavefunction of the positron in Eq. (4) was expanded up to \( l = 12 \) for the \( v_1 \) and the \( v_3 \) modes. Both values were found to describe to good numerical convergence the realistic molecular anisotropy of the interaction. In order to solve the close-coupling equations by means of standard Green’s function techniques, Eq. (6) is rewritten as an integral equation which is called a Volterra equation (for details, see [22–24]).

In the case of the \( v_1 \) mode which belongs to the \( A_1 \) symmetry, by fixing the molecular symmetry to be that of the \( T_d \) point group, the range of bond length of \( \text{C–H} \) was taken to vary from 0.87 to 1.6 \( \text{Å} \) to sufficiently take into account the effect of the nuclear displacement from the equilibrium geometry as occurring for the lowest four vibrational levels. As for the \( v_3 \) mode that has the molecular symmetry of \( C_s \) group, the vibrational normal coordinates were taken to vary in the range of \( \pm 1 \), i.e. \( r_c \pm 0.557, \mp 0.544, \pm 0.540 \) and \( \mp 0.544 \) \( \text{Å} \) for the four \( \text{C–H} \) bond lengths with six equilibrium bond angles of \( \angle \text{HCH} \). Here, \( r_c \) is the equilibrium \( \text{C–H} \) distance that is taken to be 1.082 \( \text{Å} \). For the asymptotic part of the \( V_{\text{polar}} \), i.e. \( V_{\text{pol}} \), the values of \( \alpha_1 \) are used by normalizing those obtained from the very large basis set (quintuple-zeta) of Dunning’s correlation consistent type [25] to the experimental value of \( \alpha_1 \) (17.54 a.u.) at the equilibrium geometry.

4. Discussion of results

One of the important features for treating as realistically as possible the dynamical effects of the impinging positron beam on the molecular vibrational motion is to generate the corresponding matrix elements of Eq. (9). This means, in turn, that we have to obtain both the dipole polariz-
ability behavior and the molecular potential energy curve for the range of internuclear coordinates which are involved to describe a preselected number of levels for that particular vibrational mode. We therefore show in Fig. 1 the calculated behavior of both quantities for the total symmetric stretching motion associated with the \( v_1 \) mode, while Fig. 2 reports the same quantities, but this time for the antisymmetric stretching motion for the \( v_3 \) frequency. The experimental energy spacings are 2920 cm\(^{-1}\) for the former mode and 3016 cm\(^{-1}\) for the latter [4]. As already discussed, the experimental resolution is not able to separate the two different energy loss processes [8]. One can make the following comments by observing the results shown in the two figures.

1. The variation of the dipole polarizability for the \( v_1 \) mode, the \( \alpha^{(1)}_1 \), indicates that the region of CH distances sampled by the calculations shows changes of more than 50% from its equilibrium value, thereby suggesting that such changes will be very important and, near threshold, will dominate in guiding the vibrational energy transfer dynamics.

2. With the same token, the corresponding variations for \( \alpha^{(3)}_1 \) shown in Fig. 2 indicate that the antisymmetric stretch causes less of a change in the polarizability values, a feature that seems reasonable when one considers the reduced variation of the ‘volume’ occupied by the density cloud of the bound electrons as the bonds stretch out of phase during the \( v_3 \) motions. On the other hand, one should keep in mind that this vibration will induce a transient dipole in the CH\(_4\) molecule, thereby enhancing the range of its interaction with the projectile [4].

3. The range of energies involved for both the computed potential energy curves (lower panels of Figs. 1 and 2) is very similar in both cases and corresponds to about 25,000 cm\(^{-1}\). This means that, when using the simple harmonic oscillator model to obtain the target vibrational wavefunctions, we shall need to do in order to construct the matrix elements of Eq. (9), the bond deformations of the both modes can support well above eight vibrational levels which could be coupled during the collision.

As an example of the general shape for such coupling matrix element, we report in Fig. 3 \( l = l' = 0 \) and \( p = p' = A_1 \) (top panel) and \( l = l' = 3 \) and \( p = p' = T_1 \) (lower panel) contributions associated with the radial part of the integral of Eq. (8) for the \( v_1 \) mode. For each of them, we show the couplings which exist between the vibrational ground state and the next three vibrational levels. One clearly sees that both contributions are fairly short range and show their largest coupling effects near the position of the outer nuclei (the H atoms).
and between them and the central atom (the C atom). The radial coordinate is taken from the c.o.m. of the molecular target. The calculations also show that the spherical coupling extends over a larger range of distances due to the dominant effect of the spherical dipole polarizability. Finally, we see in both panels that the dominant coupling occurs by far with the $D_n = 1$ excitations, while the transfer of two and three quanta of vibrational energy in the $m_1$ mode is associated to much smaller coupling matrix elements, a feature which will obviously affect the final cross sections.

The actual inelastic cross sections for the excitation of both the $v_1$ and the $v_3$ ($z$ component only) modes are reported in Figs. 4 and 5, where we show different aspects of the calculations which we have carried out in the present work. In both figures, the open circles denote the more simple calculations associated with the adiabatic nuclear vibration (ANV) approximation described before for electron-impact excitation processes [4, 12]. In this instance, no direct dynamical coupling is active during the scattering process and the transition $T$-matrix is computed by simple calculation over the initial and final vibrational wavefunctions for each specific normal mode of the target:

$$T_{\nu\nu'}^{l} = \int dR \{ Z_{\nu'}(R) \}^{*} T_{\nu\nu'}^{l}(R) \{ Z_{\nu}(R) \}, \quad (14)$$

and therefore no positron dynamics is obtained under the action of the coupling matrix elements of Eq. (8), as discussed before.

Only the first vibrational threshold is presented in the figures for each of the modes, and the solid line shows the BF-VCC results which reach convergence when the first closed channel ($n = 2$) is added to the expansion of Eq. (4), and the inclusion of higher closed channels essentially leaves the final cross sections unchanged. We therefore report for the $v_1$ mode only the results with two vibrational channels coupled dynamically. This
feature is a clear indication of the rather weak coupling with the motion of the molecular nuclei that the positron projectile undergoes during the scattering process. In the case of the $v_3$, we also report in the figure the Born cross sections obtained by employing the additional dipole moment induced by the $v_3$ mode [14]. One can see that the corresponding cross sections are clearly much smaller, especially in the low-energy regions of the scattering. The comparison between the exact (at least within our modelling of the interaction) treatment of the vibrational dynamics i.e. the BF-VCC method and the more approximate ANV results is really very satisfactory with the obvious exclusion of the threshold region where the physical cross sections should go to zero (as the BF-VCC calculations do) while the ANV data do not. However, the closeness between the two methods of computing the inelastic cross sections is very similar for both modes although the differences become already noticeable at around 2 eV of collision energy (i.e. well above the threshold) in the case of the $v_1$ mode. This means that the rather weak coupling between the positron and the molecular nuclei does not really require to include corrections from the projectile kinetic energy term during the scattering process and therefore, away from thresholds, a simpler, asymptotic-type of wavevector choice is already sufficient.

We report in Fig. 6 a comparison between the present calculations and the available experiments for the $(v_1 + 3v_3)$ excitation processes in CH$_4$ [9]. The following comments could be made by looking at that figure.

1. The excitation of the $v_3$ mode, given its threefold multiplicity due to the $T_2$ symmetry, is by far the dominating process during the excitation dynamics. From about 2 eV of collision energy and all the way out to 6 eV, in fact, we see from the figure that the excitation probability of the $v_3$ mode is more than five times larger than that for the $v_1$. In both cases, only two coupled levels were sufficient to reach convergence.

2. The experimental data are fairly close to the shape produced by our calculations over the whole energy region and clearly show the marked increase at threshold of the combined excitation processes. The latter is dominated by the dipole term which appears in the $v_3$ mode and confirms once more the strong effect of such an asymptotic interaction on the low-energy scattering processes [26]. On the other hand, the experiment shows a larger peak than our calculated values from below 2.0 eV down to threshold, although keeping the same energy dependence. Such differences could be due to other inelastic processes occurring in the experiments but not included by our interaction potential model into the treatment of the dynamical excitation event, as we shall discuss more extensively in a forthcoming paper [27].

5. Present conclusions

The work reported here treats, at the molecular level, the modelling of the quantum dynamics of the vibrational excitation of a polyatomic nonlinear molecule which collides with a beam of low-energy positrons. As far as we are aware of, this is the first time that the exact dynamics of the vibrational close-coupling expansion is applied to the real case of a polyatomic target undergoing gas phase scattering with positron projectiles. We have examined the scattering process for two of the four

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**Fig. 6.** Vibrational excitation cross sections computed with the BF-VCC method for the $v_1$ (dotted curve), the $v_3$ (chain curve) and the $3v_3$ (broken curve) modes of CH$_4$. The sum of the two types of modes is given by the solid curve. The present calculations are also compared with the experiments [9] for $v_1 + 3v_3$ modes (full circles with error bars).
types of normal modes which exist in the CH$_4$ molecule, our present test system. We have carried out the calculations both at the exact BF-VCC level of dynamical treatment and also using the more approximate ANV convolution procedure. We were obviously able to compute separately the two stretching mode (the total symmetric $v_1$ and the antisymmetric $v_3$) contributions, while experiments reveal their sum only [9]. The latter is therefore the quantity we have compared directly with our calculations. The following conclusions could be drawn from the results presented in this work.

1. The $v_1$ excitation probability is much smaller than the corresponding $v_3$ excitation: the latter energy loss process is shown from our results to greatly dominate the overall excitation of CH$_4$ from the energy of about 0.4 eV and all the way up to 6 eV.

2. The cross sections are found to be rather featureless even close to the threshold and to increase in size as the collision energy decreases. Due to the presence of a transient dipole moment during the $v_3$ stretching of the bonds, the latter mode shows a much more marked increase of its cross section at threshold, a well-known feature of electron-impact excitation by polar targets [26].

3. The experiments are similar to the theoretical prediction in energy behavior. Below about 2 eV, however, the measured data exhibit a much more marked peak at low energy, a feature chiefly related to the asymptotic behaviour of the interaction which is here dominated by the induced dipole moment terms [27]. At this preliminary stage of the study, it is however difficult to ascertain this discrepancy, which will be, however, further analyzed in a forthcoming paper [27].

4. The ANV approximation, due to the rather weak nature of the positron-molecule coupling with the nuclear motion, appears to hold out well for energies away from threshold while, however, exhibiting the wrong energy dependence right at threshold, as already seen in our study of electron–CH$_4$ vibrational excitation processes [3,4].

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