Vibrational excitation of CF$_4$ by electron impact: a computational analysis

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Abstract. The vibrationally inelastic cross sections are computed for the $\nu_1$ and $\nu_3$ modes of CF$_4$ using the quantum mechanical adiabatic nuclear vibrations approximation for the dynamics and using a nonempirical local interaction potential for electrons as projectiles. The results from electron excitation are compared with available, albeit indirect, experimental data. The calculations confirm the dominance of the $\nu_3$ mode at energies below the electronic excitation as the main channel for vibrational heating of CF$_4$ by electron impact.

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1. Introduction

Carbon tetrafluoride (CF₄) is certainly one of the most widely used components that is included in the feed gas mixtures used over a broad range of plasma-assisted electronic-chip-processing applications. It does not have stable excited species as electronic excitation leads to molecular dissociation [1] and, in a plasma environment, turns out to be an ideal source of reactive species, especially of fluorine atoms [2]–[4]. As a consequence of its interesting properties and its special role in chemistry under plasma conditions, this molecule constitutes an ideal source for a broad variety of reactive, neutral and ionic, fragment molecules in their ground and/or excited electronic states [4].

The possibility of predicting different aspects of its behaviour in electron-impact processes, elastic and inelastic, therefore constitutes an interesting challenge and, at the same time, a useful addition to the already impressive array of data which have been gathered on the low-energy electron interaction with the title molecule [1]. In the present study, we intend to focus our interest on the vibrational excitation efficiency by electron impact that we shall compute for CF₄ gaseous molecules before the electronic excitation becomes important (above 12.5 eV, or thereabouts).

In general, our information on the vibrational excitation of CF₄ stems from direct measurements which use electron beams [5, 6] and the indirect determinations via swarm analysis [7, 8]. Furthermore, the excitation process of vibrations in CF₄ is itself a mixture of direct excitation and of indirect excitation via resonances. Thus, we know that the excitation cross section for the $\nu_3$ mode, the antisymmetric stretching mode, increases sharply for energies approaching the vibrational threshold (0.157 eV) due to direct excitation via its large infrared (IR) activity [5]. At higher collision energies, a strong enhancement further appears in the experiments around 8 eV, while an additional broad, and weaker, ‘shoulder’ appears in the inelastic cross section around 21 eV [5, 6]. Thus, the experimental observation locates strong inelastic scattering in two distinct energy regions: one corresponds to the well-known resonance region between 6 and 11 eV and the other in the region of dominant direct excitation via dipolar interaction due to the $\nu_3$ mode and located around 2 eV [4]. The excitation of the $\nu_3$ mode is experimentally seen as the dominant energy loss process over the entire range of collision energies below the threshold for electronic excitation. The excitations of either the $\nu_1$ (symmetric stretching) or the ($\nu_2 + \nu_4$, symmetric and asymmetric bending modes) are smaller than both the elastic and the $\nu_3$ excitation under all observed conditions [1].

In the present study, we shall therefore focus on the dominant $\nu_3$ mode calculations and will also study the $\nu_1$ mode as a comparative process which shows a much lower excitation efficiency. The two stretching modes ($\nu_1$, $\nu_3$) as well as the two corresponding bending modes ($\nu_2$, $\nu_4$) are usually considered as not amenable to separate experimental resolution and are often each treated as an unresolved energy loss signal [1]. Section 2 outlines our modelling of interaction forces and dynamics, while section 3 reports our results for electron impact excitation. Section 4 presents our conclusions.

2. Theoretical method

2.1. Scattering equations

Within an ab initio, parameter-free approach, we start with the target nuclei kept fixed at some chosen geometry so that their motion during the scattering process could be decoupled from
the other dynamical variables. This simplifying scheme goes under the name of the fixed nuclei approximation and it strongly decreases the dimensionality of the coupled scattering equations for the dynamics [9]. Furthermore, the target $N$ electrons bound in a specific molecular electronic state (which is taken as unchanged during the scattering) are described within a near-Hartree–Fock, self-consistent field (SCF) approximation by using the single-determinant description of the $N$ occupied molecular orbitals (MOs). In our implementation of the scattering equations, the occupied MOs of the targets are again expanded onto a set of symmetry-adapted angular functions with their corresponding radial coefficients represented on a numerical grid [10]. In this approach, any arbitrary three-dimensional function describing a given electron, either one of the $N$ bound electrons or the scattering electron, is expanded around a single centre (SCE) usually taken to be the centre of mass of the global $(N + 1)$ electron molecular structure [11, 12]

$$F^{\mu}(r, \hat{r}|\mathbf{R}) = \sum_{l, h} r^{-1} f^{\mu}_{lh}(r|\mathbf{R}) X^{\mu}_{lh}(\hat{r}). \quad (1)$$

The above SCE representation refers to the $\mu$th element of the $p$th irreducible representation (IR) of the point group of the molecule at the nuclear geometry $\mathbf{R}$. The angular functions $X^{\mu}_{lh}(\hat{r})$ are symmetry-adapted angular functions given by a proper combination of spherical harmonics $Y_{lm}(\hat{r})$, where the $b$ coefficients have been described in [10, 13, 14],

$$X^{\mu}_{lh}(\hat{r}) = \sum_{m} b^{\mu}_{lmh} Y_{lm}(\hat{r}). \quad (2)$$

The quantum scattering equations then evaluate the unknown radial coefficients of equation (1) for the $(N + 1)$th continuum electron scattered off the molecular target

$$\left[ \frac{d^2}{dr^2} - \frac{l(l + 1)}{r^2} + 2(E - \varepsilon_{\alpha}) \right] f^{\mu\alpha}_{lh}(r|\mathbf{R}) = 2 \sum_{l'h'} \int \frac{dr'}{V^{l'h',\alpha\beta}_{lh'}(r, r'|\mathbf{R})} f^{\mu\beta}_{l'h'}(r|\mathbf{R}), \quad (3)$$

where $E$ is the collision energy, $E = k^2/2$, and $\varepsilon_{\alpha}$ is the electronic eigenvalue for the $\alpha$th asymptotic state. The $p\mu$ indices now label the specific $\mu$th component of the $p$th IR that belongs to the $\alpha$th electronic target state (initial state) coupled with the infinity of excited state IRs labelled collectively by the index $\beta$. The coupled partial integrodifferential equations (3) show on the r.h.s. the kernel of the integral operator $V$, which is a sum of diagonal and nondiagonal terms that, in principle, can fully describe the electron–molecule interaction. With the further assumption of the exchange forces being given approximately by a local interaction, one can simplify equation (3) by writing it for only one of the electronic channels, thereby dropping the $(\alpha, \beta)$ labels and considering only the ground electronic state potential

$$\left[ \frac{d^2}{dr^2} - \frac{l(l + 1)}{r^2} + k^2 \right] f^{\mu\alpha}_{ij}(r|\mathbf{R}) = 2 \sum_{n} V^{\mu\alpha}_{in}(r|\mathbf{R}) f^{\mu\beta}_{nj}(r|\mathbf{R}), \quad (4)$$

where the indices $(i, j, n)$ now collectively represent each one of the ‘angular channels’ $|lh\rangle$ and the potential coupling elements are given by

$$V^{\mu\alpha}_{in}(r|\mathbf{R}) = \langle X^{\mu\alpha}_{i}(\hat{r})|V(r|\mathbf{R})|X^{\mu\beta}_{n}(\hat{r}) \rangle = \int d\hat{r} X^{\mu\alpha}_{i}(\hat{r}) V(r|\mathbf{R}) X^{\mu\beta}_{n}(\hat{r}). \quad (5)$$

The numerical solutions of the coupled equation (4) will produce the relevant $K$-matrix elements, which will in turn yield the necessary expression for the elastic (rotationally summed)
differential cross sections, obtained for scattering off randomly oriented molecules by averaging the scattering amplitude \( f(\hat{k} \cdot \hat{r}|\alpha, \beta, \gamma) \) over all the angular values \([10]–[14]\).

Electron–molecule scattering cross sections (integral and differential), which are computed using the \( V^{ESE} \) (exact static exchange) potential outlined above, usually show some agreement with experimental data of elastic scattering at energies away from resonant features but turn out to be not at all realistic when used for resonant scattering \([16]\) or for the general treatment of low-energy (\(<10\, eV\)) scattering processes. This is chiefly due to the lack of correlation effects in the description of the \( e^-\)–molecule interaction.

We have therefore used a further correction that we had used for electron scattering from large polyatomic nonlinear targets with a good degree of success \([11]–[14]\). In particular, we have already shown elsewhere \([14, 15]\) how the combined effects of simplifying the exchange interaction between the bound electrons and the continuum projectile via a modified semiclassical (local) approach and of treating the correlation-polarization forces using a global density functional model can indeed help us to deal with vibrationally inelastic collisions, at least for the present tetrahedral molecule, with a markedly decreased computational effort and with an acceptable level of accuracy \([15, 16]\).

Briefly, the \( V^{eex} \) model potential contains a short-range correlation contribution \( V_{\text{corr}} \), which is smoothly connected to a long-range polarization contribution \( V_{\text{pol}} \), both terms being specific for an electron projectile. The short-range term is obtained by defining an average dynamical correlation energy of a single electron within the formalism of the Kohn and Sham variational orbitals representing the bound electrons. The functional derivative of such a quantity with respect to the SCF \( N\)-electron density of the molecular target provides a density-functional description of the required short-range correlation term (for a general description of density-functional-theory methods, see Parr and Yang \([17]\)). The long-range part of \( V^{eex} \) is obtained by first constructing a model polarization potential \( V_{\text{pol}} \), which asymptotically agrees with the potential obtained from the static dipole polarizability of the target in its ground electronic state. This corresponds to including the dipole term in the second-order perturbation expansion of the polarization potential \([11]–[14], [18]\).

The matching conditions between \( V_{\text{corr}} \) and \( V_{\text{pol}} \) generate in turn a crossing point located at 
\[ r_{\text{match}} = 4.1 \text{ Å for } R_{\text{eq}} \text{ and varying between 3.5 and 4.4 Å over the range of nuclear geometries required to carry out the excitation cross sections.} \]

The new, full interaction now corresponds to carrying out the scattering equations using the static-exchange-correlation-polarization \( V^{\text{SECP}} \) description of the electron–molecule interaction.

We further used a simpler form of exchange interaction in order to reduce the computational effort. Thus, we replaced the nonlocal contributions in equation (3) with a semiclassical approximate model, already used and discussed by us in our earlier work (see e.g. \([19]\) for its first presentation), which we called the semiclassical exchange \( V_{\text{ex}}^{\text{SMCE}} \). It treats the bound–continuum exchange interaction within a scheme where the local momentum of the bound electrons is initially disregarded with respect to that of the impinging particle, thereby leading to the neglect of the gradients of MOs with respect to the gradient of the wave function for the projectile \([19]\).

Hence, the final expression of the exchange forces \( V_{\text{ex}}^{\text{SMCE}}(r|k^2) \) is given by an energy-dependent function of the static interaction \( V_{\text{st}} \) and the target total electron density in terms of its MOs, \( \varphi_s(r) \),

\[
V_{\text{ex}}^{\text{SMCE}}(r|k^2) = \frac{1}{2} \{ E - V_{\text{st}}(r) \} - \frac{1}{2} \left\{ \left[ E - V_{\text{st}}(r) \right]^2 + 8\pi \sum_{s=1}^N |\varphi_s(r)|^2 \right\}^{1/2},
\]
where $E$ is the asymptotic collision energy, $E = \frac{1}{2}k^2$, and the index $s$ runs over the occupied MOs of the target. $V_{st}$ is the static interaction of the scattered electron with the target’s (electrons + nuclei) structure.

The coupled equation (3) can now be recast in an integral form [14] using the potential coupling elements defined before, $V_{st}^{\mu}(r|R)$, and using standard Green’s function techniques to obtain for the radial functions of the continuum electron

$$f_{ij}^{\mu}(r|R) = \delta_{ij}j_{li}(kr) + \sum_n \int_0^r dr' g_{li}(r, r')V_{in}(r|R)f_{ij}^{\mu}(r|R), \quad (7)$$

where the integral on the right-hand side of equation (8) terminates at $r' = r$ (integral equations with this property are called Volterra equations). The values of $j_{li}$ and $g_{li}$ describe Bessel’s and Newmann’s functions, respectively [20]–[23].

The numerical implementation and stabilization corrections for the equations given by equation (7) have been discussed for diatomics previously [20]–[22] and we have recently [12] carried out its obvious generalization for polyatomic systems. Suffice it to say here that the combined use of a local form of exchange interaction (like the $V_{ex}^{\mu}$ outlined above) with the integral formulation for the continuum solutions allows us to obtain the required $K$-matrix elements for each selected nuclear geometry with a substantial reduction of the computational time, a key element when dealing with vibrationally inelastic scattering calculations, even for very large partial wave expansions for equation (1).

The crucial question when formulating a theoretical approach to the study of low-energy inelastic vibrational excitation of polyatomic molecules by electron impact is how to correctly include the effect of nuclear kinetic energy operators on the continuum wave functions for the scattered electron. From the earlier studies which went beyond some sort of weak-scattering approximations (clearly reviewed in [23]), two types of approaches have been favoured for diatomic targets: (i) one possibility rigorously takes into account the effects of the vibrational Hamiltonian by expanding the $(N + 1)$ electron + $M$-nuclei system in a complete set of eigenfunctions of that Hamiltonian [23], thereby carrying out the vibrational close-coupling calculations, and (ii) another option is to approximate the above-mentioned effects by treating the internuclear coordinates as a set of parameters on which the scattering attributes will finally depend [24]. This approach constitutes the foundation of the adiabatic nuclear vibration (ANV) approximation and effectively extends the conventional Born–Oppenheimer theory of bound molecular states within a given electronic state to the continuum states of the whole (electron + molecule) system.

The latter formulation is computationally less demanding than the former. However, at least in the case of diatomic targets [25] and based on our previous experience on a polyatomic molecule [26]–[28], it is known to introduce significant errors into the computed vibrationally inelastic cross sections for scattering energies near and within a few eV above the relevant excitation threshold, while turning out to be more realistic at higher collision energies [16]. As a result, it still remains a powerful computational tool for yielding vibrational inelastic observables and indicators [27, 28] for collision energies away from each channel threshold.

The additional simplification introduced now by the ANV approximation starts by first making an energy sudden approximation that replaces the ‘off-shell’ situation of the wavevector with the simpler ‘on-shell’ conditions:

$$k_n^2 \sim k_0^2 \quad (8)$$
for all values of \( n' \), where \( k^2_0 \) is now a suitable energy reference level and \(|n'|\) labels all the relevant quantum numbers for each chosen final state. A solution of equation (4) could then be obtained by solving it for a fixed set of internal coordinates for the molecular nuclei \( Q \), with \( Q \) being now a collective index for all the normal coordinates of the molecule and now appearing explicitly in the matrix elements on the r.h.s. of equation (4) [15]

\[
\left\{ \frac{d^2}{dr^2} - \frac{l'(l' + 1)}{r^2} + k^2 \right\} w_{l'v'}(r|Q) = 2 \sum_{l''v''} (l''v'') V(r|Q) w_{l''v''}(r|Q),
\]

which is then solved after the coupling terms on the r.h.s. are constructed for each nuclear configuration chosen to be sampled during the vibrational transitions and treated as an adiabatic parameter.

The corresponding \( S \) matrix elements, obtained from solving equation (9) for the range of \( Q \) values selected for the calculation of a particular inelastic transition within a given mode, are produced by convolution over the initial and final vibrational wavefunctions, \( \chi_n(Q) \) and \( \chi_{n'}(Q) \), describing the relevant excitation process:

\[
S_{n'l'v'}^n(k^2_0) = \int dQ \chi_{n'}(Q) S_{l'v'}(Q) \chi_n(Q).
\]

One can thus recover for each set of \( (Q) \) values the corresponding \( T \)-matrix from the \( K \)-matrix given in the calculations since: \( T = K(1 - iK)^{-1} \) and \( S = 1 + 2iT \). The ANV result could then be seen as obtaining, for the whole range of \( Q \) values, the relevant \( T \)-matrix for any \((n \to n')\) transition by performing the following integration over the \( Q \) coordinate:

\[
T_{n'l'v'}^n(k^2_0) \sim \langle \chi_{n'}|T_{l'v'}(Q)|\chi_n \rangle_Q.
\]

### 3. Computational results

The single-determinant molecular equilibrium geometry was optimized using a basis set expansion of the (ang-cc-pVTZ) type, producing the \( T_d \) structure with a bond distance of 1.296 Å (experimental value [4] : 1.31 Å), a total energy of \(-435.821\) hartrees and a spherical polarizability value of \( 16.90 \alpha_0 \) (experimental value [4]: \( 19.60 \alpha_0 \)). The corresponding symmetric stretching (\( \nu_1 \)) and antisymmetric stretching (\( \nu_3 \)) normal coordinates were generated over a set of 15 different values of the corresponding normal coordinates \( Q_s \), using a range of C–F distances from \( R_i = 1.230 \) Å to \( R_f = 1.370 \) Å, and spanning about three bound vibrational states (numerically generated) per mode. The corresponding harmonic frequencies were 909 cm\(^{-1}\) for the \( \nu_1 \) mode and 1281 cm\(^{-1}\) for the \( \nu_3 \) mode [4]. The calculated polarizability gradient \( \frac{\partial \alpha_0}{\partial Q} |Q_{eq} \) was \( 2.11 \) amu\(^{-1/2}\) Å\(^2\) for \( \nu_1 \) and \( 7 \times 10^{-3} \) amu\(^{-1/2}\) Å\(^2\) for the \( \nu_3 \) mode. \( Q_{eq} \) represents here the molecular equilibrium geometry. For the latter antisymmetric mode, the corresponding dipole gradient value (in units of debye amu\(^{-1/2}\) Å\(^{-1}\)) was \(-1.49\) debyes.

The computed, geometry-dependent spherical polarizability values were scaled to the experimental \( \alpha_0(Q_{eq}) \) as a simple device for adjusting the calculations to the experimental quantity at the equilibrium geometry and further assuming that their dependence on the
Figure 1. Computed and measured elastic cross sections (rotationally summed) from low energy up to the resonance region: •, from [30]; ○, from [1]; ·····, from [12]; –––, from [32]; ——, present calculations.

$Q_i$ parameters would also linearly scale at other geometries. The numerical bound state wavefunctions for the two modes were used to construct the matrix elements on the r.h.s. of equation (10) and to obtain the convolution of equation (11). They were obtained by numerical integration of the corresponding one-dimensional Schrödinger equation [29] and yielded the following energy eigenvalues for the three lowest bound states: $\varepsilon_0 = 62(61)$ meV, $\varepsilon_1 = 188(189)$ meV, $\varepsilon_2 = 317(313)$ meV, $\varepsilon_3 = 456(453)$ meV for the $\nu_1 (\nu_3)$ modes, respectively. The corresponding $Q_i$ values varied between $Q_{\text{min}} = 0.486$ amu$^{-2}$ and $Q_{\text{max}} = 0.560$ amu$^{-2}$ for the $\nu_1$ mode and between $-0.514$ and $0.514$ for the $\nu_3$ mode.

Partial-wave expansions were carried out for terms up to $\ell_{\text{max}} = 50$, generating 100 multipoles in the potential for the description of the scattered electron interaction with target molecules in equation (9). A convergence level of about 1% was obtained on the inelastic $T$-matrix elements. The range of integration was extended over a ($r, \vartheta, \varphi$) grid of 710 radial points out to $r_{\text{max}} = 34a_0$, while 168 points were used over $\vartheta$ and 81 over $\varphi$. The number of coupled equations retained in the $A_1$ representation was 441. The dominant IRs for the inelastic (and also elastic) cross sections were the $A_1$ and $T_2$ IRs.

To give some evidence about the general quality of our model treatment for the present system, we report in figure 1 calculations of the fixed-nuclei total elastic cross sections over the range of energies from above threshold and up to the high-energy resonance structure: experimental data from various sources are also given, together with the results from earlier calculations. The experimental, total cross sections of Jones are from [30], while the elastic ones (Christophorou) are from [1]. The earlier calculations are from our earlier work [12] and from Isaacs et al [32]. We see that the present results follow experiments reasonably well considering the complicated structure of the present molecule and the approximation we have introduced here. We also found that our present K-matrix elements yield good agreement with experimental
Figure 2. Computed and measured \((0 \rightarrow 1)\) vibrational excitation cross sections for electron impact on \(\text{CF}_4\). Lowest panel: excitation of the \(\nu_3\) mode (——) compared with the corresponding Born results \([4]\) (– · – · –). Middle panel: computed \(\nu_1\) excitation (——). The results for the same excitation mode in \(\text{CH}_4\) are also shown in this panel (– – –), together with an enlarged view (×20) of the \(\nu_1\) excitation of \(\text{CF}_4\) at the lower energies.

angular distributions over a broad range of energies \([30]–[33]\); the most notable effect of our approximate interaction potential is the shift of the resonance to higher energies in comparison with experiments.

Our calculations are able to describe well the order of magnitude of the cross sections between the threshold energies and the resonance region. Furthermore, the broad resonance maximum is also given qualitatively in accord with experiments with an energy shift in its position and a higher peak maximum that can be attributed to the simplified nature of our treatment of (exchange) forces. We therefore expect that our computed vibrational inelasticity may also turn out to be qualitatively correct with respect to existing experiments.

The calculations for the ANV inelastic cross sections associated with \(\nu_1\) and \(\nu_3\) excitations of the \((0 \rightarrow 1)\) transition are presented in figure 2, where the top panel shows the sum of the inelastic cross sections and their comparison with indirect experiments (given by \([5, 6]\) and reported in \([1]\)). The following comments could be readily made from the reported results.

1. As indicated by various experimental findings \([1]\), the \(\nu_3\) excitation is by far the dominant excitation mode of \(\text{CF}_4\). Our calculations in the middle panel of figure 2 indeed confirm such a finding.
2. The approximate (exchange + polarization) forces which we employ here are shifting the resonance position to higher energies with respect to the experiments (see e.g. figure 1) and indicate that the \(\nu_1\) excitation is showing it more markedly than the \(\nu_3\) excitation.
Figure 3. Computed two-quanta vibrational excitations for the \( \nu_1 \) (middle panel) and \( \nu_3 \) (lowest panel) modes of CF\(_4\). The sum of the two excitation cross sections is given in the top panel.

(3) The Born approximation modelling of vibrational excitation [6] is definitely inadequate to describe correctly the size of the excitation process, as shown by the dot-dashed curve reported in the bottom panel.

(4) The excitation of the \( \nu_1 \) mode in methane is also given for comparison in the middle panel (computed earlier by us [16]) and clearly indicates that its resonant feature at lower energies strongly affects the size of the CH\(_4\) excitation in comparison with that of CF\(_4\), at those same lower energies, shown enlarged in the middle panel for comparison (dash-dotted line).

(5) The sum of the two excitation cross sections \( \sigma_{\nu_1} + \sigma_{\nu_3} \) is reported in the top panel, where comparison is made with existing experiments (taken from [1], table 9). One sees that our calculations shift the resonance at higher energies and therefore exhibit a different energy dependence over the 10–14 eV energy range. On the other hand, we see that qualitative accord exists between computed and indirectly extracted inelastic cross sections: both are dominated by the \( \nu_3 \) excitation process and remain fairly close to one another, although the calculated sum is, on average, a factor of about 2 larger than the experimentally extracted values.

As a further comparison of the excitation efficiency of the \( \nu_3 \) and \( \nu_1 \) modes, we report in figures 3 and 4 the two-quanta excitation process, the \((0 \rightarrow 2)\) excitations and the excitation of a ‘hot’ molecular target (figure 4). The two-quanta excitation processes shown by figure 3 clearly indicate that they are much smaller than the single-quantum excitations of figure 2 and are markedly dominated by resonance features: it is only within that energy range, in fact, that we can see any sizeable vibrational excitation of both modes. We see further that the energy dependence of the cross section associated with the \( \nu_3 \) mode (bottom panel) is totally changed...
Figure 4. Computed excitation cross sections of the $\nu_1$ (middle panel) and $\nu_3$ (lowest panel) modes of the CF$_4$ molecule treated as a ‘hot’ target in its $n = 1$ level for both modes. The sum of cross sections is shown by the top panel.

when the ‘double jump’ process is concerned: only at the resonance region, in fact, does it show a significant contribution. This is due to the changes in nodal structure in the wavefunctions that appear in the convolutions of equations (10) and (11). The coupling potential dependence on $Q$ remains the same, while overlap cancellation effects become now more important at the energies where that coupling is the weakest, i.e. away from the resonant region.

The ‘hot’ molecular excitation from the $n = 1$ level turns out to be again a rather efficient process, for which the total excitation cross section (figure 4, top panel) is even larger than the same cross section for the excitation from the $n = 0$ level (compare figure 2, top panel). All the computed quantities confirm the dominance of the asymmetric stretching mode in the efficiency of the vibrational heating of gaseous CF$_4$, as indicated by experiments [1].

One compact way of labelling the energy transfer efficiency per single collision is to define the average energy transfer as

$$\langle \Delta E \rangle_{\nu_i} = \frac{\sum_{n,n'} \sigma_{n\rightarrow n'}(\nu_i) \times \Delta\epsilon_{nn'}}{\sum_{n,n'} \sigma_{n\rightarrow n'}(\nu_i)}$$

(12)

at a given collision energy and for a preselected $|n\rangle$ initial state. In our case, that was the ground vibrational level for the $\nu_i$ normal mode. $\Delta\epsilon_{nn'}$ are the energy spacings between the levels (in meV) and we have chosen the numerical values given within each $\nu_i$ manifold by the computed bound states, as discussed in section 2.

Results of the present calculations are presented in figure 5.

One sees once again how dominant the asymmetric stretching mode is when it comes to estimating heating efficiencies for vibrational excitation, where the broad contribution over the 8–10 eV region of the experimental resonance is also present in the calculations reported in the middle panel. One also sees that the total amount of energy transfer over the computed modes...
is, for CF₄, markedly larger compared with that for methane, also reported in the inset of the top panel and discussed earlier by us [27, 28].

4. Conclusions

In the present study, we have analysed the low-energy vibrational excitation of CF₄ gaseous molecules by impact with electrons.

The calculations for electron impact were carried out at the ANV level using numerical wavefunctions and indicate the marked dominance of the ν₃ mode in exciting vibrations with respect to the less efficient ν₁ mode. The comparison with existing experiments, albeit only somewhat indirect data are available [1], indicate a fair agreement between our calculations and the existing data: the latter also confirm the dominance of the ν₃ mode in exciting vibrations in the gaseous CF₄ target.

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