

Vibrational-excitation cross sections by electron impact on the CH radical for nonthermal plasmas

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Vibrational excitations of the CH molecule are critical for understanding the kinetics of the interstellar medium, stellar atmospheres, and plasma-assisted combustion. Building upon previous *R*-matrix calculations—which characterized the $X^2\Pi$ and $a^4\Sigma^-$ electronic states of CH and the $^1\Sigma^+$, $^3\Pi$, and $^5\Sigma^-$ resonant states of CH^- —this study evaluates cross sections and rate coefficients for electron-impact vibrational excitation using the local complex potential method. State-to-state formalism is used to analyze electron-vibration energy exchange. Our results demonstrate that electron-driven processes provide non-negligible contributions to nonequilibrium kinetic modeling.

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I. INTRODUCTION

The CH radical (methyldyne) is a highly reactive, small molecular species that serves as a fundamental intermediate in various fields, notably planetary atmospheric chemistry, combustion, and astrophysical environments. Its exceptional reactivity stems from its electronic structure, characterized by both a singly occupied orbital and a vacant orbital localized on the carbon atom.

In astrophysical contexts, the methyldyne radical was the first molecule to be detected in space [1] and was subsequently identified and detected in diffuse molecular clouds [2,3] and in shock regions in galaxies [4] and stellar atmospheres [5]. Recently, Luo *et al.* [6] predicted abundance and evolution of CH in the Galactic Cloud Clumps, combining observations from the Arecibo telescope together with RADEX modeling [7]. In another recent work, Schroetter *et al.* [8] identified the CH molecule in the d203-506 protoplanetary disk through a detailed analysis of the JWST-NIRSpec spectrum. They reported rovibrational emission lines around 3.3 μm ; specifically, the spatial distribution of the 3.426- μm line was found to be slightly less extended than that of the vibrationally excited one, the latter being traced *via* the $v = 1 \rightarrow 0$ $S(1)$ emission line, which receives a non-negligible contribution from electron scattering.

The CH radical, particularly through its collisions with electrons, plays a crucial role in plasma-assisted combustion [9], significantly contributing to NO_x production and the

formation of higher hydrocarbons. Unlike traditional combustion, where CH forms primarily *via* high-temperature thermal reactions (Zeldovich mechanism), in low-temperature plasma chemistry its production—often associated with the Fenimore mechanism [10,11]—is enhanced by electron impact and vibrationally excited states.

While the rovibrational spectrum of the CH radical has been extensively explored experimentally [12–15], and substantial theoretical research exists on its rotational excitation [16,17], photodissociation [18], and photoionization [18], a gap remains. Despite their importance, to the best of our knowledge, no theoretical calculations of electron-impact vibrational excitation (VE) for CH have been reported in literature. The present work is motivated by the need to address this lack of theoretical data.

In a previous work [19], detailed *R*-matrix calculations of the bound and resonant states of CH were made and, subsequently—using those results for the $X^2\Pi$ ground state and for the $a^4\Sigma^-$ first excited electronic state of CH and the $^1\Sigma^+$, $^3\Pi$, and $^5\Sigma^-$ resonant states—a comprehensive study on the dissociation and dissociative electron attachment to vibrationally excited CH molecules was performed by Abidi *et al.* [20] using the local complex potential (LCP) model [21,22]. In the present work, we extend the LCP method to obtain resonant cross sections for vibrational excitations by electron impact for the CH molecule in its ground state and for the first excited electronic state:

$$e + \text{CH}(X^2\Pi; v) \rightarrow \text{CH}^-(^1\Sigma^+, ^3\Pi) \rightarrow e + \text{CH}(X^2\Pi; v'), \quad (1)$$

$$e + \text{CH}(a^4\Sigma^-; v) \rightarrow \text{CH}^-(^5\Sigma^-) \rightarrow e + \text{CH}(a^4\Sigma^-; v'), \quad (2)$$

where v and v' depict vibrational levels and the intermediate states refer to the resonant contributions.

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In the following, we will limit ourselves only to consider resonant scattering, which represents the dominant contributions at low electron energies. Direct vibrational excitation (nonresonant mechanism), which is allowed for the CH molecule by dipole transitions, will be neglected.

The paper is organized as follows: in Sec. II, we present the theoretical approaches to determine electronic states and couplings for CH and CH[−] and we introduce the LCP method to calculate the collision processes in (1) and (2). Section III reports on the results for the cross sections and rate coefficients resolved over vibrational states. In Sec. IV we study the electron-vibration energy exchange for the CH molecule in the framework of the state-to-state (StS) kinetic approach. Finally, Sec. V summarizes the conclusions of the paper.

II. THEORETICAL FRAMEWORK

In this section, we briefly describe the *R*-matrix method and the LCP model used to calculate the molecular states and the cross sections respectively.

A. *R*-matrix and MOLPRO calculations for molecular states

The *R*-matrix calculations [23,24] were performed with the diatomic version of the UK molecular *R*-MATRIX codes using the Slater-type orbitals (STOs) to represent the target molecular orbitals. The STOs were first used to perform a Hartree-Fock self-consistent field (SCF) calculation on the X²Π ground state of the CH target molecule. Subsequently, the SCF orbitals were used to perform a complete active space (CAS) configuration-interaction (CI) calculation with two electrons frozen in the 1σ orbital and the remaining five electrons allowed to move in the CAS defined as (2σ − 8σ, 1π − 3π, 1δ). The model gave vertical excitation energies and dipole moment of the X²Π ground state which compared well with available data [25] and hence were used for subsequent scattering calculations.

For scattering calculations, the scattered electron was described by continuum orbitals F_{ij} which were taken to be spherical Bessel functions since the target is neutral and partial waves with $l \leq 6$ and $|m| \leq 2$ are retained in the calculations. An inner region wave function was then constructed as a close-coupling expansion using the target CI and continuum wave function F_{ij} . An *R* matrix was then built at the boundary of the inner region, taken to be a sphere of radius 12 a_0 . The *R* matrix was then propagated in the outer region and matched with asymptotic functions.

For bound-state calculations, the *R* matrix was propagated to 50 a_0 and matched with exponentially decaying asymptotic functions, while for resonance calculations, the *R* matrix was propagated to 70 a_0 and matched to appropriate asymptotic functions to obtain a *K* matrix. For the positions E_r and widths $\Gamma_r(R)$ of the resonances, the eigenphase sums $\delta(E) = \sum_i \tan^{-1} K_{ii}$ were first obtained at each incident energy E from the diagonal elements K_{ii} of the *K* matrix. The resonance positions were then obtained by locating the change of sign of the second derivative of $\delta(E)$. Finally the resonance widths Γ_r were calculated by fitting $\delta(E)$ to Breit-Wigner profiles [26].

Applying this procedure, we identified three resonances for the CH[−] system: the ¹Σ⁺ state, generating from the neutral

TABLE I. CH bound states and CH[−] anionic states obtained by the *R*-matrix and MRCI calculations and their asymptotic limits. ¹Σ⁺, ³Π, and ⁵Σ[−] are resonant while the remaining states are bound. Shown also are the calculated (asymptotic) electron affinities (EA) for the anionic states in good agreement with the recent measurements of Ref. [31] reported in square brackets.

States	Asymptotic limit	EA (eV)
X ² Π	C(³ P)+H(² S)	
a ⁴ Σ [−]	C(³ P)+H(² S)	
X ³ Σ [−]	C [−] (⁴ S)+H(² S)	−1.21 [−1.217]
¹ Σ ⁺	C [−] (² P)+H(² S)	+0.67
³ Π	C(³ P)+H [−] (¹ S)	−0.66
⁵ Σ [−]	C [−] (⁴ S)+H(² S)	−1.21 [−1.217]

ground state ²Π; the ³Π state which is formed by attaching a *p*-wave electron to the excited A²Δ state; and the ⁵Σ[−] whose parent is the a⁴Σ[−] state. In principle, since we are considering multichannel scattering, independently from the formation process, resonances can decay in any of the open channels through the corresponding partial width [27,28]. For the scattering *e* + CH considered here, we find that the ¹Σ⁺ and ³Π states of CH[−] resonance couple with the X²Π state of the CH molecule whereas the ⁵Σ[−] resonance couples with the a⁴Σ[−] state. The details of the procedures may be found in our earlier work in Ref. [20] and are not discussed here for brevity. The calculations were repeated over a grid of 20 internuclear distances in the range $R = 1\text{--}8a_0$ to obtain the potential-energy curves of the bound and resonant states and the resonance widths Γ as a function of the internuclear distance R .

Since the asymptotic limits of the X²Π ground state and the a⁴Σ[−] first excited state calculated using the *R*-matrix procedure deviated slightly from the corresponding accurate values taken from the NIST database [29], we performed a more formal quantum chemistry calculation using the state averaged complete active space self-consistent field–multireference configuration-interaction (MRCI) calculation with the MOLPRO [30] quantum chemistry software for the X²Π and a⁴Σ[−] bound states, and the bound parts of the ³Π and ⁵Σ[−] resonant states beyond their crossing points. The *R*-matrix ³Π and ⁵Σ[−] curves were then aligned so that they smoothly joined the corresponding MRCI branches (see Abidi *et al.* [20] for details).

The final states obtained using this procedure and their electron affinities at $R = 10a_0$ are shown in Table I whereas Fig. 1 summarizes the potential-energy curves and resonance widths as a function of the internuclear distance used in the scattering calculations.

The vibrational levels ϵ_v^s and the vibrational wave functions χ_v^s corresponding to the CH potential-energy curves $V^s(R)$ with $s = \{X^2\Pi, a^4\Sigma^-\}$ were obtained by solving the radial Schrodinger equation,

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V^s(R) \right] \chi_v^s(R) = \epsilon_v^s \chi_v^s(R), \quad (3)$$

using the Fourier Grid Hamiltonian (FGH) method [32]. Here, $\mu = 1695.2a_0$ is the reduced mass of the CH molecule.

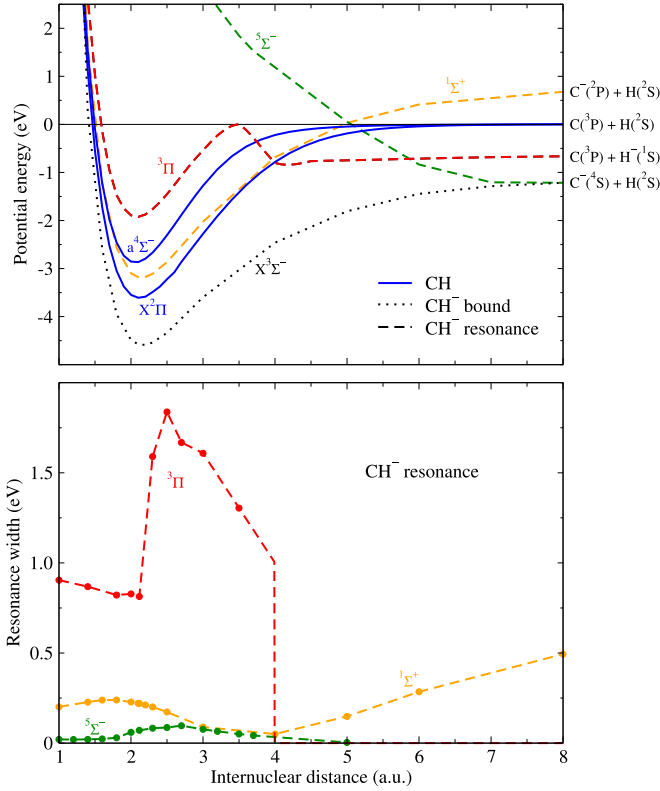


FIG. 1. Top: Potential-energy curves of CH and CH⁻ states used in the present work and symmetries as indicated in the panel. Bottom: Resonance widths for the ¹Σ⁺, ³Π, and ⁵Σ⁻ resonant states. Reproduced with permission from APS.

Because the FGH approach discretizes the Schrödinger equation in a finite box with zero boundary conditions at $R_{\max}$, we extended the internuclear distance range to $[1, 20] a_0$ and linearly extrapolated the potentials to obtain well-behaved box-discretized representations of the continuum. Within this setup, we identified 17 and 12 bound vibrational levels for the $X^2\Pi$ and $a^4\Sigma^-$ states, respectively, along with 75 and 80 box-discretized continuum levels extending up to 15 eV above the dissociation limit [20]. To validate the CH vibrational states, we compared the FGH results with calculations performed using the Numerov method obtaining the same values with a discrepancy $<0.1\%$.

B. Local complex potential method

Since the details of the LCP method are available in our earlier work [20], for brevity we give only the essentials. The LCP method was first developed by Bardsley and Mandl [21] and Domcke [22] and is used to treat resonant scattering together with the nuclear dynamics and is therefore very suitable for obtaining vibrationally resolved cross sections. Recently, the LCP method, together with the R -matrix method, has been applied successfully for studying dissociation and vibrational excitation of NO and D₂ molecules [33–36].

In the LCP approach, the cross section for a vibrational transition of a molecule between vibrational states $v \rightarrow v'$, belonging to the electronic state s , and for an incident electron

energy ϵ is given by

$$\sigma_{s,v \rightarrow s,v'}(\epsilon) = \sum_r \frac{2S_r + 1}{(2S_s + 1)2} \frac{g_r}{g_s} \frac{64\pi^5 m_e^2 k'}{\hbar^4} \frac{k'}{k} |\langle \chi_{v'}^s | \mathcal{V}_s^r | \chi_v^s \rangle|^2, \quad (4)$$

where $2S_r + 1$ and $2S_s + 1$ are the spin multiplicities of the resonant anion state and of the neutral target state respectively; g_r and g_s represent the corresponding degeneracy factors; $k(k')$ is the incoming (outgoing) electron momenta and m_e is the electron mass. $\langle \cdot | \cdot | \cdot \rangle$ stands for integration over internuclear distances R .

In Eq. (4), $\xi_{s,v}^r(R)$ is the resonant wave function, related to the initial vibrational wave function of CH, solution of the nuclear equation with total energy $E = \epsilon + \epsilon_v$:

$$\left[-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V_r^-(R) - \frac{i}{2} \Gamma_s^r(R) - E \right] \xi_{s,v}^r(R) = -\mathcal{V}_s^r(R) \chi_v^s(R), \quad (5)$$

where $V_r^-(R)$ with $r = \{^1\Sigma^+, ^3\Pi, ^5\Sigma^-\}$ is the potential energy for the three CH⁻ resonant states reported on the top of Fig. 1 (dashed lines) whereas $\Gamma_s^r(R)$ refers to the autoionization partial widths of the resonance r with respect to the neutral state s (bottom plot in Fig. 1). As discussed in Sec. II A and according to Eqs. (1) and (2) the allowed couplings are $\Gamma_{X^2\Pi}^{^1\Sigma^+}$, $\Gamma_{X^2\Pi}^{^3\Pi}$, and $\Gamma_{a^4\Sigma^-}^{^5\Sigma^-}$. In the LCP model, $\mathcal{V}_s^r(R)$ is the resonance coupling to the target state defined by

$$\mathcal{V}_s^r(R) = \frac{\hbar}{8\pi^2} \frac{\Gamma_s^r(R)}{\sqrt{2m_e[V_r^-(R) - V_s(R)]}}. \quad (6)$$

We solved for the nuclear dynamics by writing Eq. (5) in a matrix form and applying the FGH method over the same discretized grid of internuclear distance used to solve Eq. (3).

III. CROSS SECTIONS AND RATE CONSTANTS

Figures 2 and 3 present the main results of this work. Each panel reports cross sections for elastic scattering, VE, and vibrational deexcitation (VdE) between vibrational levels of the ground and the lowest electronic state of CH.

A first comparison between the $X^2\Pi$ ground state and the $a^4\Sigma^-$ excited state shows that the cross sections for the excited state are three to four orders of magnitude smaller than those for the ground state. This reduction arises because excitation from the $a^4\Sigma^-$ state of CH proceeds only *via* the $^5\Sigma^-$ resonance, located about 10 eV above the neutral state, which strongly suppresses the corresponding cross sections. Another common feature is that all the VE cross sections exhibit sharp thresholds corresponding to the gap $\epsilon_{v'} - \epsilon_v$ between the final and initial vibrational states of CH.

To understand some specific behavior of the VE cross sections for the $X^2\Pi$ state, we report in Fig. 4 the partial contributions coming from the two resonances as specified in Eq. (1) for selected cases. We note as for the elastic cross section $0 \rightarrow 0$, the first peak is attributable to the $^1\Sigma^+$ resonance and the second one to the $^3\Pi$ resonance. However, in particular for the transitions $0 \rightarrow 1$ and $10 \rightarrow 10$, due to the larger value of the resonance width of $^3\Pi$ compared with $^1\Sigma^+$ (see the plot in the bottom of Fig. 1), the contribution coming

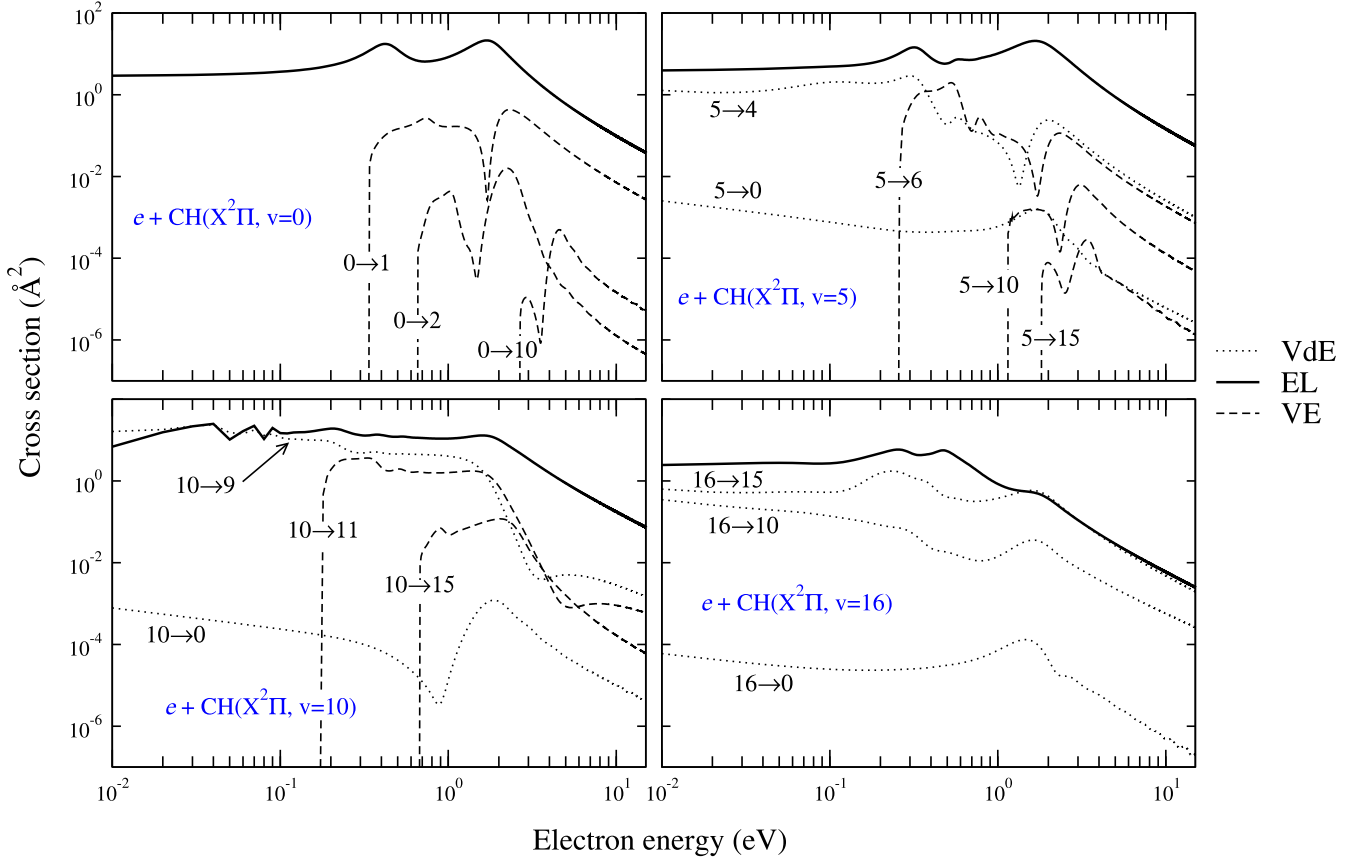


FIG. 2. Summary of the state-specific elastic (EL), vibrational-excitation (VE), and deexcitation (VdE) cross sections by electron impact for the vibrational levels $v = 0, 5, 10, 16$ of the ground electronic state $X^2\Pi$ of the CH molecule as a function of the incident electron energy.

from the $^3\Pi$ resonance to the total cross section is the large one whereas the $^1\Sigma^+$ contribution is relevant only at very low energies < 1 eV and for low vibrational levels.

On the other hand, the specific structures in the $^3\Pi$ cross sections, in particular the deep minima, are related to the shape of the corresponding potential, in particular to the presence of the predissociation state belonging to the centrifugal barrier potential of the resonance. To this end, in Fig. 4 are shown two vertical lines which refer to the region between the opening of the $^3\Pi$ potential (corresponding to the minimum of the $^3\Pi$ potential located around $2a_0$, dashed line) and the maximum of the centrifugal barrier for the $^3\Pi$ potential (located around $3.5a_0$, dot-dashed line).

For the $a^4\Sigma^-$ excited state, the VE cross sections for higher vibrationally excited states show oscillatory structures similar to dissociative attachment cross sections (see Abidi *et al.* [20]). These structures are characteristic of resonant scattering and have also been observed in resonant vibrational excitation of other systems like CO [37].

For the CH radical, the experimental value of the dipole moment is 1.46 ± 0.06 D [38]. The vibrational deexcitation process is expected to be very important in molecules with permanent dipole moment due to the high probability of spontaneous decay of high vibrational levels toward lower states. VdE cross sections are reported, for some of the vibrational states, in Figs. 2 and 3. Unlike the VE, the VdE process does not have a threshold and they actually show a large value,

in particular monoquantic deexcitations are comparable with elastic cross sections.

We have, finally, given the rate coefficients for VE and VdE in Fig. 5. The rate coefficients $k(T_e)$ were obtained as a function of the electron temperature T_e from the corresponding cross sections $\sigma(\epsilon)$ assuming the electron energy distribution is Maxwellian:

$$k(T_e) = \left(\frac{8}{\pi m_e k_B^3 T_e^3} \right)^{1/2} \int_{\epsilon_{th}}^{\infty} \epsilon \sigma(\epsilon) e^{-\epsilon/k_B T_e} d\epsilon, \quad (7)$$

where k_B is the Boltzmann constant and ϵ_{th} is the energy threshold for the corresponding process. In all cases the rates rise to a peak and fall off at higher electron temperatures beyond $T_e = 10^4$ K, which corresponds to an energy a little less than 1 eV. At this energy, many vibrational-excitation channels of the lower state $X^2\Pi$ are already open, causing a decrease of incident electron flux available for vibrational excitation or deexcitation of the $a^4\Sigma^-$ upper state. For this reason, the $v = 0$ and 5 rates also appear to be larger for the $X^2\Pi$ ground states than the corresponding rates for the $a^4\Sigma^-$ excited state.

IV. ELECTRON-VIBRATION ENERGY EXCHANGE

In this section, we investigate the energy exchange between electrons and vibrational excitations for the ground electronic state $X^2\Pi$ of the CH radical—the so-called e-V

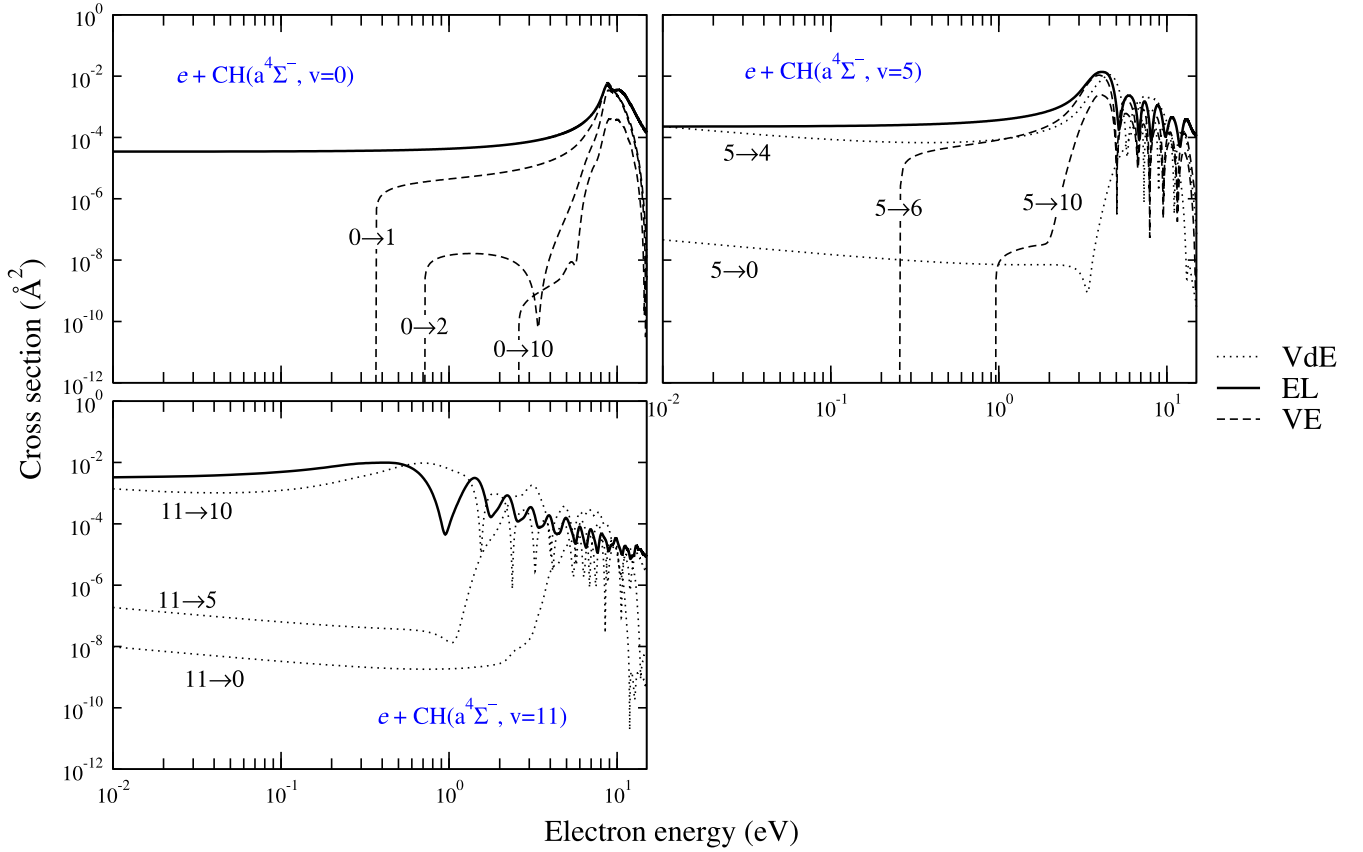


FIG. 3. Same as in Fig. 2 but for the vibrational levels $v = 0, 5, 11$ of the first excited electronic state $a^4\Sigma^-$ of the CH molecule.

processes—under nonequilibrium conditions, calculating the corresponding vibrational relaxation time (VRT).

We consider a nonequilibrium system containing free electrons, described by a Maxwell distribution at temperature T_e , and CH molecules with an initial vibrational temperature $T_{\text{vib}}^0 \neq T_e$, described by a Boltzmann distribution. Assuming T_e is kept constant, electron-CH collisions drive the system toward equilibrium, where the CH vibrational temperature approaches T_e .

In the StS kinetics formalism [39,40], the time dependence of the vibrational energy $E_{\text{vib}}(t)$ is given by

$$E_{\text{vib}}(t) = \sum_{v=0}^{16} n_v(t) \epsilon_v, \quad (8)$$

where the sum is over the vibrational levels ϵ_v calculated via Eq. (3). The nonequilibrium vibrational distribution function (VDF), $n_v(t)$, of CH molecules is obtained by solving the following set of master equations:

$$\frac{dn_v}{dt} = n_e \sum_{w=0}^{16} [k_{w,v} n_w - k_{v,w} n_v], \quad v = 0, \dots, 16, \quad (9)$$

where $k_{v,w}$ and $k_{w,v}$ are the VE and VdE rate coefficients reported in Fig. 5 and n_e is the electron density. This StS approach follows the methodology recently applied by Laporta *et al.* [33,41] to study electron-vibration relaxation time for O_2 and NO molecules.

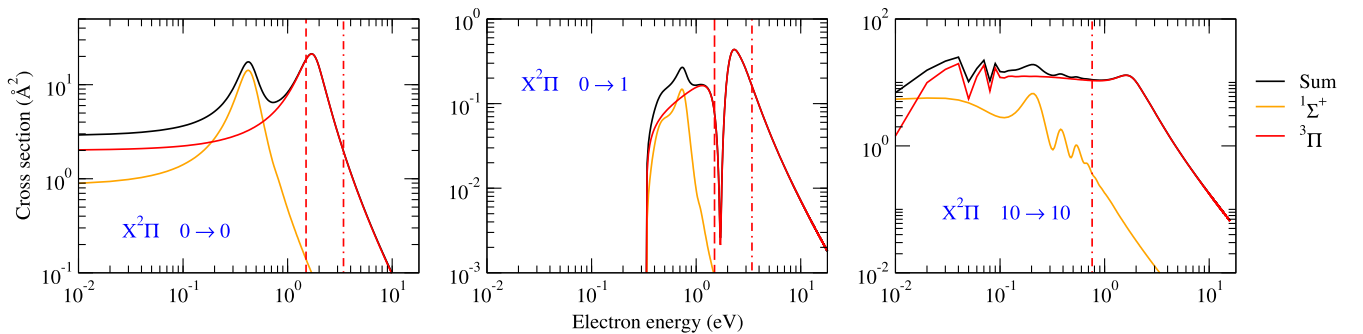


FIG. 4. Some vibrational-excitation cross sections for the $X^2\Pi$ state of CH showing the partial contributions from the $^1\Sigma^+$ and the $^3\Pi$ resonances. The vertical lines refer to the region of $^3\Pi$ resonance between the potential well (dashed line) and the centrifugal barrier (dot-dashed line).

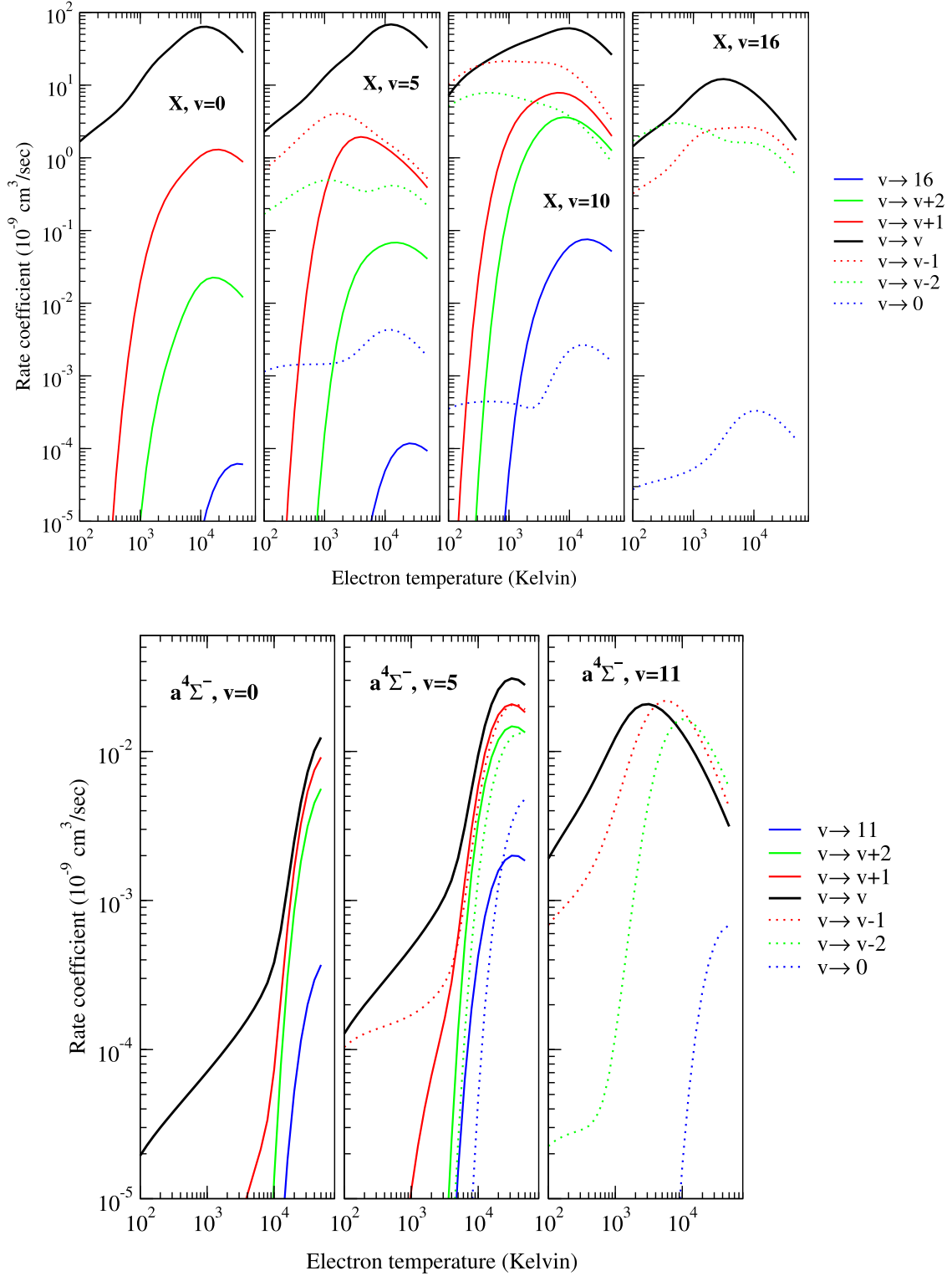


FIG. 5. State-specific vibrational-excitation (solid lines) and deexcitation (dotted lines) rate constants for the ground $X^2\Pi$ (top panel) and for the first excited $a^4\Sigma^-$ (bottom panel) electronic states of the CH molecule by electron impact as a function of the electron temperature.

Alternatively, in the Landau-Teller (LT) approach [42], the evolution of $E_{\text{vib}}(t)$ is governed by the following first-order equation:

$$\frac{dE_{\text{vib}}}{dt} = \frac{E_{\text{vib}}^* - E_{\text{vib}}}{\tau_e}, \quad (10)$$

where τ_e represents the VRT for e-V processes. Equation (10) admits the general solution:

$$E_{\text{vib}}(t) = E_{\text{vib}}^* (1 - e^{-t/\tau_e}) + E_{\text{vib}}^0 e^{-t/\tau_e}, \quad (11)$$

where $E_{\text{vib}}^* = E_{\text{vib}}(t \rightarrow \infty) = E_{\text{vib}}^*(T_e)$ is the equilibrium vibrational energy (calculated using a Boltzmann VDF at T_e)

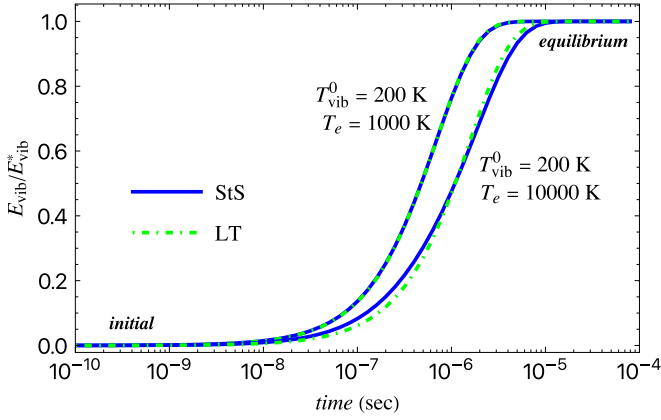


FIG. 6. Time evolution of vibrational energy obtained in the master equation StS approach (solid blue line) compared with the Landau-Teller fit (green dashed line) for two specific sets of temperatures T_{vib}^0 and T_e . Electron density was set to $n_e = 10^{-21} \text{ m}^{-3}$.

and $E_{\text{vib}}^0 = E_{\text{vib}}(t=0) = E_{\text{vib}}^0(T_{\text{vib}}^0)$ is the initial vibrational energy, obtained from Eq. (8) setting an initial Boltzmann VDF, $n_v^0(T_{\text{vib}}^0) \sim e^{-\epsilon_v/k_B T_{\text{vib}}^0}$.

The VRT, τ_e , was extracted by fitting the function $E_{\text{vib}}(t)$ obtained in the StS model in Eqs. (8) and (9) with the LT solution in Eq. (11) and it was calculated for specific sets of initial vibrational temperatures T_{vib}^0 of CH and for different electron temperatures T_e . As an explicit example, in Fig. 6, we report the time evolution of the CH vibrational energy compared with the LT fit for two configurations of temperatures with $T_{\text{vib}}^0 = 200 \text{ K}$ and $T_e = \{1000, 10\,000\} \text{ K}$. The corresponding computed values for the τ_e are 6.91×10^{-7} and $1.58 \times 10^{-6} \text{ s}$ respectively. Electron density was set to $n_e = 10^{-21} \text{ m}^{-3}$.

To obtain an electron-density-independent quantity, we report the results in terms of the product $n_e \tau_e$ which is a sort of inverse global vibrational rate constant for the CH radical. The corresponding results are summarized in Fig. 7. To compare with the first-order approximation of the electron-vibration energy exchange model proposed by Lee [43], in Fig. 7 we

also report the (inverse) of the rate coefficient $K_{1 \rightarrow 0}$ (dashed line).

As an initial observation, we observe for low electron temperature, $T_e < 1000 \text{ K}$, and for relatively low initial vibrational temperature, $T_{\text{vib}}^0 < 2000 \text{ K}$, that the vibrational energy exchange is well described by the excitation of the first vibrational level of CH (see the low-temperature branch of the dashed curve, $k_{1 \rightarrow 0}$). Moreover, due to the fact that for low temperatures only the first vibrational levels of CH can be excited, the system reacts linearly, and at least until $T_{\text{vib}}^0 < 5000 \text{ K}$ the vibrational rate $n_e \tau_e$ scales almost linearly, whereas, as the temperature increases and the excitation of high vibrational levels becomes possible, for $T_{\text{vib}}^0 > 5000 \text{ K}$, VRT tends to decrease (see the red curve).

At very low temperatures, $T_e < 250 \text{ K}$ and $T_{\text{vib}}^0 < 500 \text{ K}$ (blue and light blue curves), the slope of the rate curve $n_e \tau_e$ tends to deeply decrease as a function of the electron temperature, meaning that nonequilibrium effects due to molecular rotations, which are neglected in our model, start to be dominant.

Conversely, i.e., for $T_e > 1000 \text{ K}$, as the transferred energy from electrons is large enough to excite the full ladder of the vibrational levels of CH, the vibrational rates $n_e \tau_e$ exhibit the same behavior independently from the initial vibrational temperature T_{vib}^0 and the trend is inverted (growing) as a function of the electron temperature compared to the low electron temperature.

As a specific application of the present results, we consider first the case of the interstellar medium (ISM) where typical values of electron densities are $n_e \approx 10^8 \text{ m}^{-3}$. Assuming an electron temperature T_e in the range 10^3 – 10^4 K and an initial temperature for CH of $T_{\text{vib}}^0 = 200 \text{ K}$, we obtain a value for the VRT of $\tau_e \approx 10^7 \text{ s}$. These results confirm that in the ISM, the vibrational populations of the CH radical are primarily determined by radiative processes, for which $\tau_{\text{rad}} \approx 1 \text{ s}$ [44]. However, we remark that VRT due to the electron collisions is orders of magnitude larger compared to the collisional time arising from atoms and molecules. In fact, assuming a rate coefficient of $k_{\text{coll}} \approx 10^{-13} \text{ cm}^3/\text{s}$ for CO-H₂ collisions [45]

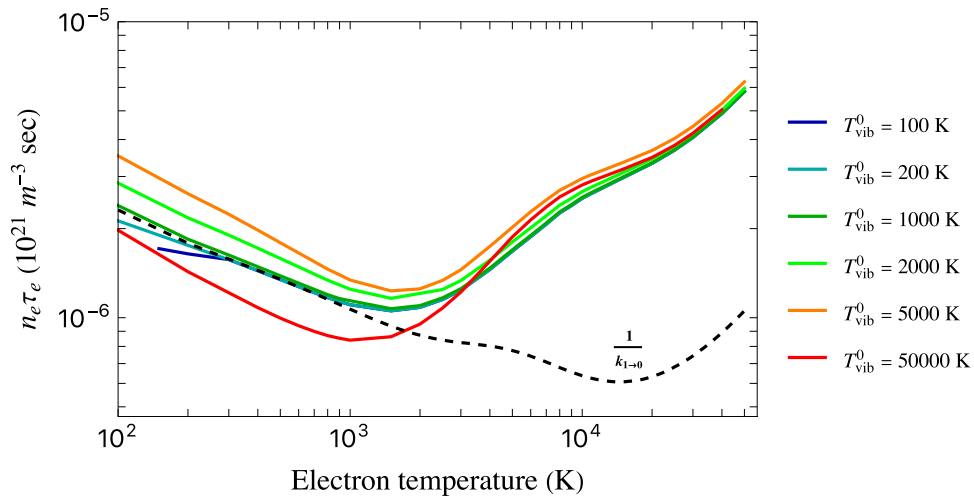


FIG. 7. Electron-vibration relaxation time for the CH molecule (solid lines) as a function of the electron temperature and for some initial vibrational temperatures of CH, compared with the first-order approximation (dashed line).

(no vibrationally resolved data are available in literature for CH-H₂ scattering) and a molecular density of $n_{\text{mol}} = 10^3 \text{ cm}^{-3}$, we obtain a value for the corresponding relaxation time of $\tau_{\text{coll}} = 1/k_{\text{coll}} n_{\text{mol}} \approx 10^{10} \text{ s}$. This indicates that, depending on the ISM density, collisions are dominated by electrons, and even a small electron fraction can significantly drive vibrational excitations.

In the case of stellar atmosphere, for which $n_e \approx 10^{15} \text{ m}^{-3}$ and departure from nonlocal thermodynamic equilibrium (non-LTE) is more realistic [46], we set an initial vibrational temperature for CH of $T_{\text{vib}}^0 = 10^3 \text{ K}$ and an electron temperature of $T_e = 10^4 \text{ K}$. This yielded a VRT value of $\tau_e = 2.55 \text{ s}$, which is comparable to the radiative time τ_{rad} . Consequently, the kinetic contributions from electron collisions become significant.

Specifically, for the plasma-assisted combustion where $n_e \approx 10^{20} \text{ m}^{-3}$, assuming a temperature of 10^4 K for electrons and a gas temperature of 300 K , the calculated relaxation time is $\tau_e \approx 10^{-5} \text{ s}$. Since this is longer than the vibrational-translation relaxation time with neutrals (for which typical values are $\tau_{\text{VT}} \approx 10^{-6} \text{ s}$), electron impact plays a dominant role in the vibrational excitation of the CH radical. In particular, the e-V processes serve as efficient mechanisms to lower the activation energy for reactions involving O₂ and OH molecules.

V. CONCLUSIONS

In this work, we presented detailed calculations of cross sections and the corresponding rate coefficients for

vibrational-excitation and deexcitation processes involving the ground $X^2\Pi$ state and the first excited $a^4\Sigma^-$ state of CH. Using these data, we examined the energy exchange between electrons and CH molecules in the $X^2\Pi$ ground state during vibrational excitation under nonequilibrium conditions. From this analysis, we derived vibrational relaxation times and applied them to specific scenarios in astrophysics and plasma-assisted combustion.

The results demonstrate that for the CH radical, vibrational relaxation due to electron scattering is comparable in magnitude to radiative relaxation—particularly within stellar atmosphere regimes. This underscores the importance of electron-driven processes in nonequilibrium kinetic modeling. Furthermore, e-V processes were found to play a dominant role in activating combustion reactions.

Future work will extend these calculations to include rotational effects, allowing for the investigation of vibrational relaxation times at very low electron temperatures.

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DATA AVAILABILITY

The full dataset of cross sections and rate coefficients described in the present work is openly available [47].

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