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Electron Nuclear Dynamics of $\text{H}^+ + \text{CO}_2(000) \rightarrow \text{H}^+ + \text{CO}_2(v_1v_2v_3)$ at $E_{\text{Lab}} = 20.5\text{--}30$ eV with Coherent-States Quantum Reconstruction Procedure

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Abstract

The simplest-level electron nuclear dynamics (SLEND) method with the coherent-states (CSs) quantum reconstruction procedure (CSQRP) is applied to the scattering system $\text{H}^+ + \text{CO}_2(000) \rightarrow \text{H}^+ + \text{CO}_2(v_1v_2v_3)$ at $E_{\text{Lab}} = 20.5\text{--}30$ eV. Relevant for astrophysics, atmospheric chemistry and proton cancer therapy, this system undergoes collision-induced vibrational excitations in CO_2 . SLEND is a time-dependent, variational, direct, and non-adiabatic method that adopts a classical-mechanics description for nuclei and a single-determinantal wavefunction for electrons. The CSQRP employs the canonical CS to reconstruct quantum state-to-state vibrational properties from the SLEND classical nuclear dynamics. Overall, the calculated collision-induced vibrational properties agree well with experimental data. SLEND total differential cross sections (DCSs) agree remarkably well with their experimental counterparts and accurately display rainbow scattering angles structures. SLEND averaged target excitation energies for vibrational + rotational and rotational motions exhibit reasonable and good agreements with experimental data, respectively. These properties show that rotational excitation is low and that the asymmetric stretch normal mode of CO_2 is much more excited than the others. SLEND/CSQRP state-to-state vibrational DCSs agree reasonably well with the sparse experimental data for final states $v_1v_2v_3 = 000\text{--}002$, but less satisfactorily for 003. These DCSs also accurately display rainbow scattering angles structures. Finally, SLEND/CSQRP vibrational proton energy loss spectra agree remarkably well with their experimental counterparts for various final vibrational states of CO_2 , collisions energies and scattering angles. Present results demonstrate the accuracy of SLEND/CSQRP to predict state-to-state vibrational properties in scattering systems with multiple normal modes.

Graphical Abstract

Canonical Coherent States Accurately Reconstruct Quantum State-to-State Vibrational Properties from Classical-Mechanics Normal Modes in Electron Nuclear Dynamics Simulations

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CONFLICTS OF INTEREST

There are no conflicts of interest to declare.

$$\begin{aligned}
 & \text{H}^+ + \text{CO}_2 \left(v_1^i v_2^i v_3^i = 000 \right) \rightarrow \text{H}^+ + \text{CO}_2 \left(v_1^f v_2^f v_3^f \right) \\
 & \mathcal{L} = \left\langle \Psi_{\text{Total}} \left| i \frac{\partial}{\partial t} - \hat{H} \right| \Psi_{\text{Total}} \right\rangle / \left\langle \Psi_{\text{Total}} \left| \Psi_{\text{Total}} \right\rangle \right. \\
 & \left\langle X_i \left| R_i^{Vib}, P_i^{Vib} \right\rangle = \exp \left(-\frac{1}{2} \left| Z_i^{Vib} \right|^2 \right) \sum_{v_i=0} \frac{\left(Z_i^{Vib} \right)^{v_i}}{\sqrt{v_i!}} \left\langle X_i \left| v_i \right\rangle \right.
 \end{aligned}$$

Keywords

Proton-molecule reactions; electron nuclear dynamics; canonical coherent states; vibrational proton energy loss spectra; state-to-state vibrational cross sections

1. Introduction

There is an upsurge of interest in studying proton-molecule reactions given their central role in astrophysics, planetary atmospheric chemistry, plasma physics, and proton cancer therapy (PCT)^{1–3}. For instance, protons in the solar wind collide with molecules in the interstellar matter and planetary atmospheres; those collisions trigger numerous chemical reactions that determine the composition and dynamics of celestial systems¹. Much closer to human concerns, PCT employs high-energy protons to obliterate cancerous cells inflicting less damage on normal cells than conventional X-ray therapy^{2, 3}. A PCT procedure comprises myriads of proton-induced reactions ranging from water radiolysis reactions to proton- and electron-induced DNA damage^{2, 3}. It follows that a detailed knowledge of proton-molecule reactions at the molecular level is crucial to understand and control the mentioned systems and procedures.

An important category of proton-molecules reactions includes those where the colliding protons excite the vibrational motion of molecules. This excitation process works as a proton-induced vibrational spectroscopy that resembles the ordinary infrared photon vibrational spectroscopy. Knowledge of these proton-induced vibrational excitation reactions is important to understand proton-to-medium energy depositions in astrophysical and PCT systems^{1–3}. Thus, prominent experimental groups have systematically studied many reactions of this type including: $\text{H}^+ + \text{H}_2$,⁴ N_2 ,⁵ CO ,^{5, 6} O_2 ,^{7, 8} H_2O ,⁹ CO_2 ,^{10–12} NO ,⁵ N_2O ,¹⁰ CH_4 ,¹³ C_2H_2 ,¹⁴ CF_4 ,¹⁵ and SF_6 ,¹⁵, *inter alia*. Those groups have measured various dynamical properties to quantify the above reactions such as proton energy loss spectra and vibrational state-to-state cross sections.

Theoretical methods can substantially expand the empirical knowledge of proton-induced vibrational excitation reactions by revealing mechanistic details and predicting properties that remain inaccessible through experiments. In contrast to the wealth of experiments, there are fewer theoretical studies on proton-induced vibration excitation reactions. The traditional way to simulate these reactions involves solving the time-independent Schrödinger equation of the corresponding scattering problem¹⁶; such an approach requires predetermined potential energy surfaces (PESs). The exact solution of the resulting close-coupling scattering equations is computationally prohibitive, so it is customary to introduce different

decoupling approximations among degrees of freedom. For instance, the infinite-order sudden (IOS^{16–19}) approximation decouples orbital and rotational angular momenta at high-energy collisions. Despite their built-in approximations, IOS methods remain computationally costly, a situation further exacerbated by their use of high-level PESs. The complexity and cost of IOS methods might in part explain the scarcity of theoretical studies on proton-induced vibration excitation reactions. Nevertheless, IOS methods have provided good results for this type of reactions such as for $\text{H}^+ + \text{H}_2$,¹⁸ N_2 ,²⁰ and CO ,^{17, 21}, *inter alia*.

In recent years, we have simulated various types of proton-molecule reactions with the electron nuclear dynamics (END) method^{22–24} as a feasible alternative to IOS methods. END is a time-dependent, variational, direct and non-adiabatic method to simulate chemical reactions^{22–24}. The simplest-level (SL) END (SLEND) version employed herein describes nuclei with classical mechanics and electrons with a single-determinantal wavefunction^{22–24}. Due to its formal structure and no reliance on predetermined PESs, SLEND is computationally less onerous than IOS methods but without any impairment on accuracy. While its nuclear description is classical, SLEND possesses an intrinsic coherent-states (CSs) quantum reconstruction procedure (CSQRP)^{23, 25} that accurately recovers quantum effects from the nuclear classical dynamics by using various types of quasi-classical CSs^{23, 25}. For proton-induced vibration excitation reactions, the CSQRP furnishes canonical (harmonic-oscillator) or Morse-oscillator CSs whose quantum dynamics correspond to a given classical nuclear dynamics^{23, 25, 26}; from that point, quantum vibrational-resolved properties are calculated by projecting the matched CS into the vibrational eigenstates of the system^{23, 25, 26} (cf. Sect. 2.2 for details). We successfully applied SLEND in conjunction with the CSQRP to various proton-induced vibrational excitation reactions such as $\text{H}^+ + \text{H}_2(v_i = 0) \rightarrow \text{H}^+ + \text{H}_2(v_f = 0-6)$ ^{27, 28}, $\text{H}^+ + \text{N}_2(v_i = 0) \rightarrow \text{H}^+ + \text{N}_2(v_f = 0-1)$ ²⁹, $\text{H}^+ + \text{CO}(v_i = 0) \rightarrow \text{H}^+ + \text{CO}(v_f = 0-2)$ ³⁰ and $\text{H}^+ + \text{NO}(v_i = 0) \rightarrow \text{H}^+ + \text{NO}(v_f = 0-2)$ ²⁶. Our SLEND results compared well with their counterparts from experiments and alternative theoretical methods, and even performed better than those methods in some cases. For instance, for $\text{H}^+ + \text{H}_2(v_i = 0) \rightarrow \text{H}^+ + \text{H}_2(v_f)$, SLEND/CSQRP provided state-to-state vibrational integral cross sections (ICSs) for $v_f = 6$ ²⁷ and differential cross sections (DCS) for $v_f = 5$ ²⁸ in very good agreement with experimental⁴ and IOS results¹⁸; moreover, the SLEND ICSs were more accurate than those from an alternative quasi-classical method⁴. In the case of $\text{H}^+ + \text{N}_2(v_i = 0) \rightarrow \text{H}^+ + \text{N}_2(v_f = 0-1)$, SLEND/CSQRP predicted a primary rainbow scattering angle value of $\theta_{Lab}^{PR} = 8.6^\circ$ that is very close to the experimental value of 9° ; in contrast, IOS and an alternative quasi-classical method under- and overestimated θ_{Lab}^{PR} by 2° and 3° , respectively. An additional advantage of SLEND over IOS methods is its time-dependent framework (IOS is time-independent) that provides a chronological record of a reaction from reactants to products (cf. the reactions animation in Sect. 4.1). In this outline, we focus on comparing SLEND/CSQRP with IOS and quasi-classical methods because the latter predominate in proton-molecule reactions studies featuring electron-nucleus effects. However, other methods are or may be relevant for these studies. In the time-independent field, we can mention the continuum distorted wave and continuum distorted wave-eikonal initial state methods³¹; in the time-dependent field, we can mention the multi-configuration time-dependent Hartree³² and the real-time nuclear-electronic orbital (NEO) methods³³.

To further advance our previous SLEND/CSQRP research, we present herein a SLEND/CSQRP study of $\text{H}^+ + \text{CO}_2(v_1^i v_2^i v_3^i = 000) \rightarrow \text{H}^+ + \text{CO}_2(v_1^f v_2^f v_3^f)$ at collision energies $E_{\text{Lab}} = 20.5, 29.5$ and 30 eV in comparison with available experimental results^{10–12}. This reaction is important in atmospheric chemistry because protons from the solar wind collide with CO_2 molecules in our atmosphere¹; those collisions initiate various reactions that regulate the composition and dynamics of the atmosphere, thus influencing climate change¹. In addition, the investigated reaction is a computationally feasible prototype of PCT reactions involving cellular CO_2 or biomolecules with ketone groups^{2, 3}. In the progress of our research, the present reaction poses a new challenge to SLEND/CSQRP: to describe accurately a proton-induced vibration excitation reaction involving a target molecule, CO_2 , with multiple normal modes—previous SLEND/CSQRP research on these reactions only involved diatomic target molecules with a single normal mode^{26–30}. Our results presented in Sect. 4 demonstrate that SLEND/CSQRP succeeds in this endeavor.

2. Method

2.1 The SLEND Theory

Lengthy reviews of the SLEND theory have been presented elsewhere^{22–24}; therefore, herein, we will provide a concise account of that method. SLEND is a time-dependent, variational, direct and non-adiabatic method to simulate chemical reactions. SLEND adopts a trial total wave function, $|\Psi_{\text{SLEND}}(t)\rangle$ that is the product of nuclear $|\mathbf{R}(t), \mathbf{P}(t)\rangle$ and electronic $|\mathbf{z}(t); \mathbf{R}(t), \mathbf{P}(t)\rangle$ wavefunctions: $|\Psi_{\text{SLEND}}(t)\rangle = |\mathbf{R}(t), \mathbf{P}(t)\rangle |\mathbf{z}(t); \mathbf{R}(t), \mathbf{P}(t)\rangle$. In a system with N_N nuclei, $|\mathbf{R}(t), \mathbf{P}(t)\rangle$ is the product of $3N_N$ 1-dimensional, frozen, narrow, Gaussian wave packets:

$$\langle \mathbf{X} | \mathbf{R}(t), \mathbf{P}(t) \rangle = \prod_{i=1}^{3N_N} \langle X_i | R_i(t), P_i(t) \rangle = \prod_{i=1}^{3N_N} \exp \left\{ - \left[\frac{X_i - R_i(t)}{2 \Delta R_i} \right]^2 + i P_i [X_i - R_i(t)] \right\} \quad (1)$$

where $R_i(t)$, $P_i(t)$, and ΔR_i are the average positions, average momenta, and widths of the wave packets, respectively. $|\mathbf{z}(t); \mathbf{R}(t), \mathbf{P}(t)\rangle$ is an unrestricted single-determinantal state in the Thouless representation³⁴. Having N_e electrons and an atomic basis set of size $K > N_e$, one can prepare N_e occupied and $K - N_e$ virtual molecular spin-orbitals (MSOs), $\{\psi_p\}$ and $\{\psi_h\}$, respectively, at the unrestricted Hartree-Fock (UHF) level. Then, the Thouless single-determinantal state $|\mathbf{z}(t); \mathbf{R}(t), \mathbf{P}(t)\rangle$ from the reference state $|0\rangle = |\psi_{N_e} \dots \psi_h \dots \psi_1\rangle$ is^{22, 23, 34}

$$|\mathbf{z}(t); \mathbf{R}(t), \mathbf{P}(t)\rangle = \exp \left(\sum_{p=N_e+1}^K \sum_{h=1}^{N_e} z_{ph}(t) b_p^\dagger b_h \right) |0\rangle; \quad (2)$$

$$\langle \mathbf{x} | \mathbf{z}(t); \mathbf{R}(t), \mathbf{P}(t) \rangle = \det \{ \chi_h[\mathbf{x}_h; \mathbf{z}(t), \mathbf{R}(t)] \} \quad 1 \leq h \leq N_e;$$

where the $\{\chi_h\}$ are the non-orthogonal and unrestricted dynamical spin-orbitals (DSOs):

$$\chi_h[\mathbf{x}; \mathbf{z}(t), \mathbf{R}(t), \mathbf{P}(t)] = \psi_h[\mathbf{x}; \mathbf{R}(t), \mathbf{P}(t)] + \sum_{p=N_e+1}^K \psi_p[\mathbf{x}; \mathbf{R}(t), \mathbf{P}(t)] z_{ph}, \quad 1 \leq h \leq N_e, \quad (3)$$

in terms of complex-valued Thouless parameters $\{z_{ph}(t)\}$; those parameters are the DSOs coefficients in the MSOs basis. The atomic basis set functions to construct the MSOs, DSOs and $|\mathbf{z}(t); \mathbf{R}(t), \mathbf{P}(t)\rangle$ are centered on the wave packets and move with positions $R_\lambda(t)$ and momenta $P_\lambda(t)$; thus, the MSOs, DSOs, and $|\mathbf{z}(t); \mathbf{R}(t), \mathbf{P}(t)\rangle$ depend parametrically on $R_\lambda(t)$ and $P_\lambda(t)$. SLEND adopts the Thouless representation³⁴ because it provides a non-redundant, invertible parameterization of a general single-determinantal state from the reference $|0\rangle$; such a representation forestalls singularities during evolution (cf. Refs. ^{22, 23}).

Application of the time dependent variational principle (TDVP)³⁵ to $|\Psi_{SLEND}(t)\rangle$ generates the SLEND dynamical equations. Like Hamilton's principle in classical mechanics, the TDVP starts with the quantum Lagrangian³⁵:

$$L_{SLEND}[\Psi_{SLEND}, \Psi_{SLEND}^*] = \langle \Psi_{SLEND} | i\partial/\partial t - \hat{H}_{Total} | \Psi_{SLEND} \rangle \text{ where } \hat{H}_{Total} \text{ is } |\Psi_{SLEND}\rangle \langle \Psi_{SLEND}|^{-1}$$

the total Hamiltonian. The TDVP imposes stationarity on the quantum action³⁵:

$$\delta A_{END}[\Psi_{SLEND}, \Psi_{SLEND}^*] = \delta \int_{t_1}^{t_2} L_{END}[\Psi_{SLEND}(t), \Psi_{SLEND}^*(t)] dt = 0, \text{ with respect}$$

to the variational parameters: $\{R_\lambda(t), P_\lambda(t), z_{ph}(t), z_{ph}^*(t)\}$ that optimization leads to a set of Euler-Lagrange equations for those parameters. To accelerate simulations, the TDVP is applied to $|\Psi_{SLEND}(t)\rangle$ in the zero-width limit of its nuclear wave packets $|R_\lambda(t), R_\lambda(t)\rangle$, $\mathbf{R}_i \rightarrow 0 \forall i$; that procedure renders a classical dynamics for the nuclei in terms of positions $R_\lambda(t)$ and momenta $P_\lambda(t)$ (the electronic dynamics remains quantum-mechanical). In that limit, SLEND dynamical equations are²²⁻²⁴

$$\begin{bmatrix} i\mathbf{C} & \mathbf{0} & i\mathbf{C}_\mathbf{R} & i\mathbf{C}_\mathbf{P} \\ \mathbf{0} & -i\mathbf{C}^* & i\mathbf{C}_\mathbf{R}^* & -i\mathbf{C}_\mathbf{P}^* \\ i\mathbf{C}_\mathbf{R}^\dagger - i\mathbf{C}_\mathbf{R}^T & \mathbf{C}_{\mathbf{RR}} & -\mathbf{I} + \mathbf{C}_{\mathbf{RP}} & \\ i\mathbf{C}_\mathbf{P}^\dagger - i\mathbf{C}_\mathbf{P}^T & \mathbf{I} + \mathbf{C}_{\mathbf{PR}} & \mathbf{C}_{\mathbf{RP}} & \end{bmatrix} \begin{bmatrix} \frac{d\mathbf{z}}{dt} \\ \frac{d\mathbf{z}^*}{dt} \\ \frac{d\mathbf{R}}{dt} \\ \frac{d\mathbf{P}}{dt} \end{bmatrix} = \begin{bmatrix} \frac{\partial E_{Total}}{\partial \mathbf{z}^*} \\ \frac{\partial E_{Total}}{\partial \mathbf{z}} \\ \frac{\partial E_{Total}}{\partial \mathbf{R}} \\ \frac{\partial E_{Total}}{\partial \mathbf{P}} \end{bmatrix} \quad (4)$$

where the total (nuclear and electronic) energy E_{Total} is

$$E_{Total} = \sum_{i=1}^{N_N} \frac{\mathbf{P}_i^2}{2M_i} + \sum_{i=1, j>i}^{N_N} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} + \frac{\langle \mathbf{z}(t), \mathbf{R}(t), \mathbf{P}(t) | \hat{H}_e | \mathbf{z}(t), \mathbf{R}(t), \mathbf{P}(t) \rangle}{\langle \mathbf{z}(t), \mathbf{R}(t), \mathbf{P}(t) | \mathbf{z}(t), \mathbf{R}(t), \mathbf{P}(t) \rangle}, \quad (5)$$

M_i and Z_i are the nuclei masses and charges and $\hat{H}_e$ is the electronic Hamiltonian. The dynamic metric matrices in Eq. (4) are

$$\begin{aligned}
 (\mathbf{C}_{XY})_{ik,jl} &= -2\text{Im} \frac{\partial^2 \ln S}{\partial X'_{ik} \partial Y_{jl}} \bigg|_{\substack{\mathbf{R}' = \mathbf{R} \\ \mathbf{P}' = \mathbf{P}}}, \quad (\mathbf{C}_{X_{ik}})_{ph} = \frac{\partial^2 \ln S}{\partial z_{ph}^* \partial X_{ik}} \bigg|_{\substack{\mathbf{R}' = \mathbf{R} \\ \mathbf{P}' = \mathbf{P}}}, \quad \mathbf{C}_{ph,qg} \\
 &= \frac{\partial^2 \ln S}{\partial z_{ph}^* \partial z_{qg}} \bigg|_{\substack{\mathbf{R}' = \mathbf{R} \\ \mathbf{P}' = \mathbf{P}}}
 \end{aligned} \quad (6)$$

where $S = \langle \mathbf{z}(t), \mathbf{R}'(t), \mathbf{P}'(t) | \mathbf{z}(t), \mathbf{R}(t), \mathbf{P}(t) \rangle$, and X and Y denote R or P . $\mathbf{C}_R$ and $\mathbf{C}_{RR}$ are equivalent to the standard non-adiabatic coupling terms³⁶ and convey the effect of the nuclear positions on the electronic dynamics. Neglect of $\mathbf{C}_R$ and $\mathbf{C}_{RR}$ considerably harms accuracy³⁷; therefore, these terms are kept in the present calculations. $\mathbf{C}_P$ and $\mathbf{C}_{PP}$ convey the explicit effect of the nuclear momenta on the electronic dynamics via electron translation factors (ETFs)³⁸ attached to the atomic basis functions. Neglect of ETFs scarcely affects accuracy at collision energies $E_{Lab} \sim 100$ eV^{22, 26, 29, 30, 39–42}. Thus, to accelerate calculations, ETFs are not included in the atomic basis set and therefore $\mathbf{C}_P = \mathbf{C}_{PR} = \mathbf{O}$.

In general, a single-determinantal/HF representation has some limitations. From a time-independent standpoint, it is well-known that HF lacks dynamic correlation effects. From a time-dependent standpoint, a recent study⁴³ on a S_N2 reaction showed that HF PESs can provide unsatisfactory results for some reactive processes when compared with highly correlated methods. However, SLEND in association with CSQRP has consistently provided good results for scattering and vibrational-resolved properties in proton-molecule reactions (cf. our numerous previous^{26–30} studies and the present results in Sect. 4). It is worth recalling that the ultimate goal of the present efforts is to simulate PCT reactions involving large biomolecules; in those systems, SLEND/CSQRP is certainly feasible³, whereas highly correlated methods may not.

2.2 Coherent-States Quantum Reconstruction Procedure of Vibrational Properties

Due to the zero-width limit applied to the Gaussian wave packets, quantum features vanish from the SLEND nuclear wavefunction. Fortunately, SLEND possesses an intrinsic CSQRP to recover quantum state-to-state properties from the nuclear classical dynamics^{23, 25}. In outline, the CSQRP first recreates narrow, finite-width wave packets corresponding to a given SLEND nuclear classical dynamics with the help of various types of CS sets^{23, 25}; then, the CSQRP calculates state-to state properties by projecting the recreated quantum entity onto appropriate eigenstates. In the following, we will summarize the CSQRP procedure; further details can be found in Refs. ^{23, 25, 44}.

In essence, Hilbert-space states $\{|\zeta_i\rangle\}$ depending on parameters $\{\zeta_i\}$ constitute a CS set if they satisfy two properties⁴⁵: (I) the states $\{|\zeta_i\rangle\}$ are continuous with respect to the parameters $\{\zeta_i\}$, and (II) the states $\{|\zeta_i\rangle\}$ attain resolution of unity with a positive measure $d\mu(\zeta_i) > 0$: $\int d\mu(\zeta_i) |\zeta_i\rangle \langle \zeta_i| = \hat{1}$. END is intimately associated with the CS theory because different END realizations employ specific types of CS sets^{22, 23, 25, 44, 46}. SLEND employs two types of CS sets^{22, 23}. First, each 1-D Gaussian wave packet $|R(t), P(t)\rangle$, in Eq. (1) is a member of the canonical CS set with real-valued parameters $\{\zeta_i\} = \{R_i, P_i\}$ ⁴⁵. Second, the Thouless single-determinantal state $|\mathbf{z}(t); \mathbf{R}(t), \mathbf{P}(t)\rangle$ ³⁴, Eq. (2), is a member of the Thouless CS set⁴⁵ with complex-valued parameters $\{\zeta_i\} = \{z_{ph}\}$. In their original roles, these CS sets

supply their parameters to appropriately represent the SLEND total wave function $|\Psi_{SLEND}(t)\rangle$ for TDVP treatments^{22, 23, 35}. In addition, the canonical CS set exhibits additional dynamical properties with respect to the harmonic-oscillator Hamiltonian that form the basis of the vibrational CSQRP. Having a 1-D harmonic-oscillator Hamiltonian $\hat{H}_{HO}$ with mass m_i and angular frequency ω_i , a normalized canonical CS $\langle X_i | R_i^{Vib}, P_i^{Vib} \rangle$ with width $\Delta R_i^{Vib} = (2m_i\omega_i)^{-1/2}$ is [cf. Eq. (1)]

$$\langle X_i | R_i^{Vib}, P_i^{Vib} \rangle = (m_i\omega_i/\pi)^{1/4} \exp \left\{ - \left[\frac{(X_i - R_i^{Vib})^2}{2 \Delta R_i^{Vib}} \right] + iP_i^{Vib}(X_i - R_i^{Vib}) \right\}. \quad (7)$$

The above CS evolves with $\hat{H}_{HO}$ satisfying temporal stability, quasi-classical behavior, and minimum uncertainty relationship, among other dynamical properties^{44, 47, 48}. Temporal stability^{44, 48} means that the CS $\langle X_i | R_i^{Vib}(t), P_i^{Vib}(t) \rangle$ evolves solely through its time-dependent parameters $R_i^{Vib}(t)$ and $P_i^{Vib}(t)$, thus remaining within its own set during dynamics. Quasi-classical behavior^{44, 47} means that the CS average position $\langle R_i^{Vib}(t), P_i^{Vib}(t) | \hat{X}_i | R_i^{Vib}(t), P_i^{Vib}(t) \rangle = R_i^{Vib}(t)$ and momentum $\langle R_i^{Vib}(t), P_i^{Vib}(t) | \hat{P}_i | R_i^{Vib}(t), P_i^{Vib}(t) \rangle = P_i^{Vib}(t)$ evolve with $\hat{H}_{HO}$ as the position and momentum of its classical-mechanics analogue with Hamiltonian $H_{HO}(R_i^{Vib}, P_i^{Vib})$. Minimum uncertain relationship^{44, 47} means that the deviations of the CS average position and momentum satisfy $\langle X_i(t) | P_i(t) \rangle = 1/2$ at all time. These properties are the foundations of the vibrational CSQRP from the SLEND nuclear classical dynamics. Specifically, if a molecule is simulated with SLEND in a vibrational motion, for each of its N_{NM} normal modes, a canonical CS $\langle X_i | R_i^{Vib}, P_i^{Vib} \rangle$ with mass m_i and angular frequency ω_i can be reconstructed so that its quasi-classical vibration matches that of the normal mode with effective mass m_i and angular frequency $\omega_i^{23, 25}$, $1 \leq i \leq N_{NM}$. The matched CS is a superposition of the normal mode vibrational eigenstates $|v_i\rangle$ ($v_i = 0, 1, 2, \dots$)⁴⁵:

$$\begin{aligned} \langle X_i | R_i^{Vib}, P_i^{Vib} \rangle &= \exp \left(-\frac{1}{2} |Z_i^{Vib}|^2 \right) \sum_{v_i=0}^{\infty} \frac{(Z_i^{Vib})^{v_i}}{\sqrt{v_i!}} \langle X_i | v_i \rangle \quad (v_i = 0, 1, \dots); \\ Z_i^{Vib} &= \sqrt{m_i\omega_i/2} R_i^{Vib} + i\sqrt{1/2m_i\omega_i} P_i^{Vib} \quad (i = 1, \dots, N_{NM}), \end{aligned} \quad (8)$$

where Z_i^{Vib} is a complex-valued CS parameter comprising the previous real-valued parameters R_i^{Vib} and P_i^{Vib} . Then, the probability of finding the SLEND-simulated molecule in the vibrational eigenstate $|v_i\rangle$ of the i -th normal mode is given by the Poisson distribution $P_i(v_i)$ ⁴⁵:

$$\begin{aligned} P_i(v_i) &= \left| \langle v_i | R_i^{Vib}, P_i^{Vib} \rangle \right|^2 = \exp \left(-|Z_i^{Vib}|^2 \right) \frac{|Z_i^{Vib}|^{2v_i}}{v_i!} = \exp \left(-E_i^{Vib}/\omega_i \right) \frac{(-E_i^{Vib}/\omega_i)^{v_i}}{v_i!} \\ v_i &= 0, 1, 2, 3, \dots \end{aligned} \quad (9)$$

where E_i^{Vib} is the SLEND classical energy of the considered normal mode of vibration.

For state-to-state properties in $H^+ + CO_2$, resolutions into the CO_2 vibrational eigenstates are only necessary at initial and some specific final times. At those times, the CO_2 molecule can be treated as an isolated entity, far away from the incoming/outgoing H^+

projectile^{23, 25, 44, 49}. In those circumstances, the CO_2 SLEND total wave function is

$|\Psi_{SLEND}^{CO_2}\rangle = |\Psi_e^{CO_2}\rangle |\Psi_N^{CO_2}\rangle$ with the dynamics of the wave packets in $|\Psi_N^{CO_2}\rangle$, cf. Eq.

(1), matching quasi-classically the SLEND nuclear classical motion of CO_2 . By switching into the center-of-mass and internal coordinates and by adopting the rigid-rotor and

harmonic approximations⁵⁰, $|\Psi_N^{CO_2}\rangle$ can be separated into translational, rotational, and

vibrational wave functions: $|\Psi_N^{CO_2}\rangle = |\Psi_{Trans}^{CO_2}\rangle |\Psi_{Rot}^{CO_2}\rangle |\Psi_{Vib}^{CO_2}\rangle$ ^{44, 49}, where all separations

are exact except for that between rotational and vibrational motions. $|\Psi_{Trans}^{CO_2}\rangle$ is a 3-D wave packet on the CO_2 center of mass that describes the CO_2 translation^{23, 25, 44, 49}; $|\Psi_{Rot}^{CO_2}\rangle$ is a

rotational CS that describes quasi-classically the CO_2 rotation⁴⁴, and $|\Psi_{Vib}^{CO_2}\rangle$ is a canonical

CS that describes quasi-classically the CO_2 vibration^{23, 25, 44, 49}. In this separation, the CO_2

rotational energy is $E_{Rot}^{CO_2} = K_{Total}^{CO_2} - K_{Trans}^{CO_2} - K_{Vib}^{CO_2}$ ^{23, 25, 44, 49}, where $K_{Total}^{CO_2}$ is the CO_2

total kinetic energy, $K_{Trans}^{CO_2}$ is the CO_2 center-of-mass translational kinetic energy, and $K_{Vib}^{CO_2}$

is the CO_2 vibrational kinetic energy; as will be shown in Sect. 4.3, the post-collision $K_{Trans}^{CO_2}$

is much smaller than the total vibrational energy $E_{Vib}^{CO_2}$. In the harmonic approximation,

$|\Psi_{Vib}^{CO_2}\rangle$ and $E_{Vib}^{CO_2}$ can be factorized and separated into their normal-mode components⁵⁰ as

$|\Psi_{Vib}^{CO_2}\rangle = \prod_{i=1}^{NNM} |R_i^{Vib}, P_i^{Vib}\rangle_i^{CO_2}$ and $E_{Vib}^{CO_2} = \sum_{i=1}^{NNM} E_i^{VibCO_2}$ respectively, where

$|R_i^{Vib}, P_i^{Vib}\rangle_i^{CO_2}$ and $E_i^{VibCO_2}$ are the canonical CS and classical vibrational energy of the i -th

normal mode, respectively; the $E_i^{VibCO_2}$ are used in Eq. (9) to resolve $|\Psi_{Vib}^{CO_2}\rangle$ and related

dynamical properties into the CO_2 normal-mode eigenstates $|v_i\rangle$ (cf. Sects. 4.4 and 4.5).

Each $E_i^{VibCO_2}$ is the sum of kinetic and potential energy components,

$E_i^{VibCO_2} = K_i^{VibCO_2} + U_i^{VibCO_2}$, which are calculated by projecting the post-collision mass-

weighted internal velocities and mass-weighted displacement coordinates onto the mass-weighted displacement coordinates corresponding to each normal mode. To set up those

projections, the post-collision CO_2 coordinates: $\mathbf{R}_X^f$, $X = C_1, C_2, O$ are aligned with the CO_2 equilibrium coordinates at initial time, $\mathbf{R}_X^i$, by a coordinate rotation that minimizes

$\sum_X |\mathbf{R}_X^f - \mathbf{R}_X^i|^2$ ⁵¹; this same coordinate rotation is applied to the CO_2 velocities. In this

scheme, the kinetic energy attributable to each normal mode is $K_i^{VibCO_2} = h_i^2/2$, where h_i is

the scalar product of the mass-weighted internal velocities projected onto the mass-weighted

normal mode displacement coordinates. Similarly, the potential energy attributable to each normal mode is $U_i^{VibCO_2} = (\omega_i)^2 g_i^2 / 2$ where g_i is the scalar product of the mass-weighted displacement coordinates projected onto the mass-weighted normal mode displacement coordinates, and ω_i is the angular frequency of the normal mode. In calculations of state-to-state vibrational properties in Sects. 4.4 and 4.5, the time to analyze the final internal state of CO₂ is a post-collision time when the H⁺ projectile is at least separated from the CO₂ target as at the initial time and the CO₂ is at a maximum in its periodically-varying internal kinetic energy.

The canonical CSQRP assumes a harmonic molecule and is therefore appropriate for nearly harmonic or moderately anharmonic molecules, a condition that CO₂ satisfies⁵²; this is corroborated by the good canonical CSQRP results presented in Sect. 4. The quasi-classical rotational CS corresponding to $|\Psi_{Rot}^{CO_2}\rangle$ has been used to calculate quantum rotational excitation probabilities in other ion-molecule collisions⁴⁴; however, this CS is not used herein because no properties resolved into rotational eigenstates were measured in the considered experiments^{10–12}. The Thouless CS does not exhibit quasi-classical behavior with respect to the electronic Hamiltonian; this is expected because this CS should describe a quantum electronic dynamics. However, an electronic quasi-classical CS has been proposed in the context of charge-equilibration models⁵³.

3. Computational Details

3.1 Software

Present SLEND simulations were conducted with our END program CSDYN 1.0 (A. Perera, T. Grimes, J. Morales, CSDYN 1.0, Texas Tech University, Lubbock, TX 79409, 2008-2010).

3.2 Initial States Preparation and Simulations Details

The vibrational CSQRP at initial and final times requires a good description of the CO₂ normal modes. Pople 6-31(1)G basis sets⁵⁴ rendered accurate results in previous vibrational SLEND/CSQRP studies^{26, 29, 30}; therefore, we will utilize those basis sets here again. Table I shows the normal mode frequencies ν_i of CO₂ from experiments⁵² and from HF/6-31G, HF/6-31G**, HF/6-31++G and HF/6-311G calculations. Following the notation of the experimental Ref.¹⁰, the normal mode frequencies are denoted as: ν_1 = single-degenerate symmetric stretch, ν_2 = double-degenerate bending, and ν_3 = single-degenerate asymmetric stretch. Table I also shows the deviations and total root mean squares (RMSs) of the calculated frequencies from the experimental ones; the RMSs indicate that the 6-311G basis set provides the best frequency description; therefore, that basis set will be used exclusively in the subsequent simulations. Correlated methods provide frequencies in better agreement with experiments than HF. For instance, frequencies calculated with the ACES IV⁵⁵ program at the level of the coupled cluster singles, doubles and perturbative triple excitations method with explicit correlation and the augmented correlation-consistent pVTZ basis set [CCSD(T)-F12/aug-cc-pVTZ] are $\nu_1 = 1354.7070$, $\nu_2 = 672.5073$, and $\nu_3 = 2396.7715$ cm⁻¹ (cf. Table I). However, we cannot adopt these frequencies in the subsequent CSQRP because

the latter should be consistent with the HF frequencies reproduced by the SLEND/6-311 dynamics of CO₂.

The nuclear parameters defining the initial conditions of the reactants H⁺ and CO₂ are shown in Fig. 1. The target molecule, CO₂, is initially at rest with moment $\mathbf{P}_{C1}^i = \mathbf{P}_{C2}^i = \mathbf{P}_O^i = \mathbf{0}$, with its center of mass at the laboratory frame origin, and in its restricted HF/6-311G electronic ground state at equilibrium geometry. From the vibrational CSQRP standpoint, these initial conditions correspond to the CO₂ vibrational ground state $|\Psi_{Vib}^{CO_2}\rangle = |v_1 v_2 v_3 = 000\rangle$, cf. Eq. (9), employed in the experiments available for comparison^{10–12}. The H⁺ projectile is first prepared with position $\mathbf{R}_{H+}^0 = (b \geq 0, 0, +15 \text{ a.u.})$, and momentum $\mathbf{P}_{H+}^0 = (0, 0, -p_{H+}^z)$ where $b = 0$ is the projectile impact parameter from the CO₂ center of mass, and p_{H+}^z corresponds to the collisional energies $E_{Lab} = 20.5, 29.5$, and 30 eV of the available experiments^{10–12}. The definite conditions $\mathbf{R}_{H+}^i$ and $\mathbf{P}_{H+}^i$ of the H⁺ projectile for our simulations are obtained by rotating $\mathbf{R}_{H+}^0$ and $\mathbf{P}_{H+}^0$ through extrinsic Euler angles⁵⁶ in the order: 1st, $0^\circ \leq \gamma < 360^\circ$, 2nd, $0^\circ \leq \beta < 180^\circ$, and 3rd, $0^\circ \leq \alpha < 360^\circ$, around the space-fixed z, y , and z axes, respectively⁵⁶. These rotations generate various projectile-target relative orientations $\omega_i = (\alpha_i, \beta_i, \gamma_i)$ (cf. our Ref. ² for a detailed description of these Euler angles and their relationship to the ordinary intrinsic Euler angles around body-fixed axes⁵⁶). The obtained $\mathbf{R}_{H+}^0$ and $\mathbf{P}_{H+}^0$ for the selected orientations ω_i are the initial conditions of the H⁺ projectile. Nine selected orientations ω_i are generated from $\omega_0 = (0^\circ, 0^\circ, 0^\circ)$ by varying independently each Euler angle in 45° increments; these ω_i lead to unique (symmetrically non-equivalent) trajectories. For each ω_i , b is varied from $b = 0.0$ to 8.9 a.u. in steps of $b = 0.1 \text{ a.u.}$ Three sets of simulations from the described initial conditions are conducted with the three investigated energies. Each individual simulation runs for a total time of $1,200 \text{ a.u.}$ (29.0280 fs) when $E_{Lab} = 20.5 \text{ eV}$ and of $1,600 \text{ a.u.}$ (38.7040 fs) when $E_{Lab} = 29.5$ and 30 eV . These times are long enough to obtain a final projectile-target separation that is equal to or longer than the initial projectile-target separation (i.e., 15.0 a.u. of length).

4. Results and discussion

4.1 Predicted Reactions

If the impact parameters b are above a critical value $b_{\text{critical}} = 1.3 \text{ a.u.}$, present SLEND/6-311 simulations only predict collision-induced vibrational scattering processes:

where the H⁺ projectiles wander off into scattering angles θ_{Lab} within the range of the experimental measurements: $0^\circ \leq \theta_{Lab} \leq 19^\circ$ ^{10, 12}; these processes also exhibit a slight degree of collision-induced rotational excitations as discussed in Sect. 4.3. In Eq. (10), following the notation of the experimental Ref.¹⁰, the initial/final normal mode quantum

numbers $v_k^{i/f}$ are denoted as: $v_1^{i/f}$ = single-degenerate symmetric stretch, $v_2^{i/f}$ = double-degenerate bending, and $v_3^{i/f}$ = single-degenerate asymmetric stretch. Experiments^{10, 11} cannot distinguish processes from the double-degenerate bending normal modes; therefore, the measured data of those modes were reported together with a single total quantum number $v_2^{i/f}$ ^{10, 11}. If the impact parameters b are below $b_{\text{critical}} = 1.3$ a.u., SLEND/6-311 simulations predict either the same processes in Eq. (10) but with $\theta_{\text{Lab}} > 19^\circ$ (i.e. outside the experimental range^{10, 12}) or reactive processes (e.g., C=O bond fragmentation: $\text{H}^+ + \text{CO}_2 \rightarrow \text{H}^+ + \text{CO} + \text{O}$). All these last processes do not contribute to the collision-induced vibration excitation processes observed in the available experiments¹⁰⁻¹² and, for that reason, they will not be considered further herein (cf. our Ref.⁵⁷ for a detailed quantitative study of reactive processes in $\text{H}^+ + \text{CO}_2$). All the subsequent calculations will correspond to the collision-induced vibrational scattering processes described in Eq. (9).

For illustration's sake, Fig. 2 shows four sequential snapshots of a representative collision-induced vibration excitation process from the initial conditions: $E_{\text{Lab}} = 30$ eV, $b = 1.8$ a.u., $\alpha = \gamma = 0^\circ$ and $\beta = 45^\circ$. In Fig. 2, gray, black and red spheres represent the H, C and O classical nuclei, respectively, and colored clouds depict isovalue contours of the electron density; those clouds are shown via a rainbow color code where red and blue correspond to the maximum and minimum selected values of the density, respectively. The first snapshot of Fig. 2 (time = 5.3 fs) shows the incoming H^+ projectile approaching an unperturbed CO_2 molecule. The second snapshot (time = 8.5 fs) shows the H^+ projectile nearly colliding with one of the O nuclei and submerging into the perturbed electron density of CO_2 . The third snapshot (time = 11.6 fs) shows the H^+ projectile scattering off to the upper left. Finally, the fourth snapshot (time = 24.2 fs) shows the post-collision CO_2 exhibiting collision-induced vibrational and electronic excitations (nuclei positions and electron density contours depart from their equilibrium values shown in the first snapshot).

4.2 Total Differential Cross Sections:

Two important types of experimental data of $\text{H}^+ + \text{CO}_2$ are its total and state-resolved DCSs. For the scattering process $\text{H}^+ + \text{M}(i) \rightarrow \text{H}^+ + \text{M}(f)$, where the target molecule M transitions from initial (i) to final (f) states, the state-to-state DCS $d\sigma_{(\alpha, \beta, \gamma)}^{i \rightarrow f}(\theta_{\text{CM}})/d\Omega$ of SLEND simulations from the initial orientation (α, β, γ) is in the center-of-mass (CM) frame^{23, 36}:

$$\frac{d\sigma_{(\alpha, \beta, \gamma)}^{i \rightarrow f}(\theta_{\text{CM}})}{d\Omega} = \frac{k_f}{k_i} \left| f_{(\alpha, \beta, \gamma)}^{i \rightarrow f}(\theta_{\text{CM}}) \right|^2 = \frac{1}{4k_i^2} \left| \sum_{l=0}^{\infty} (2l+1) T_{(\alpha, \beta, \gamma)}^{i \rightarrow f}(l) P_l(\cos\theta_{\text{CM}}) \right|^2, \quad (11)$$

where $f_{(\alpha, \beta, \gamma)}^{i \rightarrow f}(\theta_{\text{CM}})$ is the scattering amplitude, k_i and k_f are the projectile initial and final wave vector magnitudes, respectively, l is the final orbital angular momentum quantum number of the projectile, $T_{(\alpha, \beta, \gamma)}^{i \rightarrow f}(l)$ is the T-matrix, and the $P_l(\cos\theta_{\text{CM}})$ are Legendre polynomials. SLEND employs classical nuclear dynamics; therefore, the l values are obtained from the impact parameters b through the semi-classical relationship $l = k_i b$ ³⁶. The SLEND expression of $T_{(\alpha, \beta, \gamma)}^{i \rightarrow f}(l)$ depends on the specific scattering process under

consideration as illustrated in the next paragraph and in Sect. 4.3. The CM DCSs $d\sigma_{(\alpha,\beta,\gamma)}^{i \rightarrow f}(\theta_{CM})/d\Omega$ are calculated with Eq. (11) employing the SLEND data transformed into the CM frame; the obtained DCSs are transformed back to the laboratory frame and averaged over initial orientations (α, β, γ) to obtain the finally reported DCSs $d\bar{\sigma}_{SLEND}^{i \rightarrow f}(\theta_{Lab})/d\Omega$ to compare with experiments.

In this section, we will consider the simpler total DCS for the scattering process:

i.e. the DCS unresolved into the final vibrational states. We will discuss the more complex state-to-state vibrational DCS in Sect. 4.4 because prior to that, in Sect. 4.3, we should scrutinize other vibrational properties that affect the accuracy of the vibrational states resolution. In SLEND, the T-matrix for the total DCS, $T_{(\alpha,\beta,\gamma)}^{i \rightarrow \text{all}}$, is²³

$$T_{(\alpha,\beta,\gamma)}^{i \rightarrow \text{all}}(l = k_i b) = \exp[i2\eta_{(\alpha,\beta,\gamma)}(l = k_i b)], \quad (13)$$

where $\eta_{(\alpha,\beta,\gamma)}(l)$ is the phase shift³⁶ calculated from the semi-classical expression $\Theta_{CM}(b) = (2/k_i)[\eta(b) - b]$, where $|\Theta_{CM}(b)| = \Theta_{CM}(b)$ is the deflection function in the CM frame³⁶. The CM total DCSs $d\sigma_{(\alpha,\beta,\gamma)}^{i \rightarrow \text{all}}(\theta_{CM})/d\Omega$ are obtained with Eq. (9) using the $T_{(\alpha,\beta,\gamma)}^{i \rightarrow \text{all}}$ in Eq. (13); from those CM DCSs, the averaged total DCS $d\bar{\sigma}_{SLEND}^{i \rightarrow \text{all}}(\theta_{Lab})/d\Omega$ in the laboratory frame is calculated as explained in the previous paragraph. Fig. 3 plots experimental^{10, 12} and SLEND/6-311 $d\bar{\sigma}_{SLEND}^{i \rightarrow \text{all}}(\theta_{Lab})/d\Omega$ vs. the scattering angle θ_{Lab} for collision energies $E_{Lab} = 20.5^{12}$ and 30 eV¹⁰. SLEND/6-311 DCSs correctly display quantum oscillatory patterns caused by the phase shift $\eta_{(\alpha,\beta,\gamma)}(l)$ in Eq. (13)³⁶; experimental DCSs cannot reveal those quantum patterns because they are damped averaged values over long periods of measurements. Except for that feature, the agreement between SLEND/6-311 and experimental results is excellent over the whole range of the considered scattering angles. This agreement is significant because it indicates that SLEND/6-311 accurately reproduces the projectile-target interaction forces and scattering dynamics³⁶. Furthermore, the SLEND/6-311 DCSs can accurately reproduce the rainbow scattering angle structures observed in their experimental counterparts^{10, 12}. In Fig. 3, for $E_{Lab} = 30$ eV¹², experimental and SLEND/6-311 DCSs agree in showing a broad primary rainbow scattering structure in the interval $\theta_{Lab} = 7.5^\circ - 13^\circ$ with a primary rainbow scattering angle peak at $\theta_{Lab}^{PR} \approx 10^\circ$ (a primary rainbow scattering angle peak corresponds to the maximum projectile-target attractive deflection³⁶). Similarly, for $E_{Lab} = 20.5$ eV¹⁰, experimental and SLEND/6-311 DCSs agree in showing two rainbow scattering structures in the intervals $\theta_{Lab} = 11^\circ - 18^\circ$ and $\theta_{Lab} = 7^\circ - 11^\circ$ with peaks at $\theta_{Lab}^{PR} \approx 14^\circ$ and 9.5° , respectively, that correspond to the primary rainbow scattering angle peak and its first supernumerary peak³⁶, respectively. Furthermore, experimental and SLEND/6-311 DCSs show faint secondary rainbow scattering angle peaks at $\theta_{Lab}^{SR} \approx 5.5^\circ$ for both $E_{Lab} = 20.5$ and 30 eV (a secondary rainbow scattering angle peak corresponds to the maximum projectile scattering off the initial

projectile-target plane⁴). The values of the rainbow scattering angles θ_{Lab}^{PR} and θ_{Lab}^{SR} are related to parameters defining the projectile-molecule interaction forces³⁶; thus, SLEND's good prediction of rainbow scattering angle features and values confirms its good description of the projectile-target interaction.

4.3 Averaged Target Excitation Energies

The averaged excitation energy $\langle E_{DF}(\theta_{Lab}) \rangle_{(\alpha, \beta, \gamma)}$ of the target degree of freedom DF (DF = translational, rotational, vibrational, etc.) in the $H^+ + M$ scattering from the initial projectile-target orientation (α, β, γ) is^{58, 59}

$$\langle \Delta E_{DF}(\theta_{Lab}) \rangle_{(\alpha, \beta, \gamma)} = \frac{\sum_{m=1}^N \left[\frac{d\sigma(\theta_{Lab})}{d\Omega} \right]_m \Delta E_{DF}^m(\theta_{Lab})}{\sum_{m=1}^N \left[\frac{d\sigma(\theta_{Lab})}{d\Omega} \right]_m} \Bigg|_{(\alpha, \beta, \gamma)} ; \quad (14)$$

where $\Delta E_{DF}^m(\theta_{Lab})$ is the energy transferred to the target DF from the projectile H^+ in the m ($m = 1, 2, 3 \dots N$) branch (trajectory) with H^+ scattering into the direction θ_{Lab} ; in addition, $[d\sigma(\theta_{Lab})/d\Omega]_m$ is the classical total DCS of branch m :

$$\left[\frac{d\sigma(\theta_{Lab})}{d\Omega} \right]_m = \frac{b_m}{\sin(\theta_{Lab}) \left| \frac{d\theta_{Lab}(b)}{db} \right|_{b=b_m}} . \quad (15)$$

The $\langle E_{DF}(\theta_{Lab}) \rangle_{(\alpha, \beta, \gamma)}$ are subsequently averaged over the initial orientations (α, β, γ) to obtain the completely averaged energy $\langle \Delta \bar{E}_{DF}(\theta_{Lab}) \rangle$ to compare with their experimental counterparts¹⁰. Fig. 4 plots various SLEND/6-311 $\langle \Delta \bar{E}_{DF}(\theta_{Lab}) \rangle$ at $E_{Lab} = 30$ eV for the DFs = translational + vibrational (all normal modes) + rotational, vibrational (all normal modes) + rotational, vibrational (all normal modes), symmetric stretch normal mode v_1^f , bending normal modes $0v_2^f$, asymmetric stretch normal mode $00v_3^f$, and rotational. The calculations of the DF energies were explained in Sect. 2.2. Fig. 4 also plots the only available experimental $\langle \Delta \bar{E}_{DF}(\theta_{Lab}) \rangle$ for DF = vibrational (all normal modes) + rotational¹⁰. Quantitatively, SLEND/6-311 $\langle \Delta \bar{E}_{Vib + Rot}(\theta_{Lab}) \rangle$ agrees well with its experimental counterpart at low scattering angles, $0^\circ < \theta_{Lab} < 3.5^\circ$, but becomes somewhat overestimated at higher scattering angles, $3.5^\circ < \theta_{Lab} < 12^\circ$. Interestingly, SLEND/6-311 $\langle \Delta \bar{E}_{00v_3^f}(\theta_{Lab}) \rangle$ tends to coincide with the experimental $\langle \Delta \bar{E}_{Vib + Rot}(\theta_{Lab}) \rangle$ at medium and high scattering angles. In any case, SLEND/6-311 $\langle \Delta \bar{E}_{Vib + Rot}(\theta_{Lab}) \rangle$ is qualitatively correct because it reproduces the nearly monotonic increase of its experimental counterpart with respect to θ_{Lab} — all other SLEND/6-311 $\langle \Delta \bar{E}_{DF}(\theta_{Lab}) \rangle$ exhibit the same monotonic pattern. It is worth noticing that the asymmetric stretch normal mode $00v_3^f$ gets much more excited by collision than the other two types: $\langle \Delta \bar{E}_{00v_3^f}(\theta_{Lab}) \rangle = \langle \Delta \bar{E}_{v_1^f 00}(\theta_{Lab}) \rangle \approx \langle \Delta \bar{E}_{0v_2^f 0}(\theta_{Lab}) \rangle \forall \theta_{Lab}$. These relative excitations

might result from symmetry properties and constraints that regulate the dynamics. Also noteworthy, SLEND/6-311 rotational excitation $\langle \Delta \bar{E}_{Rot}(\theta_{Lab}) \rangle$ is very low $\forall \theta_{Lab}$ and lies within the experimentally inferred range of $\langle \Delta \bar{E}_{Rot}(\theta_{Lab}) \rangle$ 12-18 meV¹⁰. SLEND/6-311 $\langle \Delta \bar{E}_{Vib+Rot}(\theta_{Lab}) \rangle$ and $\langle \Delta \bar{E}_{Rot}(\theta_{Lab}) \rangle$ together suggest that SLEND accurately reproduces the final rotational energy of CO₂ $\forall \theta_{Lab}$ but somewhat overestimates the vibrational energy at $\theta_{Lab} > 3.5^\circ$. The latter energy affects the accuracy of state-to-state vibrational properties calculated with Eq. (9); nevertheless, the SLEND/6-311 vibrational energy leads to accurate state-to-state vibrational DCSs and vibrational proton energy spectra as will be shown in Sects. 4.4 and 4.5, respectively. Eqs. (14) and (15) for $\langle \Delta \bar{E}_{DF}(\theta_{Lab}) \rangle$ are based on classical-mechanics scattering theory. For that reason, SLEND/6-311 $\langle \Delta \bar{E}_{DF}(\theta_{Lab}) \rangle$ displays singularity peaks in Fig. 4 (e.g., the peaks at $\theta_{Lab} \approx 4^\circ$ and 6°); these peaks correspond to classical-mechanics rainbow scattering angles that, as quantum scattering theory proves, have lower values than their quantum-mechanics counterparts in Fig. 3³⁶.

4.4 State-to-State Vibrational Differential Cross Sections:

State-to-state vibrational DCSs are key properties to characterize the investigated scattering system; these properties are more challenging to calculate than the unresolved total DCSs in Sect. 4.2. The current DCSs are calculated with Eq. (11) for $d\sigma_{(\alpha,\beta,\gamma)}^{i \rightarrow f}(\theta_{CM})/d\Omega$ by setting $i \rightarrow f = v_1^i v_2^i v_3^i = 000 \rightarrow v_1^f v_2^f v_3^f$ and $T_{(\alpha,\beta,\gamma)}^{i \rightarrow f}(l)$ as

$$T_{(\alpha,\beta,\gamma)}^{000 \rightarrow v_1^f v_2^f v_3^f}(l = k_i b) = \sqrt{\prod_{j=1}^3 P_j(v_j^f)} \exp[i2\eta_{(\alpha,\beta,\gamma)}(l = k_i b)], \quad (16)$$

where the Poisson probabilities per normal mode $P_j(v_j^f)$ are given in Eq. (9); like previous properties, the finally reported DCSs $d\bar{\sigma}_{SLEND}^{000 \rightarrow v_1^f v_2^f v_3^f}(\theta_{Lab})/d\Omega$ are averages of the CM DCSs from Eqs. (11) and (16) over the initial projectile-target orientations (α, β, γ) and expressed in the laboratory frame. Fig. 5 plots available experimental state-to-state vibrational DCSs¹¹ and their SLEND/6-311 counterparts, $d\bar{\sigma}_{SLEND}^{000 \rightarrow v_1^f v_2^f v_3^f}(\theta_{Lab})/d\Omega$, for the CO₂ final vibrational states $v_1^f v_2^f v_3^f = 000, 001, 002$ and 003 as a function of the scattering angle θ_{Lab} and at $E_{Lab} = 29.5$ eV. Insofar as the sparse experimental data points permit discerning¹¹, Fig. 5 indicates that SLEND/6-311 DCSs agree reasonably well with their experimental counterparts for $v_1^f v_2^f v_3^f = 000 - 002$ and less satisfactorily for $v_1^f v_2^f v_3^f = 003$. Notice that SLEND/6-311 DCSs fall within the available experimental error bars or slightly outside. In addition, both experimental and SLEND/6-311 DCSs show primary rainbow scattering angles structures with a rainbow peak at $\theta_{Lab}^{PR} = 9^\circ$ for all the considered final states $v_1^f v_2^f v_3^f$.

4.5 Vibrational Proton Energy Loss Spectra:

The most important and challenging property to predict for the studied scattering system is its vibrational proton energy loss spectra $\langle \bar{P}_{000} \rightarrow v_1^f v_2^f v_3^f(\theta_{Lab}) \rangle$. This proton-induced spectroscopy on CO₂ resembles infrared photon spectroscopy. Vibrational proton energy loss spectra $\langle P_{000} \rightarrow v_1^f v_2^f v_3^f(\theta_{Lab}) \rangle_{(\alpha, \beta, \gamma)}$ from the initial projectile-target orientation (α, β, γ) are calculated similar to the average energies $\langle E_{DF}(\theta_{Lab}) \rangle_{(\alpha, \beta, \gamma)}$ with Eqs. (14)–(15):

$$\langle P_{000} \rightarrow v_1^f v_2^f v_3^f(\theta_{Lab}) \rangle_{(\alpha, \beta, \gamma)} = \frac{\sum_{i=m}^N \left[\frac{d\sigma(\theta_{Lab})}{d\Omega} \prod_{j=1}^3 P_j(v_j^f) \right]_m}{\sum_{m=i}^N \left[\frac{d\sigma(\theta_{Lab})}{d\Omega} \right]_m} \Bigg|_{(\alpha, \beta, \gamma)} ; \quad (17)$$

where the Poisson probabilities per normal modes $P_j(v_j^f)$ are given in Eq. (9) and the remaining terms are defined just after Eqs. (14)–(15). Like previous properties, the reported spectra $\langle \bar{P}_{000} \rightarrow v_1^f v_2^f v_3^f(\theta_{Lab}) \rangle$ are averages of the corresponding $\langle P_{000} \rightarrow v_1^f v_2^f v_3^f(\theta_{Lab}) \rangle_{(\alpha, \beta, \gamma)}$ over initial projectile-target orientation (α, β, γ) . Fig. 6 displays the available experimental^{10, 11} and SLEND/6-311 $\langle \bar{P}_{000} \rightarrow v_1^f v_2^f v_3^f(\theta_{Lab}) \rangle$, as a function of the H⁺ energy loss, for various final vibrational states $v_1^f v_2^f v_3^f$ of CO₂. and for some combinations of collision energies/scattering angles: $E_{Lab} = 30$ eV/ $\theta_{Lab} = 3, 6, 9, 12^\circ$ and $E_{Lab} = 29.5$ eV/ $\theta_{Lab} = 7, 10^\circ$. Experimental spectra lines were originally reported in arbitrary units^{10, 11}; then, to allow comparisons in Fig. 6, the relative experimental lines were normalized to match the absolute SLEND lines for $v_1^f v_2^f v_3^f = 000$ at each considered collision energy/scattering angle. Fig. 6 shows that the agreement between experimental and SLEND/6-311 spectra is excellent regarding both the positions and intensities of the lines at all the considered collision energies and scattering angles. Results in Fig. 6 conclusively demonstrate the accuracy of SLEND/CSQRP to reproduce state-to-state vibrational properties in scattering processes.

5. Conclusions and Future Research

The SLEND/CSQRP method^{22–25} has been applied to the scattering system $H^+ + CO_2(v_1^i v_2^i v_3^i = 000) \rightarrow H^+ + CO_2(v_1^f v_2^f v_3^f)$ at collision energies $E_{Lab} = 20.5, 29.5$ and 30 eV in comparison with available experimental results^{10–12}. The investigated system is relevant in astrophysics, planetary atmospheric chemistry and proton cancer therapy (PCT)^{1–3}. SLEND describes nuclei with frozen Gaussian wave packets in their zero-width limit and electrons with a single-determinantal wave function^{22–24}. The SLEND nuclear dynamics is classical; therefore, the CSQRP^{22–25} with the canonical CS has been utilized to reconstruct quantum state-to-state vibrational properties from the classical nuclear dynamics. The theoretical challenge herein posed to SLEND/CSQRP is to describe a system with a target molecule, CO₂, which has more than one normal mode of vibration. Overall, the calculated SLEND/CSQRP properties agree well with their experimental

counterparts^{10–12}. SLEND total DCSs for $\text{H}^+ + \text{CO}_2(v_1^i v_2^i v_3^i = 000) \rightarrow \text{H}^+ + \text{CO}_2(v_1^f v_2^f v_3^f = \text{all})$ agree very well with the available experimental results at $E_{\text{Lab}} = 20.5^{12}$ and 30 eV^{10} . This good SLEND agreement includes the correct prediction of rainbow scattering structures and of the specific values of primary and secondary rainbow scattering angles from the DCSs. At $E_{\text{Lab}} = 30 \text{ eV}$, all SLEND averaged target excitation energies $\langle \Delta \bar{E}_{DF}(\theta_{\text{Lab}}) \rangle$ for various final internal degrees of freedom (DFs) of CO_2 exhibit a nearly monotonic increase as a function of the scattering angle θ_{Lab} . SLEND $\langle \Delta \bar{E}_{\text{Rot}}(\theta_{\text{Lab}}) \rangle$ agrees well with its experimentally inferred counterpart and reveals that the collision-induced rotational excitation is low. SLEND $\langle \Delta \bar{E}_{DF}(\theta_{\text{Lab}}) \rangle$ for the vibrational normal modes show that the asymmetric stretch mode of CO_2 gets much more excited by H^+ collision than the symmetric stretch and bending modes. The only available experimental data for $\langle \Delta \bar{E}_{DF}(\theta_{\text{Lab}}) \rangle$ is for DF = vibrational (all normal modes) + rotational; SLEND $\langle \Delta \bar{E}_{\text{Vib} + \text{Rot}}(\theta_{\text{Lab}}) \rangle$ agrees well with its experimental counterpart at low scattering angles, $0^\circ < \theta_{\text{Lab}} < 3.5^\circ$, but becomes overestimated at higher scattering angles, $3.5^\circ < \theta_{\text{Lab}} < 12^\circ$; however, qualitatively, SLEND $\langle \Delta \bar{E}_{\text{Vib} + \text{Rot}}(\theta_{\text{Lab}}) \rangle$ correctly reproduces the nearly monotonic increase of its experimental counterpart as a function of the scattering angle. Despite vibrational energy overestimation, all the SLEND state-to-state vibrational properties calculated with the SLEND vibrational energy agree mostly well with experimental data. Insofar as the sparse experimental data points permit discerning¹¹, SLEND/CSQRP state-to-state vibrational DCSs of $\text{H}^+ + \text{CO}_2(v_1^i v_2^i v_3^i = 000) \rightarrow \text{H}^+ + \text{CO}_2(v_1^f v_2^f v_3^f)$ agree reasonably well with their experimental counterparts¹¹ for $v_1^f v_2^f v_3^f = 000 - 002$ and only less satisfactorily for $v_1^f v_2^f v_3^f = 003$. These SLEND/CSQRP DCSs fall within the available experimental error bars or slightly outside¹¹. In addition, SLEND/CSQRP DCSs correctly reproduce the experimental rainbow scattering structures and the values of the primary rainbow angles. Finally, SLEND/CSQRP vibrational proton energy loss spectra agrees remarkably well with its experimental counterparts^{10, 11} for various final vibrational states of CO_2 and at various collision energies and scattering angles; this excellent agreement is in both the positions and intensities of the spectral lines. The present results persuasively demonstrate the accuracy of SLEND/CSQRP to predict state-to-state vibrational properties in scattering systems with multiple normal modes. Further applications of SLEND/CSQRP will be conducted with larger scattering systems relevant in astrophysics, planetary atmospheric chemistry and PCT research.

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Fig. 1:
 $\text{H}^+ + \text{CO}_2$ reactants initial conditions; red, black and gray spheres represent O, C and H classical nuclei; the H^+ projectile has impact parameter b and projectile-target orientation ($\alpha\beta\gamma$).

Fig. 2:
Four sequential snapshots of a SLEND/6-311G simulation of $\text{H}^+ + \text{CO}_2$ at collision energy = 30 eV and from impact parameter = 1.8 a.u. and initial projectile-target orientation (0° , 45° , 0°). Simulation times are in femtoseconds.

Fig. 3:
Experimental and SLEND/6-311G total differential cross sections of $\text{H}^+ + \text{CO}_2$ vs. H^+ scattering angle at collision energies = 20.5^{12} and 30 eV^{10} .

Fig. 4:
Experimental¹⁰ and SLEND/6-311G averaged target excitation energy of $\text{H}^+ + \text{CO}_2$ for various final degrees of freedom of CO_2 vs. H^+ scattering angle and at collision energy = 30 eV.

Fig. 5: Experimental¹¹ and SLEND/6-311G state-to-state vibrational differential cross sections of $\text{H}^+ + \text{CO}_2$ from CO_2 initial vibrational state 000 to final vibrational states 00 v_3 (v_3 = asymmetric stretch mode, cf. Table I). Data plotted vs. H^+ scattering angle and at collision energy = 29.5 eV.

Fig. 6: Experimental^{10, 11} and SLEND/6-311G vibrational proton energy loss spectra of $\text{H}^+ + \text{CO}_2$ from CO_2 in initial state 000 (cf. Table I for normal modes notation) and in final vibrational states $v_1^f v_2^f v_3^f$. Data at collision energies = 29.5 and 30 eV and for various H^+ scattering angles.

Table I:

Comparison of the normal modes frequencies of CO₂ from experiments and from Hartree-Fock calculations with four Pople 6-31(1)G basis sets, ν_1 = single-degenerate symmetric stretch, ν_2 = double-degenerate bending, and ν_3 = single-degenerate asymmetric stretch frequencies, respectively. Deviations and total root mean squares (RMSs) of the calculated frequencies with respect to the experimental ones are also listed.

Basis set	ν_1 (cm ⁻¹)	ν_2 (cm ⁻¹)	ν_3 (cm ⁻¹)	RMS
Experiment	1333	667	2349	-
6-31G	1407.59 (+74.59)	656.56 (-10.44)	2374.90 (+25.90)	45.98
6-31G**	1518.61 (+185.61)	745.81 (+78.81)	2585.32 (+236.32)	179.36
6-31++G	1401.01 (+68.01)	596.44 (-70.56)	2356.12 (+7.12)	56.73
6-311G	1397.96 (+64.96)	648.63 (-18.37)	2338.38 (-10.62)	39.45