Nonadiabatic phenomena in molecular vibrational polaritons

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Abstract

Nonadiabatic phenomena are investigated in the rovibrational motion of molecules confined in an infrared cavity. Conical intersections (CIs) between vibrational polaritons, similar to CIs between electronic polaritonic surfaces, are found. The spectral, topological, and dynamic properties of the vibrational polaritons show clear fingerprints of nonadiabatic couplings between molecular vibration, rotation and the cavity photonic mode. Furthermore, it is found that for the investigated system, composed of two rovibrating HCl molecules and the cavity mode, breaking the molecular permutational symmetry, by changing $^{35}\text{Cl}$ to $^{37}\text{Cl}$ in one of the HCl molecules, the polaritonic surfaces, nonadiabatic couplings, and related spectral, topological, and dynamic properties can deviate substantially. This implies that the natural occurrence of different molecular isotopologues needs to be considered when modeling realistic polaritonic systems.

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I. INTRODUCTION

Cavity quantum electrodynamics (CQED) deals with the interaction of matter with a quantized light field enclosed in a cavity [42, 61]. Experimental and theoretical studies have revealed that the quantum nature of the light can significantly modify the different chemical, physical or energetic properties of material structures [1, 6–12, 14–20, 24–27, 29, 30, 32–34, 37, 39, 40, 44, 46, 48, 49, 52, 54–59]. Most of the works consider only a single confined photonic mode in an optical or plasmonic cavity which can strongly interact with atoms, molecules or nano materials. The strong coupling regime is reached when the light–matter coupling is stronger than the loss of the cavity mode and the decay rates in the matter. In the case of molecules, the confined photonic mode of the cavity can efficiently couple both electronic or vibrational states, depending on the cavity mode wavelength. In the first situation the different electronic molecular states mix with the UV–visible cavity photon forming hybrid light–matter, so-called electronic or vibronic polariton states carrying both characters of matter and light. Several experimental [15, 29] and theoretical [8, 9, 11, 16–20, 24, 26, 32, 33, 37, 39, 46, 48, 49, 52, 56, 57] studies have demonstrated that this phenomenon gives rise to a variety of interesting effects such as modification of the chemical landscapes [15, 18, 29, 46], cavity-induced nonadiabatic phenomena [8, 9, 11, 16–20, 32, 33, 48, 52, 56, 57], or controlling photochemistry [19, 20, 32, 33, 37, 39].

Recently efforts have been made to study the vibrational strong coupling (VSC) within one molecular electronic state [6, 12, 27, 30, 34, 44, 47]. In this regime experiments focus on the cavity-induced manipulation of chemical reactions in the ground electronic state or studying the effects of vibrational polaritons in solid and liquid phase inside infrared Fabry–Pérot cavities [1, 7, 14, 54, 55, 58, 59]. The presence of the vibrational strong coupling may lead to the suppression or enhancement of reactive pathways for molecules even in the absence of external photon pumping, implying that they involve thermally activated processes [6, 30, 54, 59].

In the present work we extend the theoretical approach by incorporating the effect of molecular rotation with vibrational polaritons. We employ realistic and highly-accurate molecular models, based on accurate quantum chemical and variational nuclear motion computations. This allows for a high-resolution insight into the formation, the spectroscopy and the dynamics of rovibrational polaritons, including cavity photon-mediated energy transfer.
between the different types of molecules. Because utilizing microfluidic cavities allows for
the experimental realization of vibrational polaritons in the liquid phase, and because gas
phase molecular polaritons are likely to be investigated eventually, special emphasis is given
to the role of molecular rotations. The coupling strength between the cavity mode and
the vibrational transition of the molecule naturally depends on the spatial orientation of
the molecule. If molecular rotation is feasible, such as in the liquid or gas phase, then a
simple averaging over different orientations is in principle erroneous, because the orientation
dependent coupling strength couples the rotational degrees of freedom with the vibrational
ones. Such couplings give rise to nonadiabatic effects [3, 4, 13, 31, 62, 63] or in some cases
to the formation of light-induced conical intersections (LICIs) [22, 23, 43], which can have
a significant impact on the polaritonic properties [8, 52].

We introduce the concept of vibrational potential energy surfaces, on which rotational
dynamics proceed, and show the impact of the cavity-induced nonadiabatic coupling – be-
tween rotations and vibrations – on spectroscopic, dynamical and topological properties of
molecules. Our showcase system is a mixture of H\textsuperscript{35}Cl and H\textsuperscript{37}Cl molecules interacting with
a photonic mode.

II. THEORETICAL APPROACH

A. Rovibrational polaritons

The hamiltonian of rotating-vibrating molecules interacting with a single lossless cavity
mode can be written in the dipole approximation as

\[
\hat{H} = \sum_{i=1}^{N_{\text{mol}}} (\hat{H}_{m}^{(i)} - \hat{E}_{c}\hat{\mu}^{(i)}) + \hat{H}_{c} = \sum_{i=1}^{N_{\text{mol}}} \left( \hat{H}_{m}^{(i)} - \sqrt{\frac{\hbar\omega_c}{\varepsilon_0 V}} e_{\mu}^{(i)} (\hat{a}_{c}^{\dagger} + \hat{a}_{c}) \right) + \hbar\omega_{c} \hat{a}_{c}^{\dagger} \hat{a}_{c}. \tag{1}
\]

where \(\hat{H}_{m}^{(i)}\) is the \(i\)th field-free molecular rovibrational Hamiltonian, \(\hat{a}_{c}^{\dagger}\) and \(\hat{a}_{c}\) are photon
creation and annihilation operators, respectively, \(\omega_{c}\) is the frequency of the cavity mode,
\(\hbar\) is Planck’s constant divided by \(2\pi\), \(\varepsilon_0\) is the electric constant, \(V\) is the volume of the
electromagnetic mode, \(e\) is the polarization vector of the cavity mode, and \(\hat{\mu}^{(i)}\) is the dipole
moment of the \(i\)th molecule.
We assume the cavity electric field to be polarized along the lab-fixed z-axis, \( \mathbf{e} = (0, 0, 1) \), and we consider an IR cavity, which allows restricting the molecular model to a single electronic state. Then, the direct-product functions, also called diabatic states, provide a complete basis, where the field-free rovibrational eigenstates satisfy
\[
\hat{H}_m^{(i)} | \Psi_{\text{rovib}}^{i,n,J,M} \rangle = E_{\text{rovib}}^{(i),n_J} | \Psi_{\text{rovib}}^{i,n,J,M} \rangle, \tag{3}
\]
\( J \) and \( M \) are the rotational angular momentum and its projection onto the space-fixed z-axis, respectively, \( n \) is all other quantum numbers uniquely defining the rovibrational states, and \( | N \rangle \) is a photon number state of the cavity radiation. The matrix representation of Eq. (1) using the basis of Eq. (2) gives matrix elements of the following form:
\[
\left( \langle N | \prod_{i=1}^{N_{\text{mol}}} \langle \Psi_{\text{rovib}}^{i,n_i,J_i,M_i} | \right) \hat{H} \left( \prod_{j=1}^{N_{\text{mol}}} | \Psi_{\text{rovib}}^{j,n'_j,J'_j,M'_j} \rangle \right) = \sum_{i=1}^{N_{\text{mol}}} \left[ E_{\text{rovib}}^{(i),n_J} \delta_{n_i,n'_i} \delta_{J_i,J'_i} \delta_{M_i,M'_i} \delta_{NN'} - \sqrt{\frac{\hbar \omega_c}{\epsilon_0 V}} \langle \Psi_{\text{rovib}}^{i,n_i,J_i,M_i} | \mathbf{e} \mu^{(i)} | \Psi_{\text{rovib}}^{i,n'_j,J'_j,M'_j} \rangle \langle N | (\hat{a}_c^\dagger + \hat{a}_c) | N' \rangle \right] \times \prod_{j \neq i} \delta_{n_j,n'_j} \delta_{J_j,J'_j} \delta_{M_j,M'_j} + \hbar \omega_c (N + 1/2) \delta_{NN'} \prod_{j} \delta_{n_j,n'_j} \delta_{J_j,J'_j} \delta_{M_j,M'_j}. \tag{4}
\]
For a diatomic molecule \( n \) can be identified with the single vibrational quantum number \( v \), and using the notation \( | \Psi_{\text{rovib}}^{i,n,J,M} \rangle \equiv | v_i J_i M_i \rangle \), Eq. (4) takes the form
\[
\left( \langle N | \prod_{i=1}^{N_{\text{mol}}} \langle v_i J_i M_i | \right) \hat{H} \left( \prod_{j=1}^{N_{\text{mol}}} | v'_j J'_j M'_j \rangle \right) = \sum_{i=1}^{N_{\text{mol}}} \delta_{M_i,M'_i} \left[ E_{\text{rovib}}^{(i),v_i^J} \delta_{v_i,v'_i} \delta_{J_i,J'_i} \delta_{NN'} - \sqrt{\frac{\hbar \omega_c}{\epsilon_0 V}} \langle v_i | \mu^{(i)} (R_i) | v'_i \rangle \langle J_i M_i | \cos(\theta_i) | J'_i M_i \rangle \times \right. \tag{5}
\left. \left( \sqrt{N} \delta_{NN'+1} + \sqrt{N+1} \delta_{NN'-1} \right) \right] \prod_{j \neq i} \delta_{v_j,v'_j} \delta_{J_j,J'_j} \delta_{M_j,M'_j} + \hbar \omega_c \delta_{NN'} \prod_{j} \delta_{v_j,v'_j} \delta_{J_j,J'_j} \delta_{M_j,M'_j},
\]
where \( \mu^{(i)}(R_i) \) is the permanent dipole moment as a function of the internuclear distance \( R_i \), \( \theta_i \) is the angle between the space-fixed z axis and the \( i \)th molecule, and the energy scale was set so that the zero point energy of the photonic mode, \( \hbar \omega_c/2 \), is omitted.
The rovibrational polaritonic states are the eigenstates of the Hamiltonian of Eq. (1). The \( k \)th polariton can be written as

\[
|\Psi^k_{\text{pol}}\rangle = \sum_{N, v_i, J_i, M_i} C^k_{N, v_i, J_i, M_i} \prod_j (v_j, J_j, M_j) |N\rangle,
\]

where \( C^k_{N, v_i, J_i, M_i} \) are the coefficients of the \( k \)th eigenvector of the matrix having the elements given in Eq. (5).

### B. Computational details

The field-free rovibrational energies of the \( \text{H}^{35}\text{Cl} \) and \( \text{H}^{37}\text{Cl} \) molecules were computed as

\[
E_{\text{rovib}}(i, v_i J_i) = E_{\text{vib}}(i, v_i) + B_v(i) J(J+1),
\]

where the \( E_{\text{vib}}(i, v_i) \) vibrational energies were obtained from converged variational computations utilizing the spherical-DVR discrete variable representation (DVR) [50] and the potential energy curve (PEC) of Ref. [38]. The \( B_v \) rotational constants (given in energy units) were evaluated for each vibrational state as

\[
B_v(i) = \langle v_i | \frac{\hbar^2}{2m_{\text{red}}^i} R^2 | v_i \rangle,
\]

where \( m_{\text{red}}^i \) is the reduced vibrational mass of the \( i \)th molecule.

The nuclear masses used in the computations were \( m_{\text{H}} = 1.00784 \) u, \( m_{\text{35Cl}} = 34.9689 \) u, and \( m_{\text{37Cl}} = 36.9659 \) u.

For computing the \( \langle v_i | \mu(i)(R) | v_i' \rangle \) vibrational (transition) dipole elements, the dipole moment curve of Ref. [66] was used. The \( \langle J_i M_i | \cos(\theta) | J_i' M_i \rangle \) terms were evaluated using an expression involving 3-j symbols,

\[
\langle J M | \cos(\theta) | J' M' \rangle = \sqrt{(2J+1)(2J'+1)(-1)^{J+1}} \left( \begin{array}{c} J & 1 & J' \\ M & 0 & -M' \end{array} \right) \left( \begin{array}{c} J & 1 & J' \\ 0 & 0 & 0 \end{array} \right),
\]

which can be derived using the relations \( \langle \phi, \theta | J M \rangle = Y_{J M}(\phi, \theta) = D_{M0}^{J+1}(\phi, \theta, \chi), \)

\begin{align*}
\cos(\theta) &= D_{00}^{J1}(\phi, \theta, \chi), \\
\int D_{K_1 M_1}^{J_1}(\Omega) D_{K_2 M_2}^{J_2}(\Omega) D_{K_3 M_3}^{J_3}(\Omega) d\Omega &= 8\pi \left( \begin{array}{c} J_1 & J_2 & J_3 \\ K_1 & K_2 & K_3 \end{array} \right) \left( \begin{array}{c} J_1 & J_2 & J_3 \\ M_1 & M_2 & M_3 \end{array} \right),
\end{align*}

[64], where \( D_{K M}^{J}(\Omega) \) is the Wigner D-matrix and \( \Omega \) represents the three Euler angles \( \phi, \theta, \) and \( \chi \).

### III. RESULTS AND DISCUSSION

#### A. Vibrational polaritonic energy surfaces (VPES)

For understanding the underlying physics, it is useful to construct the matrix representation of the Hamiltonian in Eq. (1) using vibrational-photonic basis functions.
\[ |N\rangle \prod_{i=1}^{N_{\text{mol}}} |\Psi_{\text{vib}}^{i}\rangle. \] The matrix elements of the resulting vibro-photonic Hamiltonian depend on the \( \theta \) rotational coordinates. After removing the rotational kinetic energy terms, the eigenvalues of the vibro-photonic Hamiltonian form vibrational polaritonic energy surfaces (VPES), which are functions of the \( N_{\text{mol}} \) rotational coordinates. Note the analogy that the VPESs provide effective potential energy surfaces (PES) for the rotational motion the same way as the usual light-dressed electronic potentials provide effective PESs for vibrational motion in polyatomics.

For two diatomic molecules (denoted as molecule 1 and 2, respectively) coupled to a single IR cavity mode, the first \( 4 \times 4 \) block in the vibro-photonic Hamiltonian reads

\[
H_{4 \times 4} = T_{\text{rot}} + V_{\text{rot}},
\]

where

\[
T_{\text{rot}} = 
\begin{bmatrix}
B^{(1)}_0 \hat{T}^{(1)}_{\text{rot}} + B^{(2)}_0 \hat{T}^{(2)}_{\text{rot}} & 0 & 0 & 0 \\
0 & B^{(1)}_0 \hat{T}^{(1)}_{\text{rot}} + B^{(2)}_0 \hat{T}^{(2)}_{\text{rot}} & 0 & 0 \\
0 & 0 & B^{(1)}_0 \hat{T}^{(1)}_{\text{rot}} + B^{(2)}_0 \hat{T}^{(2)}_{\text{rot}} & 0 \\
0 & 0 & 0 & B^{(1)}_0 \hat{T}^{(1)}_{\text{rot}} + B^{(2)}_0 \hat{T}^{(2)}_{\text{rot}}
\end{bmatrix},
\]

\[
V_{\text{rot}} = 
\begin{bmatrix}
E_{\text{vib}}^{(1),0} + E_{\text{vib}}^{(2),0} & 0 & 0 & 0 \\
0 & E_{\text{vib}}^{(1),0} + E_{\text{vib}}^{(2),0} + \hbar \omega_c & 0 & 0 \\
0 & 0 & E_{\text{vib}}^{(1),1} + E_{\text{vib}}^{(2),0} & 0 \\
0 & 0 & 0 & E_{\text{vib}}^{(1),0} + E_{\text{vib}}^{(2),1}
\end{bmatrix} - \sqrt{\hbar \omega_c / (\varepsilon_0 V)} \times
\]

\[
\begin{bmatrix}
\mu^{(1)}_{00} \cos(\theta_1) + \mu^{(2)}_{00} \cos(\theta_2) & 0 & 0 & 0 \\
0 & \mu^{(1)}_{00} \cos(\theta_1) + \mu^{(2)}_{00} \cos(\theta_2) & \mu^{(1)}_{01} \cos(\theta_1) & \mu^{(2)}_{01} \cos(\theta_2) \\
0 & \mu^{(1)}_{10} \cos(\theta_1) & \mu^{(1)}_{11} \cos(\theta_1) + \mu^{(2)}_{10} \cos(\theta_2) & 0 \\
0 & \mu^{(2)}_{10} \cos(\theta_2) & 0 & \mu^{(1)}_{00} \cos(\theta_1) + \mu^{(2)}_{11} \cos(\theta_2)
\end{bmatrix},
\]

where \( \mu^{(i)}_{kl} = \langle v_i = k | \mu^{(i)}(R) | v_i = l \rangle \), \( \hat{T}^{(i)}_{\text{rot}} \) is the squared rotational angular momentum of the \( i \)th molecule, and \( B^{(i)}_v \) is the rotational constant of the \( i \)th molecule in its \( v \)th vibrational state. For the specific case of a H\textsuperscript{35}Cl and a H\textsuperscript{37}Cl molecule, Figure 1 show the three largest eigenvalues of the \( V_{\text{rot}} \) matrix in Eq. (10) as a function of the \( \theta_i \) variables for \( g \equiv \sqrt{\hbar \omega_c / (\varepsilon_0 V)} = 0.001 / \sqrt{2} \). Because the \( \mu^{(i)}_{00} \) and \( \mu^{(i)}_{11} \) dipole expectation values are
nearly identical for the two molecules and are much larger than the \( \mu_{01}^{(i)} = \mu_{10}^{(i)} \) transition elements, it is worth plotting the VPESs by omitting the diagonal dipole terms to obtain more transparent figures. These are shown in Figures 2 and 3 for the cases of a \( \text{H}^{35}\text{Cl} \) and a \( \text{H}^{37}\text{Cl} \) molecule or two identical \( \text{H}^{35}\text{Cl} \) molecules, respectively. Fig. 2 demonstrates that in the case of the two different isotopologues, three bright polaritons are formed, as expected \([28, 53]\), and conical intersections (CI) can be formed between the VPESs. In the case of two identical \( \text{H}^{35}\text{Cl} \) molecules, Fig. 3 shows that two bright and a dark polariton is formed, and the upper (lower) VPES touches the dark state for red (blue) shifted cavity wave lengths.

B. Topological properties

A well-known consequence of CIs or LICIs between adiabatic electronic PESs is that the electronic wave functions of the connected surfaces become double valued, i.e., propagating the electronic wave function of a single surface along a closed curve around the CI leads to the accumulation of a topological phase of \( \pi \) \([5, 21, 22, 35, 36, 41]\). In order to verify that the LICIs between VPESs are indeed true LICIs (and to confirm the existence of LICIs between VPESs even when the diagonal dipole terms are not omitted from the VPESs), the numerical verification of the topological phases was carried out. Now, we borrow a well-established framework developed for natural nonadiabatic phenomena, which was successfully applied to study the topological properties of “natural” electronic degeneracies \([2–4, 60]\).

Let us start from the adiabatic-to-diabatic transformation (ADT)

\[
W = A^\dagger VA
\]  

(11)

where \( W \) and \( V \) denote the diabatic and adiabatic PES, respectively. \( A \) is a unitary matrix called ADT matrix, which can be obtained by solving the equation

\[
\nabla A + \tau A = 0.
\]

(12)

Its solution can be written in the following form

\[
A(s) = \gamma \exp \left( - \int_{s_0}^{s} \tau(s) \, ds \right) A(s_0)
\]

(13)

where \( \gamma \) is a path ordering operator and \( \tau(s) \) is the nonadiabatic coupling matrix which contains the nonadiabatic coupling terms (NAC)s

\[
\tau_{i,j} = <\Psi_i | \nabla | \Psi_j >.
\]

(14)
Here $\Psi_i$ and $\Psi_j$ are $ith$ and $jth$ adiabatic vibrational wave functions, respectively and $\nabla$ is the gradient operator corresponding to the rotational coordinates.

The necessary condition for the $A$-matrix to yield single-valued diabatic wave function is that the $D$-matrix,

$$D(\Gamma) = \gamma \exp \left( - \oint_{\Gamma} \tau \, ds \right)$$  \hspace{1cm} (15)

needs to be diagonal and has, in its diagonal, numbers of $(+1)$s or $(-1)$s. The number of $(-1)$s in the $D$ is designated as $K$ which is the number of the adiabatic vibrational eigenfunctions that flip their sign. The $D$-matrix is the topological matrix which contains all topological features of a vibrational manifold in a region surrounded by its contour $\Gamma$ and $K$ is the topological number. The positions of the $(-1)$s in the $D$-matrix correspond with the vibrational eigenfunctions that flip their sign. The equation for $D(\Gamma)$ is a kind of quantization condition to be fulfilled by the nonadiabatic coupling matrix $\tau$ along any closed contour $\Gamma$ in configuration space (CP).

In case of two quasi-isolated adiabatic states $(j, j + 1)$ the quantization condition reads:

$$\alpha_{j,j+1}(\Gamma) = \oint_{\Gamma} \tau_{j,j+1}(s|\Gamma) \, ds = n_j \pi$$  \hspace{1cm} (16)

where $\alpha_{j,j+1}(\Gamma)$ is the topological phase. When the closed contour $\Gamma$ is a circle with radii $q$:

$$\alpha_{j,j+1}(q) = \int_0^{2\pi} \tau_{j,j+1}(\varphi|q) \, d\varphi.$$  \hspace{1cm} (17)

The adiabatic-to-diabatic transformation angle can be defined as:

$$\gamma_{j,j+1}(\varphi|q) = \int_0^\varphi \tau_{\varphi,j+1}(\varphi|q) \, d\varphi.$$  \hspace{1cm} (18)

In the related numerical calculations of this study we concentrate on LICIs between the lower and middle as well as the middle and upper vibrational polaritonic states (see Figs. 2 and 3). In Figure 2 these are the two (1,2) and two (2,3) LICIs, corresponding to the three bright states, which are formed for the “$\text{H}^{35}\text{Cl} + \text{H}^{37}\text{Cl} + \text{IR cavity mode}$” system. These are “true” LICIs, i.e., first-order degeneracy points, as the two HCl molecules are distinguishable. However, for the two indistinguishable confined $\text{H}^{35}\text{Cl}$ molecules, only a second-order degeneracy point is formed, as demonstrated in Fig. 3.

In Fig. 4 we report on results for the “$\text{H}^{35}\text{Cl} + \text{H}^{37}\text{Cl} + \text{IR cavity mode}$” system. At first we calculated the $\tau_{1,2}$ along a circle located at the (1,2)LICI point. In Fig. 4 panel A the related ADT angle $\gamma_{1,2}$ and the corresponding topological phase $\alpha_{1,2} = -1.0169\pi$ are shown.
Similar quantities are presented for the (2,3)LICI in panel B. Here we obtain $\alpha_{2,3} = 1.0077\pi$. It is well noticed that both $\alpha_{1,2}$ and $\alpha_{2,3}$ are close to $\pi$ as expected. This means that there is only one (1,2)LICI and one (2,3)LICI in the studied CS region of panel A and B, respectively, and the two-state approximation works well. In panel C the closed contour, in contrast to the two previous ones, surrounds two LICI points. The calculated $\alpha_{1,2} = -1.1227\pi$ and $\alpha_{2,3} = -0.3436\pi$ topological phases are far from being close to $\pi$, indicating that the two-state approximation fails to describe accurately the topological behavior. The third state is needed to be involved in the calculations for the proper topological description. In order to derive the three-state ADT matrix elements and the corresponding $D$ matrix one has to calculate all off-diagonal matrix elements of the $\tau(s)$ NAC matrix and then apply Eqs. [13] and [15]. On panel D of Fig. 4 the values for the $D$ matrix elements are presented for the closed curve indicated as an inset in the panel. The values of the diagonal elements $(-1,+1,-1)$ clearly imply that the distribution contains an odd number (presumably one) of LICI for each type (1,2)LICI and (2,3)LICI. Therefore, the first and third vibrational wave functions change their sign while the sign of the second vibrational wave function remains unchanged after flipping its sign twice.

In Fig. 5 topological results are presented for the “2×H$^{35}$Cl + IR cavity mode” system in which, due to the symmetry, only a second-order degeneracy point is formed (see on Fig. 3). Consequently, if the two-state approximation worked, one would have to obtain $2\pi$ for the value of the topological phase $\alpha_{1,2}$. Instead, we obtained values of $\alpha_{1,2} = 1.0878\pi$ and $\alpha_{2,3} = 1.6789\pi$, which clearly show that the two-state approximation does not work in the studied region of the CS. At this point, one has to derive again the three-state ADT matrix elements and the corresponding $D$ matrix by employing the appropriate nonadiabatic coupling terms. The obtained (1,1,1) values in the diagonal of the $D$ matrix clearly demonstrate that the three-state approximation works perfectly and none of the vibrational wave functions change sign.

The above studies undoubtedly proved that the topological features of VPES and electronic PES are very similar. Earlier results [3, 4, 60] obtained for the latter situation can almost be transferred one by one so as to understand the topological features of the VPESs.
FIG. 1: Vibrational polaritonic energy surfaces (VPES) of the \(^{35}\text{HCl} + {^{37}\text{HCl} + \text{IR cavity mode}}\) system, obtained by diagonalizing the \(V_{\text{rot}}\) matrix in Eq. (10) with the parameters \(E_{\text{vib}}^{1,0} + E_{\text{vib}}^{2,0} + \hbar \omega_c = 2904.5\ \text{cm}^{-1}\), \(E_{\text{vib}}^{1,1} + E_{\text{vib}}^{2,0} = 2905.9\ \text{cm}^{-1}\), and \(E_{\text{vib}}^{1,0} + E_{\text{vib}}^{2,1} = 2903.7\ \text{cm}^{-1}\). The \(\sqrt{\hbar \omega_c/(\varepsilon_0 V)}\) coupling strength is \(0.0001/\sqrt{2}\) a.u.

FIG. 2: Vibrational polaritonic energy surfaces (VPES) of the \(^{35}\text{HCl} + {^{37}\text{HCl} + \text{IR cavity mode}}\) system, obtained by diagonalizing the \(V_{\text{rot}}\) matrix in Eq. (10) after removing the diagonal dipole terms and using the parameters \(E_{\text{vib}}^{1,0} + E_{\text{vib}}^{2,0} + \hbar \omega_c = 2904.5\ \text{cm}^{-1}\), \(E_{\text{vib}}^{1,1} + E_{\text{vib}}^{2,0} = 2905.9\ \text{cm}^{-1}\), and \(E_{\text{vib}}^{1,0} + E_{\text{vib}}^{2,1} = 2903.7\ \text{cm}^{-1}\). The \(\sqrt{\hbar \omega_c/(\varepsilon_0 V)}\) coupling strength is 0.0005 a.u. Two types of light-induced conical intersections (LICI) are also highlighted, see text.
FIG. 3: Same as Fig. 1 but for two identical H\textsuperscript{35}Cl molecules in the cavity. The parameters are $E_{\text{vib}}^{1,0} + E_{\text{vib}}^{2,0} = E_{\text{vib}}^{1,0} + E_{\text{vib}}^{2,1} = 2905.9 \text{ cm}^{-1}$, $\sqrt{\hbar \omega_c/(\varepsilon_0 V)} = 0.001 \text{ a.u.}$, while $E_{\text{vib}}^{1,0} + E_{\text{vib}}^{2,0} + \hbar \omega_c = 2907.2 \text{ cm}^{-1}$. 
FIG. 4: The adiabatic-to-diabatic transformation angle $\gamma_{i,j}$ and the diagonal elements of the A-topological matrix as a function of $\varphi \in [0, 2\pi]$. $\varphi$ defines the position on the closed curve. The topological phase $\alpha_{i,j}$ and the $D$-topological matrix elements are both shown for the "H$^{35}$Cl + H$^{37}$Cl + IR cavity mode" system.
FIG. 5: The adiabatic-to-diabatic transformation angle $\gamma_{ij}$ and the diagonal elements of the A-topological matrix as a function of $\varphi \in [0, 2\pi]$. $\varphi$ defines the position on the closed curve. The topological phase $\alpha_{ij}$ and the $D$-topological matrix elements are both shown for the “$2 \times H^{35}\text{Cl} + \text{IR cavity mode}$” system.
C. Light-dressed spectroscopy

Another physical property which can be effected by CIs or LICIs is the spectrum. The spectroscopy of polaritonic systems is a valuable tool for providing insight into their various physiochemical properties \[45, 52, 53, 65\], and nonadiabatic effects resulting from the strong coupling of the electronic, vibrational, rotational, and photonic degrees of freedom can cause a significant modification on the molecular absorption spectra. In one possible theoretical formulation of light-dressed spectroscopy \[51\], transitions between light-dressed states are evaluated using first-order time-dependent perturbation theory, that is, for the \(T_{l\leftarrow k}\) transition amplitude between the \(k\)th and \(l\)th light-dressed state \(T_{l\leftarrow k} \propto \langle \Psi_l | \hat{d} e^{(p)} | \Psi_k \rangle \delta (E_l - E_k \pm \hbar \omega_p)\) is assumed, where \(e^{(p)}\) and \(\hbar \omega_p\) are the polarization vector and photon energy of the probe pulse, respectively, while \(|\Psi_i\rangle\) and \(E_i\) are the light-dressed wave functions and energies, respectively. In this work the light-dressed states (polaritonic states), \(|\Psi_i\rangle\), have the form shown in Eq. \(6\), and the \(T_{l\leftarrow k}\) transition amplitudes can be computed with formulae similar to that in Eq. \(5\).

Figure 6 shows the IR absorption spectra of \(\text{H}^{35}\text{Cl}\) molecules and the mixture of \(\text{H}^{35}\text{Cl}\) and \(\text{H}^{37}\text{Cl}\) molecules, confined in IR cavities of different coupling strengths. The weight of different types of basis functions in the final polaritonic states of the transitions are indicated by the color of the transition lines. Blue, red, and green components represent vibrational excitation in \(\text{H}^{35}\text{Cl}\), vibrational excitation in \(\text{H}^{37}\text{Cl}\), and photonic excitation, respectively. The panel (A1) in Fig. 6 demonstrates that at the weakest coupling strength presented in this work, the light-dressed spectrum of two confined \(\text{H}^{35}\text{Cl}\) molecules shows two significant peaks, arising from the splitting of the single \(|v = 1, J = 1, M = 0\rangle \leftarrow |v = 0, J = 0, M = 0\rangle\) field-free transition. Each peak is further split into two in panel (B1) of Fig. 6 due to the slight differences in the rovibrational energies of \(\text{H}^{35}\text{Cl}\) and \(\text{H}^{37}\text{Cl}\). No significant difference can be seen in the low-resolution envelopes of the two panels. The light dressed spectra at larger cavity coupling strengths demonstrate that the individual peak positions and peak heights can be different for the confined \(2\times\text{H}^{35}\text{Cl}\) and \(\text{H}^{35}\text{Cl} + \text{H}^{37}\text{Cl}\) systems, but no significant differences arise in their spectrum envelope. Panels (B2),(B3) and (B4) of Fig. 6 show that most peaks are dominated by either a \(\text{H}^{35}\text{Cl}\), \(\text{H}^{37}\text{Cl}\) or photonic transition. On the other hand, the color of the largest peaks in the panels (A4) and (B4) of Fig. 6 near 2880 cm\(^{-1}\) show significant mixing between the rovibrational modes of \(\text{H}^{35}\text{Cl}\) and the
photonic mode.

Although the low-resolution spectrum envelopes remain similar, the spectra of the “2×H$^{35}$Cl + cavity mode” and “H$^{35}$Cl + H$^{37}$Cl cavity mode” systems seem to become increasingly different with increasing coupling strength. Because the rovibrational energies of the H$^{35}$Cl and H$^{37}$Cl isotopologues are nearly identical on the scale of Fig. 6, we attribute the spectral differences to the nonadiabatic couplings between the VPESs.
FIG. 6: Light-dressed spectrum of the “2×H\textsuperscript{35}Cl + IR cavity mode” system (left panels) and “H\textsuperscript{35}Cl + H\textsuperscript{37}Cl + IR cavity mode” system (right panels). Parameters are $E\text{\text{\textsubscript{1,0}}} + E\text{\text{\textsubscript{2,0}}} + \hbar\omega_c = 2904.5 \text{ cm}^{-1}$, $E\text{\text{\textsubscript{1,1}}} + E\text{\text{\textsubscript{2,0}}} = 2905.9 \text{ cm}^{-1}$, $E\text{\text{\textsubscript{1,0}}} + E\text{\text{\textsubscript{2,1}}} = 2903.7 \text{ cm}^{-1}$, and the value of the coupling strength $\sqrt{\hbar\omega_c/(\varepsilon_0 V)}$ equals $0.0001/\sqrt{2}$, $0.0005/\sqrt{2}$, $0.0010/\sqrt{2}$, and $0.0050/\sqrt{2}$ a.u in the different rows from top to bottom, in order.
D. Laser-induced dynamics

As already demonstrated for the vibrational dynamics on electronic PESs \cite{22}, an efficient way to pinpoint nonadiabatic effects is to monitor the populations on the adiabatic surfaces during the dynamics. Here we perform similar studies for the case of adiabatic vibrational polaritons. In the case of VPESs, the population on the $a$th adiabatic state is evaluated as

$$p^{(a)} = |\hat{P}^{(a)}|\langle \Psi(t) \rangle|^2,$$

where $|\Psi(t)\rangle$ is the time-dependent wave function expanded in terms of the direct-product diabatic states, see Eq. (2), and $\hat{P}^{(a)} = |\psi^{(a)}\rangle\langle \psi^{(a)}|$ is a projector onto the $a$th adiabatic state, $i.e.$, the $a$th eigenstate of the matrix in Eq. (10). Note that

$$|\psi^{(a)}\rangle = \sum_{N,v_1,v_2} C^{(a)}_{N,v_1,v_2}(\theta_1, \theta_2) |N\rangle |\Psi^{1,v_1}_{\text{vib}}\rangle |\Psi^{2,v_2}_{\text{vib}}\rangle,$$

that is, the $C^{(a)}_{N,v_1,v_2}(\theta_1, \theta_2)$ expansion coefficients depend on the rotational coordinates, $\theta_1$ and $\theta_2$, as predictable from Figs. 2 and 3.

Fig. 7 shows the temporal evolution of the adiabatic populations for the “$2 \times H^{35}Cl + IR$ cavity mode” system and the “$H^{35}Cl + H^{37}Cl + IR$ cavity mode” system, when a short IR laser pulse, tuned to the field-free vibrational fundamental of $H^{35}Cl$ (2926.1 cm$^{-1}$), is used to excite these systems from their ground states. The numerical results were obtained by directly solving the time-dependent Schrödinger equation in the diabatic direct-product basis representation. As presented by the ground state populations (dashed lines) in Fig. 7, the degree of laser-induced molecular vibrational excitation is identical within numerical error for the two systems. For the “$2 \times H^{35}Cl + IR$ cavity mode” system, the upper panel of Fig. 7 shows that the laser populates two adiabatic states and the third adiabatic state is a dark polaritonic state, which is not populated by the light field, as expected. However, due to the strong nonadiabatic couplings between the VPESs, rapid, hundred-femtosecond timescale population transfer proceeds among all three adiabatic states following the excitation by the laser field. The situation is similar for the “$H^{35}Cl + H^{37}Cl + IR$ cavity mode” system, although in this case, due to the isotope difference, the dark state is not completely dark and obtains a slight amount of population during the laser excitation. Overall, Fig. 7 demonstrates that when molecular rotations are feasible, strong nonadiabatic couplings influence the dynamics of multimolecule (ro)vibrational polaritons.
Furthermore, the nonadiabatic dynamics shown in Fig. 7 verify that breaking the molecular permutational symmetry, in this case by introducing a different Cl isotope, the polariton dynamics can deviate substantially.

![Graph showing adiabatic populations](image)

**FIG. 7**: Adiabatic populations in the laser-induced dynamics of the “2×H^{35}Cl + IR cavity mode” system (upper) and “H^{35}Cl + H^{37}Cl + IR cavity mode” system (lower panel). Squares, crosses, and triangles stand for the upper, middle, and lower adiabatic polaritonic VPESs, respectively, color coded according to Figs. 2 and 3. The dashed line shows the ground state VPES population, and the continuous line represents the electric field of the laser pulse. Parameters are $E_{vib}^1 + E_{vib}^2 + \hbar \omega_c = 2904.5 \text{ cm}^{-1}$, $E_{vib}^1 + E_{vib}^0 = 2905.9 \text{ cm}^{-1}$, $E_{vib}^1 + E_{vib}^2 = 2903.7 \text{ cm}^{-1}$, and $\sqrt{\hbar \omega_c/(\varepsilon_0 V)} = 0.0005/\sqrt{2} \text{ a.u.}$ The pump laser has a field strength of $0.1/\sqrt{2} \text{ a.u.}$, and its central wavenumber equals the field-free $|11\rangle \leftarrow |00\rangle$ rovibrational transition of H^{35}Cl (2926.1 cm$^{-1}$).

As an alternative approach to probe the presence of nonadiabatic couplings in the laser-
induced dynamics of our rovibrational polaritonic test systems, the orientation, \( i.e., \) the \( \langle \cos(\theta) \rangle \) expectation value, was evaluated for a single \( ^{35}\text{HCl} \) (\( ^{37}\text{Cl} \)) molecule, when confined in an IR cavity with another \( ^{35}\text{HCl} \) (\( ^{37}\text{Cl} \)) molecule or a \( ^{37}\text{HCl} \) (\( ^{35}\text{Cl} \)) isotopologue. The computed results for \( ^{35}\text{HCl} \) and \( ^{37}\text{Cl} \) are shown in the upper and lower panels of Figure 8, respectively. Figure 8 shows that after around three picoseconds, the rotational dynamics of the HCl molecules clearly reflect whether they share the cavity with the same or a different isotopologue. Although the exact value of the numerical results presented here should be treated with caution, because cavity loss was neglected in this work, such a dependence of the orientation on the partner molecule is a clear fingerprint of molecular distinguishability on the VPESs (and corresponding nonadiabatic couplings) and, therefore, on the rotational dynamics.
FIG. 8: Upper panel: the laser-induced orientation, i.e., the $\langle \cos(\theta) \rangle$ expectation value for a confined H$^{35}$Cl molecule, when sharing the cavity with another H$^{35}$Cl molecule (blue continuous line) or a H$^{37}$Cl molecule (red dashed line). Lower panel: the laser-induced orientation of a confined H$^{37}$Cl molecule, when sharing the cavity with another H$^{37}$Cl molecule (blue continuous line) or a H$^{35}$Cl molecule (red dashed line). The molecular, cavity mode and laser parameters are the same as in Fig. 7.
IV. SUMMARY AND CONCLUSIONS

A general framework for computing the rovibrational polaritons of molecular ensembles in a lossless cavity was presented. Based on this formulation, the concept of vibrational potential energy surfaces (VPES) was introduced, which provide effective potential energy surfaces for the rotational motion of the confined molecules. For the test system of two rovibrating HCl molecules interacting with a single lossless infrared cavity mode, degeneracies were identified between the VPESs: light-induced conical intersections (LICI) were found when two different isotopologues, H\textsuperscript{35}Cl and H\textsuperscript{37}Cl, are in the cavity, and a second-order degeneracy was found in the case of two same isotopologues. The degeneracies between the VPESs were characterized based on their topological properties, and their nonadiabatic fingerprints were identified in the light-dressed spectra and the laser-induced dynamical properties of the investigated rovibrational polaritons.

The presented results clearly show that breaking molecular permutational symmetry due to different isotopes can play an important role in rovibrational polaritonic properties; the polaritonic surfaces, nonadiabatic couplings, and related spectral, topological, and dynamic properties can be influenced substantially. This implies that the natural abundance of different isotopologues should be accounted for if one aims for a realistic simulation on confined molecular ensembles.

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