Violation of electronic optical selection rules in x-ray emission by nuclear dynamics: Time-dependent formulation

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The resonant photon emission following the excitation of a fully symmetric system to core-excited electronic states is discussed within a time-dependent formulation. Two types of vibrational modes—localizing modes and symmetry breaking but nonlocalizing modes—are considered, named according to their impact on dynamical symmetry breaking and localization accompanying the process. The decay rates are proportional to the population of a coherent superposition of the relevant core states vibronically coupled via the appropriate vibrational modes. This population is essentially a product of partial contributions of the two types of vibrational modes mentioned above. The general arguments are illustrated on the CO₂ molecule. Here, the bending mode is the symmetry breaking but nonlocalizing mode and the asymmetric stretching mode is the localizing mode. The decay rates and total resonant photon emission intensities are calculated in the leading terms approximation of the potential matrix Hamiltonian. The impact of the asymmetric mode on localization and hence on the optical selection rules as a function of time is discussed in detail. It is shown that the vibronic coupling via the bending mode changes the polarization of the emitted light and exerts an impact on the effect of vibronic coupling via the asymmetric stretching mode.

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I. INTRODUCTION

Owing to modern technologies in synchrotron radiation systematic studies on the impact of nuclear dynamics in various fields of molecular spectroscopy can nowadays be performed [1]. Nuclear dynamics of molecules undergoing electronic ionization or excitation are subjects to different kinds of vibronic coupling effects [2]. Vibronic coupling effects are topical both for core and valence ionization or excitation and the subsequent decay. The present paper is devoted to core processes; for work on core processes see, e.g., Refs. [3–8]. Systems possessing atoms equivalent by symmetry and, consequently, equivalent ls or other core orbitals exhibit a peculiar manifold of vibronic coupling effects. These lead to the phenomenon of dynamical core hole localization which is an essential feature of such systems [9,10]. More precisely, vibronic coupling between core excited electronic states of different spatial symmetry leads to excitation of appropriate nontotally symmetric vibrational modes which lowers the original symmetry of the system and makes originally equivalent atoms inequivalent. In principle, this type of dynamical symmetry breaking prevails to all symmetric polyatomic systems, but some care must be taken studying systems with adjacent equivalent atoms (see Ref. [11] for details). Owing to the initial equivalence of the atoms, the core-excited states are nearly degenerate and easily split into core-localized nondegenerate ones by vibronic coupling. The effect of dynamical core hole localization was first predicted and discussed in Ref. [9].

From the detection of ionization or absorption spectra alone it is impossible to deduce whether the excited states are truly localized or delocalized because in both cases the spectra are formally identical [9,10,12,13]. It has first been shown in Refs. [12] and [13] that vibronic coupling of core excited states and the related phenomenon of dynamical symmetry breaking and localization can be observed via emission spectra such as x-ray and Auger spectra. For other interesting investigations see Refs. [14–16]. X-ray emission spectra are fingerprints of vibronic coupling effects and therefore of the vital dynamical core hole localization since they unlock transitions between decaying and final electronic states which are forbidden by pure electronic optical selection rules. For example see Fig. 1: if the core excitation takes place from a gerade ground state |i⟩ to an ungerade intermediate core-excited state |Φ⟩, then by optical selection rules only a final state |f⟩ of g symmetry is bright, while the optical transition to a final state of u symmetry is forbidden. However, ungerade final states can also acquire photon emission intensity if the intermediate |Φ⟩ state couples vibronically to the energetically close state of g symmetry. This coupling will populate the |Φ⟩ intermediate state and a decay to final ungerade states takes place. The higher the intensity of x-ray emission to these states the stronger the excitation of the mode responsible for the vibronic coupling within the manifold of decaying states and, consequently, the stronger the localization effect.

The main goal of the present paper is to arrive at a transparent time-dependent description of the formation of resonant photon emission intensity during the process of core excitation and the subsequent decay, mediated by vibronic coupling in the manifold of core states. Of particular interest is the identification of the effects of different types of nuclear motions (see below). The results obtained are of general va-
modes of this type "symmetry breaking nonlocalizing modes."

The paper is organized as follows. In Sec. II we discuss the matrix Hamiltonian of nuclear motion for various interacting states and derive the working equations for the rates of photon emission intensities as a function of time. Considered are excitations of localizing modes, of symmetry breaking nonlocalizing modes and their mutual action. The general results of Sec. II are supported and illuminated by examples in Sec. III. The main results are briefly summarized and analyzed in Sec. IV.

II. THEORETICAL FRAMEWORK

A. Resonant photon emission intensity

We introduce $\mu$ as a column vector of dipole matrix elements between an initial electronic state $|i\rangle$ and a manifold of intermediate electronic states $|\Phi_f\rangle$, and $W$ as a row vector of dipole matrix elements between this manifold of intermediate states $|\Phi_f\rangle$ and a final state $|f\rangle$ to which these states may decay radiatively. Then at time $t=0$ the vibrational ground state $|0\rangle$ of the initial electronic state $|i\rangle$ is excited to the manifold of intermediate states and arrives there as $|\mu(0)\rangle$.

The wave packet which describes the nuclear motion on the decaying manifold as a function of time then reads [13]

$$|\Psi_d(t)\rangle = e^{-iH_d^t_0} |\mu(0)\rangle.$$  (1)

Here $H_d$ is the matrix Hamiltonian governing the nuclear motion on the decaying manifold of states. The intensity of resonant x-ray emission to the final state $|f\rangle$ is subjected to the nuclear dynamics on the decaying intermediate states and can be expressed as [12]

$$I_f = \alpha \int_0^\infty dt \langle \Psi_d(t) | W^\dagger W | \Psi_d(t) \rangle.$$  (2)

The proportionality factor $\alpha$ depends on the kinematic factors and is not of relevance here. We shall show below in Sec. II C that expression (2) also holds if the excitation is not instantaneous, but performed with a pulse of finite duration. In other words, Eq. (2) is of general validity.

Matrix elements of the dipole moment operator are functions of nuclear coordinates and hence $\mu$, $W$ do not commute with the kinetic energy operator in $H_d$ in general. Here we work in a diabatic basis and the effects of a nuclear coordinates dependence are small compared to the effects induced by vibronic coupling. In this case we may use the Franck-Condon principle and consider $\mu$, $W$ as constants. In those special cases where $\mu$ and/or $W$ do depend substantially on the nuclear coordinates, expression (2) cannot be further simplified and should be used as it is.

For simplicity of presentation we first consider in the following without loss of generality the situation indicated in Fig. 1, i.e., two intermediate electronic states $|\Phi_f\rangle$ and $|\Phi_i\rangle$. By optical selection rules only $|\Phi_f\rangle$ can be reached by photon absorption from the totally symmetric ground state $|i\rangle$ and decay to final gerade states via photon emission. Ungerade final states are dark. We have that
and:

\[ W = W(1,0) \text{ if } |f\rangle \text{ is gerade,} \]
\[ W = W(0,1) \text{ if } |f\rangle \text{ is ungerade.} \]

The quantity \( W W^\dagger W \) introduced in Eq. (2), is in general a matrix of the dimension of the decaying manifold of states.

Now let us discuss the Hamiltonian of nuclear motion \( H_d \). The two diabatic symmetry adapted, i.e., delocalized electronic states \( |\Phi_{\sigma}\rangle \) and \( |\Phi_{\sigma}\rangle \) chosen as the basis for the representation of the Hamiltonian \( H_d \). For example, for \( O1s-\sigma^* \) transition in the \( CO_2 \) molecule these states correspond to the two resulting nearly degenerate \( |\Sigma_{\sigma}\rangle \) and \( |\Sigma_{\sigma}\rangle \) core states (due to the nearly degenerate oxygen core orbitals \( 1\sigma_g \) and \( 1\sigma_u \)), while for a \( O1s-\pi^* \) transition they correspond to the nearly degenerate \( |\Pi_{\sigma}\rangle \) and \( |\Pi_{\sigma}\rangle \) core states. Each of the states \( |\Pi_{\sigma}\rangle \) and \( |\Pi_{\sigma}\rangle \) is, of course, by itself degenerate because of symmetry. In this basis the Hamiltonian of nuclear motion is a matrix which takes on the following appearance [12]:

\[ H_d = \begin{pmatrix} \langle \Phi_{\sigma}|H|\Phi_{\sigma}\rangle & \langle \Phi_{\sigma}|V|\Phi_{\sigma}\rangle \\ \langle \Phi_{\sigma}|V|\Phi_{\sigma}\rangle & \langle \Phi_{\sigma}|H|\Phi_{\sigma}\rangle \end{pmatrix} - \frac{i}{2} \Gamma 1. \]  

(3)

\( H \) describes the nuclear motion in \( |\Phi_{\sigma}\rangle \) and \( |\Phi_{\sigma}\rangle \), \( V \) is the potential coupling between these states (interstate vibronic coupling), \( \Gamma \) is the inverse lifetime of the core excited states, and \( 1 \) denotes a unit matrix. For the set \( |\Sigma_{\sigma}\rangle \), \( |\Sigma_{\sigma}\rangle \) of core states the dimension of \( H_d \) is 2, while for the set \( |\Pi_{\sigma}\rangle \), \( |\Pi_{\sigma}\rangle \) the dimension is 4 and each matrix element presents a \( 2 \times 2 \) block owing to the two degenerate electronic components of each state (more details will be given below). The present structure of the Hamiltonian is typical for core excitations in highly symmetrical molecules. The nondiagonal elements of Eq. (3) describe the interstate vibronic coupling between the electronic states, while a diagonal element reproduces the vibrational structure of the corresponding individual electronic state. For degenerate decaying states the blocks on the diagonal carry additional information on intra state vibronic coupling between the electronic components of the degenerate state. Examples are the dynamical Renner-Teller effect via symmetry breaking nonlocalizing modes which will be discussed below and the distorted Jahn-Teller effect [10].

It is useful to transform the Hamiltonian of nuclear motion from the symmetry adapted delocalized to a localized representation. In the present case the transformation matrix is particularly simple

\[ S = \begin{pmatrix} 1 & 1 \\ \sqrt{2} & 1 \\ 1 & -1 \end{pmatrix}, \]

(4)

and transforms the basis \( |\Phi_{\sigma}\rangle, |\Phi_{\sigma}\rangle \) to the localized basis \( |\Phi_1\rangle, |\Phi_2\rangle \), where the indices 1 and 2 refer to the local sites, e.g., the left and right oxygen atoms in \( OC \). The construction of \( S \) in a general case is discussed in Ref. [20]. After this transformation the Hamiltonian assumes the diagonal form

\[ H_{dL} = \begin{pmatrix} \langle \Phi_1|(H+V)|\Phi_1\rangle & 0 \\ 0 & \langle \Phi_2|(H-V)|\Phi_2\rangle \end{pmatrix} - \frac{i}{2} \Gamma 1, \]

(5)

For the set \( |\Sigma_{\sigma}\rangle \), \( |\Sigma_{\sigma}\rangle \) of core states the Hamiltonian \( H_{dL} \) is a two-dimensional matrix, and for the set \( |\Pi_{\sigma}\rangle \), \( |\Pi_{\sigma}\rangle \) of core states \( H_{dL} \) and \( H_{dL} \) are themselves blocks of dimension 2. \( H_{dL} \) and \( H_{dL} \) describe the nuclear motion in the localized electronic states each associated to one local site. In general, the number of blocks on the diagonal is equal to the number of equivalent atoms in a system [10,20].

The transformation to a localized representation significantly simplifies the Hamiltonian of nuclear motion and allows us to derive more explicit expressions for the resonant photon emission intensity and to arrive at a transparent time-dependent description of the process. We will turn to the explicit time dependent description in the next section in detail. Here we only mention one result obtained in Ref. [12] using a different description. The total photon emission intensity is not given by intensities from \textit{a priori} localized states, i.e., \( I_f \neq I_{f1} = I_{f2} \), where \( I_{f1} \) and \( I_{f2} \) are the intensities computed for the localized states \( |\Phi_1\rangle \) and \( |\Phi_2\rangle \), respectively. Interestingly, these intensities are \( I_{f1} = I_{f2} = a|\mu|^2|W|^2/2\Gamma \) and do not depend on the nuclear dynamics while the exact intensity \( I_f \) does.

The total photon emission intensity \( I_f \) can be expressed as a sum of two contributions, one of which is just the incoherent contribution \( (I_{f1} + I_{f2})/2 \) of photon emission intensities from both localized states \( |\Phi_1\rangle \), \( |\Phi_2\rangle \) and the second term is related to a “coherence strength” which decreases with increasing interstate vibronic coupling. The total photon emission intensity to gerade and ungerade \textit{final} states reads [12]

\[ I_{f,u} = \frac{a|\mu|^2|W|^2}{2\Gamma}(1 \pm C_{12}), \]

(6)

where \( C_{12} \) is the coherence strength

\[ C_{12} = \text{Re} \int_0^\infty dt \ e^{-\Gamma t} \langle 0|e^{iH_{dL}t}e^{-iH_{dL}t}|0 \rangle. \]

(7)

Without vibronic coupling \( C_{12} = 1 \) and, hence, \( I_g = a|\mu|^2|W|^2/\Gamma \) and \( I_u = 0 \) as dictated by optical selection rules. Vibronic coupling lowers the value of \( C_{12} \) and reduces the coherence of photon emission from the localized states \( |\Phi_1\rangle \), \( |\Phi_2\rangle \) until finally for \( C_{12} \leq 0 \, I_g = I_u = I_{f1} = I_{f2} \), as if the states were \textit{a priori} localized.

The above mentioned result the optical selection rules in resonant x-ray emission are violated in symmetric systems by vibronic coupling and its relation to dynamic localization are of general validity. The particular expression for the emission intensity \( I_f \) depends, however, on the number of equivalent atoms and on the type of modes active in the system. Expression (6) is valid for a set of two vibronically
interacting core excited states of any symmetric molecule with two equivalent atoms, for example, the $|\Sigma_g\rangle$ and $|\Sigma_u\rangle$ states of CO$_2$. The energy gap between these states is small compared to the frequency of the vibrational mode (i.e., they are nearly degenerate) and can be neglected in practical calculations [9]. It is also valid for states like the $|\Pi_g\rangle$ and $|\Pi_u\rangle$ states of CO$_2$ as long as we are not concerned with nuclear modes which lift the degeneracy of the states. In CO$_2$ this degeneracy is lifted by the bending mode which is a symmetry breaking but nonlocalizing mode. The influence of such modes on selection rules and dynamic localization is one of the subjects of the present paper.

In principle, the two manifolds $\{|\Sigma_g\rangle, |\Sigma_u\rangle\}$ and $\{|\Pi_g\rangle, |\Pi_u\rangle\}$ can also interact vibronically with each other. In CO$_2$ there are indeed indications [21] that both manifolds may be close in energy and, therefore, vibronic coupling between them cannot be a priori excluded. Many results of the present theory, in particular the basic expression (2), are also valid in such cases with the appropriate $H_d$. The explicit discussion of these more intricate situations is, however, beyond the scope of the present paper.

B. Time-dependent formulation: State populations and decay rates

It is convenient to express the relevant quantities in the delocalized, symmetry adapted, as well as in the localized picture. The wave packet (1) of the nuclear motion in the decaying manifold of symmetry adapted core excited states is easily rewritten with the use of the Hamiltonian $H_{dl}$ (5) describing the dynamics in the localized states:

$$|\Psi_d(t)\rangle = S e^{-iH_{dl}t} \mu_L |0\rangle,$$

where $S$ is the delocalized-to-localized transformation matrix (4) and $\mu_L$ is the dipole column vector in the localized representation

$$\mu_L = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix}.\tag{9}$$

The wave packet has components of g and u symmetry and reads

$$|\Psi_d(t)\rangle = \begin{pmatrix} |\Psi_g(t)\rangle \\ |\Psi_u(t)\rangle \end{pmatrix},$$

$$|\Psi_{g(u)}(t)\rangle = \frac{1}{\sqrt{2}} e^{-i(\Gamma/2)t} (e^{-iH_{dl}t} + e^{-iH_{dl}t}) \mu |0\rangle.$$

It is readily seen that initially, i.e., at time $t = 0$, the gerade component vanishes $|\Psi_g(0)\rangle = 0$ according to the optical selection rule. At later times $|\Psi_g(t)\rangle$ acquires nonvanishing contributions if and only if vibronic coupling between the core excited states $|\Phi_g\rangle$ and $|\Phi_u\rangle$ is present (see Sec. III for explicit examples).

The wave packet in the localized representation reads

$$|\Psi_{dl}(t)\rangle = e^{-iH_{dl}t} \mu_L |0\rangle.\tag{11}$$

FIG. 2. Schematic drawing of the diabatic potential curves of the ground and the core excited localized states in the antisymmetric stretching direction. Propagation of the components of the excited wave packet on two localized potential surfaces: The wave packet which is vertically excited from the electronic ground state into the core excited localized states splits into two components $|\Psi_1(t)\rangle$ and $|\Psi_2(t)\rangle$ which propagate each on the potential surface of its “own” localized state. The coherent superpositions $|\Psi_1(t)\rangle \pm |\Psi_2(t)\rangle$ determine the emission intensity.

Similarly to $|\Psi_d(t)\rangle$, this wave packet also possesses two components

$$|\Psi_{dl}(t)\rangle = \begin{pmatrix} |\Psi_1(t)\rangle \\ |\Psi_2(t)\rangle \end{pmatrix},$$

$$|\Psi_{1(2)}(t)\rangle = \frac{1}{\sqrt{2}} e^{-i(\Gamma/2)t} e^{-iH_{dl(2)}t} \mu |0\rangle.$$

The consideration of the evolution of the wave packet (11) on the localized potential energy surfaces, schematically shown in Fig. 2, gives a transparent dynamical picture of the photon emission process. Initially the wave packet $|\Psi_d(0)\rangle$ is created in the vicinity of the crossing point of the two potential surfaces. This point is at the equilibrium geometry of the system before excitation. In time the wave packet splits into the two components $|\Psi_1(t)\rangle$ and $|\Psi_2(t)\rangle$ which propagate independently each on a localized potential surface and decay coherently to a final state.

A comparison of Eqs. (10) and (12) immediately gives

$$|\Psi_{g(u)}(t)\rangle = \frac{1}{\sqrt{2}} (|\Psi_1(t)\rangle \mp |\Psi_2(t)\rangle).\tag{13}$$

Note that the minus sign relates to the gerade wave packet, i.e., to that wave packet which is associated with the gerade core excited electronic state $|\Phi_g\rangle$.

We now introduce the populations

$$n_{g(u)}(t) = \langle \Psi_{g(u)}(t) | \Psi_{g(u)}(t) \rangle$$

which are the weights of the total wave packet $|\Psi_d(t)\rangle$ on the gerade and ungerade core excited electronic states. To
express this quantity by the wave packets on the localized states we use Eq. (13) and obtain

$$n_{g(u)}(t) = \frac{1}{2} [n_1(t) + n_2(t)] = Re \langle \Psi_1(t) | \Psi_2(t) \rangle,$$

(15)

$$n_1(t) = n_2(t) = \frac{|\mu|^2}{2} e^{-\gamma t},$$

where $n_1(t)$ and $n_2(t)$ are the populations of the localized core excited states. These populations are equal and simply decay exponentially. They do not depend on the nuclear dynamics. The populations of the symmetry adapted states, on the other hand, are modified by an interference term, which provides a transfer of population from the $|\Phi_g\rangle$ electronic state to $|\Phi_u\rangle$ and backwards depending on the details of the prevailing nuclear dynamics. This interference term is related to the coherence strength (7).

In the following we make contact between the state populations and emission intensities. The intensity of resonant photon emission as a function of time is

$$I_f(t) = \int_0^t dt' \langle \Psi_d(t') | W^\dagger W | \Psi_d(t') \rangle.$$  

(16)

Introducing the rate of emission

$$\frac{dI_f(t)}{dt} = \langle \Psi_d(t) | W^\dagger W | \Psi_d(t) \rangle,$$

(17)

and assuming the Franck-Condon approximation for $W^\dagger W$ (see Sec. II A) the rates of emission to gerade and ungerade final states read

$$\frac{dI_g(t)}{dt} = |W|^2 n_g(t), \quad \frac{dI_u(t)}{dt} = |W|^2 n_u(t).$$

(18)

The rate of emission to a gerade (ungerade) final state is proportional to the population of the ungerade (gerade) decaying (core excited) intermediate state. This result is very sound: by dipole selection rules a gerade (ungerade) state can only decay to an ungerade (gerade) state and the decay depends on how strongly the decaying state is occupied. The populations change in time due to vibronic coupling. Initially only the $|\Phi_g\rangle$ decaying state is populated. As time advances population flows to the $|\Phi_g\rangle$ decaying state via vibronic coupling and opens the channel for emission to a final state of $u$ symmetry.

Using Eqs. (14) and (13) the rate of emission can readily be expressed by the wave packets on the potential surfaces of the localized core excited states

$$\frac{dI_g(t)}{dt} = \frac{|W|^2}{2} \langle \Psi_1(t) + \Psi_2(t) | \Psi_1(t) + \Psi_2(t) \rangle,$$

$$\frac{dI_u(t)}{dt} = \frac{|W|^2}{2} \langle \Psi_1(t) - \Psi_2(t) | \Psi_1(t) - \Psi_2(t) \rangle.$$  

(19)

It is seen that the rate of resonant x-ray emission intensity is proportional to the population of the coherent superposition of the localized core states. What happens if the core excited states were a priori localized? This would lead to an incoherent superposition of these states and neglecting the interference term in Eq. (19) we obtain

$$\frac{dI_g(t)}{dt} = \frac{|W|^2}{2} \langle n_1(t) + n_2(t) \rangle = \frac{|W|^2 |\mu|^2}{2} e^{-\gamma t}.$$  

(20)

The emission rates are equal and do not depend on nuclear dynamics.

Now let us consider more explicitly the situation of decaying states such as the $|\Pi_g\rangle$ and $|\Pi_u\rangle$ core states in CO$_2$. Each of these states is degenerate by symmetry and has two components, e.g., $|\Pi_{g\ell\ell}\rangle$ and $|\Pi_{u\ell\ell}\rangle$. The equations derived above can readily be transferred to explicitly exhibit the degenerate character of the states (see Sec. II C for additional details). In doing so it is important to take into account the orientation of the polarization vectors of the polarized exciting and emitted light. For the sake of transparency of presentation we concentrate here on linearly polarized light propagating along the molecular axis. As shown in the Appendix the anisotropy of the emission intensity is then a function of only one angular parameter—the angle $\Theta$ between the polarization vectors of exciting and emitted light. We denote the molecular axis by $z$ and the angle between the polarization vector of the exciting and emitted light and the $x$ axis by $\phi$ and $\theta$, respectively. The basic equation (17) then reads

$$\frac{dI_g(\theta - \phi,t)}{dt} = |W|^2 (\cos \theta \Psi_{u_\ell\ell}(t) + \sin \theta \Psi_{u_\ell\ell}(t)) | \Psi_{u_\ell\ell}(t)$$

+ $\sin \theta \Psi_{u_\ell\ell}(t)$$

(21)

and by interchanging the $g$ and $u$ subscripts one obtains the equation for the rate of intensity of a final ungerade state. The intensity rates now depend on $\Theta = \theta - \phi$ and are proportional to the self-overlap of the coherent superposition $\cos (\Psi_{u_\ell\ell}(t)) + \sin (\Psi_{u_\ell\ell}(t))$ of the nuclear wave packet components on the $|\Pi_{g\ell\ell}\rangle$ and $|\Pi_{u\ell\ell}\rangle$ states.

Because the emission intensity is a function of one angular parameter only, the choice of the polarization of the exciting light, which determines the initial condition at time $t = 0$ of $|\Psi_{u_\ell\ell}\rangle$, is irrelevant by itself. In the present work we choose the initial condition which leads to equal populations of $|\Pi_{g\ell\ell}\rangle$ and $|\Pi_{u\ell\ell}\rangle$, i.e., $\phi = \pi/4$. If desired, it is easy to rewrite all the equations derived below for other initial conditions using the Appendix. The rate of emission intensity with the same polarization as the exciting light, $\Theta = \theta - \phi = 0$, takes the following appearance:

$$\frac{dI_g(0,t)}{dt} = \frac{|W|^2}{2} \langle \Psi_{a_\ell\ell}(t) + \Psi_{u_\ell\ell}(t) | \Psi_{a_\ell\ell}(t) + \Psi_{u_\ell\ell}(t) \rangle.$$  

(22a)

We recover expression (18) if we interpret $|\Psi_g\rangle$ and $|\Psi_u\rangle$ as the superposition of their components, i.e., as $|\Psi_{a_\ell\ell} + \Psi_{u_\ell\ell}\rangle$.  

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and analogously for the gerade symmetry. The total coherent ungerade population of the core excited states then reads

\[ n_u(t) = \langle \Psi_{ax}(t) + \Psi_{ay}(t) | \Psi_{ax}(t) + \Psi_{ay}(t) \rangle \]  \hspace{1cm} (22b)

and an identical expression is valid for the gerade population. Equation (19) holds as well if we note that \[ |\Psi_{12}(t)\rangle \] there has to be interpreted as \[ |\Psi_{12}(t) + \Psi_{12}(t)\rangle \].

A few relevant remarks on the impact of various kinds of nuclear modes are in order. In the absence of vibronic coupling the gerade state will not be populated and the usual optical selection rules hold, i.e., there is no influence of nuclear dynamics. In the presence of interstate vibronic coupling and absence of intrastate coupling (e.g., Renner-Teller coupling within a \( |\Pi\rangle \) state) only the localizing modes are active. The symmetry breaking nonlocalizing modes, such as the bending mode in \( \text{CO}_2 \), stay inactive and can be neglected. In this case \( \langle \Psi_u | \Psi_u \rangle = \langle \Psi_g | \Psi_g \rangle = \langle \Psi \psi | \Psi \psi \rangle \), and Eq. (22) boil down to the same equations as those found for nondegenerate core excited states. Except for a trivial factor 2 the degeneracy can be discarded. As soon as symmetry breaking nonlocalizing modes are active, i.e., intrastate vibronic coupling constants are non-negligible, the full expressions (22) must be considered. Some subtle effects then arise even if the localizing modes are inactive. The above is illustrated in some detail by the examples studied in Sec. III.

Until now we did not mention totally symmetric modes, i.e., modes which do not break the symmetry of the molecule. The impact of these modes on absorption and emission spectra is very prominent in many cases. They also have a considerable impact in vibronic coupling situations where they are denoted tuning modes [2]. In spite of their importance for the understanding of the spectra, their impact on the total intensities of absorption and emission spectra of core excited states is usually negligible [12]. Since small variations of totally symmetric modes do not lift the quasidegeneracy of the vibronically interacting core states, they become separable from the other modes to a good approximation and do not influence the total intensity. This intensity changes only due to dynamical localization which is not done by the totally symmetric modes. These modes are only of relevance if different sets of states (such as \( \{\Sigma_g, \Sigma_u\} \) and \( \{\Pi_g, \Pi_u\} \)) interact with each other. This nongeneric case is not in the scope of the present work. We, therefore, discard totally symmetric modes in the examples discussed in Sec. III.

In nonlinear polyatomic molecules and in linear ones with more than three atoms we can easily anticipate that the classes of localizing and symmetry breaking nonlocalizing modes can be broken down to subclasses of modes each having its own typical impact on dynamical localization. For instance, if several atoms equivalent by symmetry are present, some of the localizing modes may lead to a localization on a group of atoms rather than on a single atom. In a \( X_4 \) molecule of symmetry \( D_{4h} \), for example, all four atoms are equivalent and the excitation of the antisymmetric out-of-plane vibration \( B_{1u} \) distorts the symmetry to \( C_{2v} \) and the core component of the core excited state localizes on a group of two equivalent atoms.

C. Generalization to narrow-band excitation

In the preceding subsections we have discussed the interrelation between the population of the core excited states and the intensity emission rate after a sudden excitation from an initial electronic state which is typically the ground state of the system. In the next section we investigate these quantities as a function of time for several examples. A sudden excitation at time \( t = 0 \) corresponds to an excitation with a light pulse \( \sim \delta(t) \), i.e., to a broad-band excitation in frequency space. Modern technologies enable the use of pulses of variable band width. And recently it has been beautifully demonstrated that the x-ray emission intensities after pulse excitation of \( \text{CO}_2 \) vary strongly with detuning of the pulse off resonance [14,15].

In the following we show that the results derived in the preceding subsections for broad-band excitation hold also for a general pulse. The only change which has to be made is to substitute the nuclear wave packet \( |\psi_d(t)\rangle \) on the manifold of core excited states after broad-band excitation (1) by the correct expression for that after excitation with a general pulse [22]

\[ |\psi_d(t)\rangle = -i \int_{-\infty}^{t} d\tau \ e^{iH_d(\tau - t)} g(\tau) \mu |0\rangle, \]  \hspace{1cm} (23)

where \( g(t) \) is the excitation function of the pulse. For broad-band excitation, \( g(t) \sim \delta(t) \), and Eq. (1) is immediately recovered.

To establish the relation of Eq. (23) to the rate of emission intensity we use equation (16) of Ref. [22] for the nuclear wave packet \( |\psi(E,t)\rangle \) on the final electronic state and the basic expression [13]

\[ I_j(E,t) = \langle \psi_j(E,t) | \psi_j(E,t) \rangle \]  \hspace{1cm} (24)

for the emission intensity collected up to time \( t \) at the energy \( E \) of the emitted particle, here photon. For \( t \rightarrow \infty \) the above expression gives the Auger or the x-ray emission spectrum. The total intensity collected up to time \( t \) is determined by integrating \( I_j(E,t) \) over the energy \( E \). After this integration one obtains with the aid of Eqs. (16) and (12) from Ref. [22]

\[ \frac{dI_j(t)}{dt} = 2 \text{Im} \int_{-\infty}^{\infty} dE \langle \psi_j(E,t) | \mathbf{W} | \psi_d(t) \rangle. \]  \hspace{1cm} (25)

Using Eq. (16) of Ref. [22] again leads to

\[ \int_{-\infty}^{\infty} dE \langle \psi_j(E,t) | = i \pi \langle \psi_d(t) | \mathbf{W}^\dagger \]  \hspace{1cm} (26)

and inserted into Eq. (25) readily gives

\[ \frac{dI_j(t)}{dt} = \langle \psi_d(t) | \mathbf{W}^\dagger \mathbf{W} | \psi_d(t) \rangle, \]  \hspace{1cm} (27)

where we have incorporated trivial factors into the definition of \( \mathbf{W} \). Obviously, this expression is identical to that derived in the preceding subsection for broad-band excitation, see Eq. (17).

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All relations derived in the preceding subsections are thus also valid for excitation with a general pulse \( g(t) \). For nuclear wave packets on the core excited states one must use the above expression (23).

The numerical evaluation of the wave packet \( |\Psi_d(t)\rangle \) excited with a general pulse is discussed in detail in Ref. [22]. Once this wave packet is computed the evaluation of the intensity rate (25) is straightforward. Nevertheless, one may expect a variety of interesting phenomena by varying the excitation function \( g(t) \). Their investigation is beyond the scope of the present paper. Here we would just like to discuss briefly the interesting case of strong detuning of the excitation pulse off resonance. It has been explicitly shown in Ref. [22] that due to strong detuning the wave packet \( |\Psi_d(t)\rangle \) generally vanishes fast after the pulse duration. This shortens the lifetime of the wave packet from \( 1/\Gamma \), in the cases of broad-band and narrow-band on resonance excitations, to some effective value \( \tau_{\text{eff}} \). Consequently, the vibronic coupling has less time to be active and the intensity of those final states which are dark without vibronic coupling is substantially reduced. At very strong detuning nuclear dynamics does not take place at all and these states are dark as predicted by purely electronic optical selection rules.

### III. SPECIFIC EXAMPLES

In this section we discuss three time-dependent examples of nuclear dynamics involved in the process of core excitation and the subsequent decay via resonant x-ray emission. Schematically this process is described in Fig. 1. In the first example the vibronic coupling of the decaying states will be considered via excitation of a localizing mode. This model applies, for instance, to \( \text{O}_1\text{s} \rightarrow \sigma^* \) core-valence transitions in CO\(_2\), where the localizing mode is the asymmetric stretching mode. By this mode the symmetry of the molecule is reduced from \( D_{\infty h} \) to \( C_{2v} \) and the phenomenon of dynamical core localization can take place. The model is also applicable to those \( \text{O}_1\text{s} \rightarrow \pi^* \) transitions where the Renner-Teller coupling (via the bending mode) is weak. Of course, the model can also be applied to any polyatomic molecule with two atoms equivalent by symmetry, where the action of the localizing mode(s) dominates over that of the other modes. The second example is devoted to the study of the impact of a symmetry breaking nonlocalizing mode in a symmetric linear molecule. It applies, for instance, to \( \text{O}_1\text{s} \rightarrow \pi^* \) excitations in CO\(_2\), where bending reduces the symmetry from \( D_{\infty h} \) to \( C_{2v} \), but preserves the equivalence of the two oxygen atoms. In the last example the combined action of a localizing and a symmetry breaking nonlocalizing mode is investigated.

Here, a remark on the numerical evaluation of the rates of photon emission intensities is in order. If the decaying state is excited with a general pulse and/or several modes are active, we refer to Ref. [22] for an efficient algorithm. In the specific examples discussed below (broad-band excitation) it sufficed to diagonalize the matrix Hamiltonians \( H_d \) and to compute the rates by inserting completeness into the corresponding expressions. The \( H_d \) were represented in a basis of one- and two-dimensional harmonic oscillators for the stretching and bending modes, respectively. The diagonalization and integration over time were performed using standard methods [23].

**A. \( \text{O}_1\text{s} \rightarrow \sigma^* \) transition: Excitation of the asymmetric stretching mode**

Owing to the two nearly degenerate core orbitals \( 1\sigma_g, 1\sigma_u \), the transition \( \text{O}_1\text{s} \rightarrow \sigma^* \) originates in two (nearly) degenerate core excited states \( |\Sigma_g \rangle \) and \( |\Sigma_u \rangle \), vibronically coupled via the asymmetric stretching mode. The energy gap between these core states is negligibly small, \( \sim 10^{-3} \) eV, compared to the frequency of the vibrational mode \( \omega_u = 0.291 \) eV and these states are considered as exactly degenerated. Then in a linear vibronic coupling model the Hamiltonian of nuclear motion in the delocalized representation reads [9,12,13]

\[
H_d = \begin{pmatrix}
H_0 & \lambda Q_u \\
\lambda Q_u & H_0
\end{pmatrix} - i \frac{\Gamma}{2} \mathbb{1},
\]

where \( H_0 = \frac{1}{2} \omega_u (P_u^2 + Q_u^2) + E_g, E_g \) is vertical energy difference between the initial and decaying states, \( Q_u \) is the (dimensionless) asymmetric stretch coordinate, and \( P_u \) is the corresponding conjugate momentum; the vibronic coupling between electronic states of different spatial symmetry \( |\Sigma_g \rangle, |\Sigma_u \rangle \) is described by interstate coupling constant \( \lambda \). With the transformation (4) to the localized representation \( H_d \) is readily diagonalized giving \( H_{d1,2} = H_0 \pm \lambda Q_u \). Using Eq. (15) and the results obtained in Ref. [12], the population of the core excited decaying states can be expressed explicitly in this model

\[
n_{\Sigma u}(t) = \frac{|\mu|^2}{2} e^{-\Gamma t} (1 + e^{2\Gamma t/\omega_u} - e^{-\Gamma t/\omega_u}),
\]

where \( f^2 = 2(\lambda/\omega_u)^2 \). As shown in Sec. II B, the rate of photon emission intensity to a final state is proportional to the population of the decaying state of appropriate symmetry for the transition to this final state [see Eq. (18)].

The populations \( n_{\Sigma u}, n_{\Sigma u} \) as a function of time are depicted in Fig. 3 in units of \( |\mu|^2 \) for the parameter values \( \omega_u = 0.291 \) eV [24], \( \Gamma = 0.14 \) eV [25] (\( \Gamma/\omega_u = 0.48 \)), and \( \lambda/\omega_u = 0.68 \) [26]. The physical quantities discussed here depend only on the ratios \( \Gamma/\omega_u \) and \( \lambda/\omega_u \). We have chosen these ratios to apply to a real system (CO\(_2\)) and that is why we have also reported above the individual underlying parameter values.

From Fig. 3 it is clear, that only the ungerade core excited state is initially populated and thus only the final gerade state is bright at \( t = 0 \). The population oscillates in time and flows from the \( |\Sigma_u \rangle \) to the \( |\Sigma_g \rangle \) state and vice versa via the vibronic coupling mechanism. At short time the flow is to \( |\Sigma_g \rangle \), i.e., \( n_{\Sigma u} \sim t^5 \), and the final ungerade state becomes bright too. In the figure the sum over populations \( n_{\Sigma u} + n_{\Sigma u} \) is shown as a solid line, is nothing but the function \( |\mu|^2 e^{-\Gamma t} \) and demonstrates the exponential decay of the total population of the intermediate state manifold.
The flow of population and, hence, the increase of emission intensity to the final ungerade state, which is dark in the absence of vibronic coupling, increases if the vibronic coupling increases. This is best demonstrated in Fig. 4, where the total photon emission intensity as a function of the interstate coupling constant $\lambda$ is presented (see also Ref. [12]). Figure 4 also demonstrates an increase of the intensity of originally dark states on the cost of the bright ones as the lifetime of the decaying states grows. This can be easily understood from the time dependence of the populations $n_g(t)$ and $n_u(t)$ depicted in Fig. 3. The longer the lifetime, i.e., the smaller $G$, the smaller the exponential damping and, hence, the larger the absolute amount of population flow.

$$\frac{n_g(t)}{n_u(t)} = \frac{1 - e^{2(\cos \omega \mu t - 1)}}{1 + e^{2(\cos \omega \mu t - 1)}}$$

and does not depend on the inverse lifetime $\Gamma$. In Fig. 5(a) this ratio is depicted as a function of time for two values of $\lambda/\omega_u$. In the present paper it is periodic because $H_0$ in Eq. (28) is harmonic and takes on its maximum at multiples of $t = \pi/\omega_u$.
This value increases with the magnitude of the interstate coupling constant $\lambda$ and approaches unity for infinitely strong vibronic coupling. It is interesting to note that the ratio of populations of the fully localized states is simply given by $n_1(t)/n_{-1}(t)=1$ and does not depend on nuclear dynamics [see Eq. (15)]. This value is indicated for comparison in Fig. 5(a) by a horizontal line. In Fig. 5(b) we show the population ratio of the delocalized states for an extremely large value of $\lambda/\omega_a$. Even for such values localization is not achieved at all times. As one can see from Eq. (30), the function $n_1(t)/n_{-1}(t)$ cannot be identical 1 at all times as $n_1(t)$ vanishes periodically. The “dips” in the function $n_1(t)/n_{-1}(t)$ become, however, narrower and narrower and the function approaches a horizontal line as the interstate coupling constant $\lambda$ grows. We conclude that full dynamical localization can be approached only asymptotically. The interstate coupling constant thereby characterizes the degree of exchange between the components $\Sigma^u$ and $\Sigma^g$ states, whereas the lifetime of the core states governs duration of the emission process.

For the discussion of Fig. 5 it is illuminating to consider Fig. 2 and Eq. (15). The larger $\lambda/\omega_a$, the steeper are the diabatic potential curves shown in the latter figure at their crossing point. The wave packet is created at $t=0$ in the vicinity of this crossing point. The larger $\lambda/\omega_a$, the faster the components $|\Psi_1(t)\rangle$ and $|\Psi_2(t)\rangle$ propagate away from each other and their overlap decreases. At the time interval when this overlap is negligible, the system behaves as if the states were localized. After a period of vibration the wave packets $|\Psi_1(t)\rangle$ and $|\Psi_2(t)\rangle$ return to their original position, their overlap is maximal and the system behaves as if the states were delocalized.

**B. O1s $\rightarrow \pi^*$ transition: Excitation of the bending mode**

The transition O1s $\rightarrow \pi^*$ leads to two nearly degenerate core excited states $|\Pi_0^+\rangle$ and $|\Pi_0^-\rangle$ and, therefore, four electronic component states are involved in the nuclear dynamics: $|\Pi_0^+,\Pi_0^+\rangle$, $|\Pi_0^+,\Pi_0^+\rangle$, and $|\Pi_0^-,\Pi_0^+\rangle$. The nuclear dynamics coupling the components of different inversion symmetry is governed by the asymmetric stretching mode, whereas the bending mode governs the dynamics coupling the $x$ and $y$ components of the same degenerate state. In this subsection we study the impact of the bending mode alone. In the next subsection the joint action of both modes is discussed.

At time $t=0$ the CO$_2$ molecule is excited from the totally symmetric ground electronic state to the $|\Pi_0^+\rangle$ core state. If only the excitation of the bending mode is taken into account, interstate vibronic coupling with the $|\Pi_0^+\rangle$ intermediate state is not operative and the decay from the $|\Pi_0^+\rangle$ state to final gerade states is the only decay possible. As the state $|\Pi_0^+\rangle$ does not appear in our discussions we omit for simplicity in the following also the index $\mu$ labeling the $|\Pi_0^+\rangle$ state whenever unambiguous.

\[
\begin{aligned}
\frac{n_1(t)}{n_{-1}(t)}_{\text{max}} &= \frac{1-e^{-2\gamma t}}{1+e^{-2\gamma t}}.
\end{aligned}
\]

Bending breaks the symmetry of the CO$_2$ molecule from D$_{sh}$ to C$_{2v}$ so that two oxygen atoms maintain their equivalence. In spite of the reduction of symmetry there is no localization of the core states and the nuclear dynamics problem consists in the vibronic coupling between the two doubly degenerate states $|\Pi_0^+\rangle,|\Pi_0^-\rangle$ via the doubly degenerate bending mode. In other words, in the present subsection we study the dynamical Renner-Teller effect in emission spectra.

Let us first study how the bending mode influences the population of the components $|\Pi_0^+\rangle$ and $|\Pi_0^-\rangle$ as a function of time and, hence, the rate of photon emission intensity. It is convenient to work in a complex electronic and vibrational basis and to use polar coordinates instead of the cartesian $x$ and $y$ for the degenerate bending coordinate. The transformation matrix to the complex basis $|\Pi_0^+,\Pi_0^-\rangle$ and coordinates reads [2,19,27]

\[
U_c = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ i & -i \end{pmatrix},
\]

\[
x = \rho \cos \varphi, \quad y = \rho \sin \varphi.
\]

The wave packet on the $|\Pi_0^+,\Pi_0^-\rangle$ manifold $|\Psi_0(t)\rangle$ has four components and its propagation is governed by the multidimensional Hamiltonian $H_d$, see Eq. (1). In the absence of interstate vibronic coupling $H_d$ has a block diagonal structure, each block is two dimensional and describes the bending nuclear motion in a degenerate $|\Pi_0\rangle$ state. These Hamiltonians are essentially identical and we denote them by $H_b$. In the leading order in the expansion of the potential matrix in terms of the bending coordinate $|\Psi_0(t)\rangle$, corresponding to the weak Renner-Teller coupling regime, this Hamiltonian reads

\[
H_b = \begin{pmatrix} H_{0(b)} & \gamma \rho^2 e^{2i\varphi} \\ \gamma \rho^2 e^{-2i\varphi} & H_{0(b)} \end{pmatrix} - \frac{i}{2} \Gamma 1,
\]

where $\gamma$ is the intrastate Renner-Teller coupling constant, $H_{0(b)}$ denotes the Hamiltonian of the bending motion in the ground state which is approximated by the two-dimensional harmonic oscillator with frequency $\omega_b$, and $\Gamma$ is the inverse lifetime of the decaying state.

The wave packet $|\Psi_0(t)\rangle$, propagating on the coupled $|\Pi_0^+\rangle$ and $|\Pi_0^-\rangle$ potential surfaces consists of two components $|\Psi_0^+(t)\rangle$ and $|\Psi_0^-(t)\rangle$. Since the Hamiltonian $H_b$ is nondiagonal, the motion of these two wave packets is interconnected. They read

\[
|\Psi_0(t)\rangle = \begin{pmatrix} |\Psi_0^+(t)\rangle \\ |\Psi_0^-(t)\rangle \end{pmatrix} = U_c \begin{pmatrix} |\Psi^+(t)\rangle \\ |\Psi^-(t)\rangle \end{pmatrix} = U_c e^{-iH_0 t} |\mu(0)\rangle,
\]

where $|\Psi^+(t)\rangle,|\Psi^-(t)\rangle$ are the wave packets in a complex basis, $\mu$ is a two-dimensional column vector of matrix elements of the dipole moment operator for the transitions from the initial totally symmetric ground state to the $|\Pi_0^+\rangle,|\Pi_0^-\rangle$ states of $\mu$. Following Sec. II B and the Appendix we note that the emission intensity depends on the angle $(\theta - \phi)$ between the polarizaton vectors of the emitted and ext-
citing light. We may, therefore, choose the initial population of the \(|\Pi,\rangle\) and \(|\Pi,\rangle\) components, which determines \(\phi\) according to our convenience. We assume that these states are initially equally populated, i.e., \(\phi = \pi/4\). The column vector \(\mu\) has the following appearance in the complex basis:

\[
\mu = \frac{1}{\sqrt{2}} \mu \begin{pmatrix} 1 - i \\ 1 + i \end{pmatrix}.
\] (35)

Since \(|\Pi,\rangle\) and \(|\Pi,\rangle\) are the components of a degenerate state, a number of simplifying relations hold. First,

\[
\text{Re}(\Psi^-(t)|\Psi^+(t)) = 0
\] (36a)

and, therefore, the populations of the electronic components \(n_x(t)\) and \(n_y(t)\) are equal to each other:

\[
n_x(t) = n_y(t) = \langle \Psi_{x(y)}(t)|\Psi_{x(y)}(t) \rangle = \langle \Psi^+(t)|\Psi^+(t) \rangle + \langle \Psi^-(t)|\Psi^-(t) \rangle / 2,
\] (36b)

Second, since the norm of \(|\Psi_b(t)\rangle\) is just an exponential, we find

\[
n_x(t) = n_y(t) = \frac{1}{2} \langle 0|\mu \mu^\dagger|0 \rangle e^{-\Gamma t},
\] (36c)

which is just \(|\mu|^2 e^{-\Gamma t}/2\) in the Condon approximation. Obviously, the populations of the \(|\Pi,\rangle\) and \(|\Pi,\rangle\) electronic components do not depend on the nuclear dynamics.

For later purposes it is useful to address the overlap of the two wave packets, propagating on the coupled \(|\Pi,\rangle\) and \(|\Pi,\rangle\) potential surfaces which depends on the Renner-Teller coupling constant

\[
\langle \Psi_x(t)|\Psi_x(t) \rangle = \langle \Psi_y(t)|\Psi_y(t) \rangle = -\text{Im}(\langle \Psi^-(t)|\Psi^+(t) \rangle).
\] (37)

Now we can evaluate the rate of the x-ray emission intensity. We may either use the general expression (21) derived in Sec. II B or compute the intensity explicitly for the particular case discussed here. The results are, of course, identical. We follow here the latter approach. The electronic components \(|\Pi,\rangle\) and \(|\Pi,\rangle\) of \(u\) symmetry decay to a final state of \(g\) symmetry, assumed for simplicity to be nondegenerate. The row vector \(W\) of dipole matrix elements between the ungerade \(|\Pi,\rangle\) and \(|\Pi,\rangle\) states and a final gerade state \(|f\rangle\) is equal to \(W = W_\text{cos} \theta \sin \theta, \theta\) determines the polarization of emission, and \(W/\sqrt{2} \{\text{exp}(i\theta),\text{exp}(-i\theta)\}\) in the complex basis \(|\Pi,\rangle, |\Pi,\rangle\). The matrix \(W^\dagger W\) in the complex basis reads

\[
W^\dagger W = \frac{|W|^2}{2} \begin{pmatrix} 1 & e^{-2i\theta} \\ e^{2i\theta} & 1 \end{pmatrix}.
\] (38)

Using the above relations (35),(36) the rate of intensity follows from the basic expression (17) in terms of the physically relevant quantity \(\Theta\) which is the angle between the direction of polarization of the excitation and the direction of the polarization of the emission.

\[
\frac{dI_\text{e}(\Theta,t)}{dt} = \langle \Psi_b(t)|W^\dagger W|\Psi_b(t) \rangle
\]

\[
= |W|^2 \left\{ \cos^2 \Theta |\mu|^2 e^{-\Gamma t} + \cos 2\Theta \left[ \langle \Psi_x(t)|\Psi_x(t) \rangle - \langle \Psi_y(t)|\Psi_y(t) \rangle \right] \right\}.
\] (39)

In the absence of Renner-Teller coupling \(\langle \Psi_x(t)|\Psi_x(t) \rangle = (|\mu|^2/2) e^{-\Gamma t}\) and the rate of emission becomes \(\cos^2 \Theta |W|^2 |\mu|^2 e^{-\Gamma t}\) as expected. The overlap \(\langle \Psi_y(t)|\Psi_y(t) \rangle\) governs the coherence of the emission. Renner-Teller vibronic coupling reduces this quantity and, hence, also the coherence of photon emission. We may introduce a term which describes the dynamical reduction of the coherence of emission and, consequently, the reduction of the interference of emission from the electronic states \(|\Pi,\rangle\) and \(|\Pi,\rangle\): cos \(2\Theta\{(\Psi_x(t)|\Psi_x(t)) - (|\mu|^2/2)e^{-\Gamma t}\}\). We denote this quantity dynamical interference term. It obviously vanishes in the absence of Renner-Teller coupling. It is also zero at time \(t = 0\). From Eq. (39) it is also evident that the angularly integrated rate of emission is \((|W|^2 |\mu|^2/2) e^{-\Gamma t}\) and does not depend on the Renner-Teller activity.

We note that the presence of the Renner-Teller coupling does not change the populations of the components [see Eq. (36c)] but influences the emission intensity via dynamical interferences. These lead to oscillations in the rate of photon emission at a given polarization \(\Theta\) which intensify with the increase of the Renner-Teller coupling constant (see Fig. 6). The dynamical interference term evolves oscillatory and induces oscillations in the intensity rate of photon emission as a function of time. These oscillations arise due to excitations of the bending vibronic levels. Our numerical analysis shows that several excitations contribute to the oscillations. The dominant one is the excitation from the ground vibronic level to the level which can be essentially characterized by two quanta of the bending mode.

In Fig. 6 the rate of emission is depicted for the same polarization as that of the excitation (solid lines in the main frame). For comparison the rate of photon emission in the absence of the Renner-Teller vibronic coupling is also presented (dashed lines). One observes the reduction of the rate of emission via Renner-Teller vibronic coupling. A reduction in the emission intensity which has the same polarization as the excitation is accompanied by an increase of intensity with a polarization orthogonal to that of the excitation. The dependence of the intensity on \(\Theta\) is shown in the inset of Fig. 6. A departure from the \(\cos^2 \Theta\) distribution is observed due to the activity of the Renner-Teller vibronic coupling.

In Fig. 6 the value of \(\Gamma/\omega_b\) used in computing curve (a) is characteristic for the \(\text{CO}_2\) molecule where \(\omega_b = 0.083\ \text{eV}\) and \(\Gamma = 0.14\ \text{eV}\). Because of the small bending frequency \(\omega_b\), the period of vibration \(2\pi\omega_b\) is long compared to the lifetime of the core excited states of \(\text{CO}_2\). This diminishes
C. O1s → π* transition: Mutual influence of asymmetric stretching and bending modes

Here we discuss the joint impact of the asymmetric stretching and the bending modes on the formation of resonant photon emission from the core excited |Π_s⟩ and |Π_u⟩ states. Two types of vibronic couplings are considered: interstate coupling between the states with different inversion symmetry, gerade and ungerade, via the asymmetric stretching mode and interstate coupling between the x, y components of each of these states via the bending mode. The Hamiltonian of nuclear motion $H_d$ in Eq. (3) is built in the diabatic delocalized basis $|Π_s⟩, |Π_u⟩, |Π_x⟩, |Π_y⟩$. Again we assume that $|Π_u⟩, |Π_y⟩$ states are equally populated (see Secs. II B and III B). The column vector $μ$ in this basis reads

$$μ = μ \begin{pmatrix} 1 \\ 1 \\ 0 \\ 0 \end{pmatrix},$$

and the row vector W is

$$W = W(\cos θ, \sin θ, 0, 0) \quad \text{if } |f⟩ \text{ is gerade},$$

$$W = W(0, 0, \cos θ, \sin θ) \quad \text{if } |f⟩ \text{ is ungerade},$$

where $θ$ is the polarization angle of emission. After transformation to a localized complex representation with the sequential use of the matrices $S$ (4) and $U_c$ (32), the Hamiltonian of nuclear motion $H_{dl}$ assumes a block-diagonal form. Each block $H_{dl,2}$, corresponding to one localized site, has the dimension 2 and contains operators of both stretching and bending modes. $H_{dl}$ and $H_{d2}$ differ by the sign in front of the interstate vibronic coupling constant $λ$. The matrix elements of the bending mode are the same in both site Hamiltonians. These Hamiltonians read

$$H_{dl,2} = \frac{H_0 ± λQ_u}{γρ^2 e^{2iϕ}} - \frac{i}{2} Γ_1.$$
One can represent the Hamiltonian $H_{d,1,2}$ as an additive sum of Hamiltonians containing operators of a single mode:

$$H_{d,1,2} = H_{1,2} + H_b - \frac{i}{2} \Gamma 1,$$

(42b)

where

$$H_{1,2} = \begin{pmatrix} H_{0(Q_u)} \pm \lambda Q_u & 0 \\ 0 & H_{0(Q_g)} \pm \lambda Q_u \end{pmatrix}$$

$$H_b = \begin{pmatrix} H_{0(b)} & \gamma \rho e^{2i\varphi} \\ \gamma \rho e^{-2i\varphi} & H_{0(b)} \end{pmatrix}$$

(42c)

$H_{1,2}$ are the Hamiltonians containing the stretching mode operators only; $H_b$ is the Hamiltonian for the bending motion only and is identical with that in the preceding example.

Of great importance is the fact that $H_{1,2}$ commutes with $H_b$. Consequently, the $|\Psi_r(t)\rangle$ and $|\Psi_s(t)\rangle$ wave packets are each a product of the wave packets propagating separately along stretching and bending normal coordinates

$$\left| \Psi_{uAx}(t) \right\rangle = \frac{1}{\sqrt{2}} \left( |\Psi_1(t)\rangle \pm |\Psi_2(t)\rangle \right),$$

(43)

$$\left| \Psi_{uAy}(t) \right\rangle = \frac{1}{\sqrt{2}} \left( |\Psi_1(t)\rangle \pm |\Psi_2(t)\rangle \right),$$

The upper sign belongs to the $u$ state, the lower one to the $g$ state. Note that $|\Psi_1(t)\rangle$ and $|\Psi_2(t)\rangle$ are exactly those wave packets propagating on the potential energy surfaces of the localized core states introduced in our first example (Sec. III A) where the same notation is used. $|\Psi^+(t)\rangle$ and $|\Psi^-(t)\rangle$ are the same wave packets as those in our second example (pure Renner-Teller case, Sec. III B) apart from a trivial factor: $|\Psi^+(t)\rangle$ and $|\Psi^-(t)\rangle$ in Eq. (43) must be multiplied by $(\mu/\sqrt{2})e^{-1/2}$ in order to obtain the $|\Psi^+(t)\rangle$ and $|\Psi^-(t)\rangle$ introduced in Sec. III B.

The individual populations of the decaying states $|\Pi_{Ax}, \Pi_{Ay}, \Pi_{xg}, \Pi_{yg}\rangle$ boil down with the aid of Eq. (36) to

$$n_{uAx}(t) = n_{uAy}(t) = \frac{1}{2} \left| \frac{|\mu|^2}{2} e^{-1/2} \pm \text{Re}(\Psi_1(t)|\Psi_2(t)) \right|,$$

(44a)
i.e., they do not depend on the bending motion. The result is identical to $n_{uAx}(t)$ found in Sec. III A for the localizing asymmetric stretching mode. The mixed term

$$\langle \Psi_{uAx}(t)| \Psi_{uAy}(t) \rangle$$

$$= -\frac{1}{2} \text{Im}(\Psi^-(t)|\Psi^+(t))$$

$$\times \left( \frac{|\mu|^2}{2} e^{-1/2} \pm \text{Re}(\Psi_1(t)|\Psi_2(t)) \right)$$

(44b)
on the other hand, depends on both types of motion. This implies that there is a combined impact of symmetry breaking nonlocalizing and of localizing modes on the emission intensity.

The rate of photon emission follows from the general equation (17), but can also be obtained from Eq. (21). The emission rate is proportional to the appropriate (coherent) population of a degenerate decaying state. Using Eq. (44) it can be conveniently written as a product

$$\frac{dI_{g(u)}(\Theta,t)}{dt} = |W|^2 \left( \cos^2 \Theta - \cos 2\Theta \frac{1 + \text{Im}(\langle \Psi^-(t)|\Psi^+(t)\rangle)}{2} \right)$$

$$\times \left( \frac{|\mu|^2}{2} e^{-1/2} \pm \text{Re}(\langle \Psi_1(t)|\Psi_2(t)\rangle) \right),$$

(45)
of a bending and a stretching contribution. Nontrivial effects are manifested by interferences of individual wave packets; of wave packets corresponding to different atomic sites 1 and 2, and of wave packets corresponding to the two components of the Renner-Teller active states. Of course, the bending mode has no impact on the angularly integrated decay rate.

It is useful to discuss the ratio of the photon emission rates computed with and without the presence of the bending mode. From Eqs. (45) and (15) we see that this ratio is nothing but $\frac{1}{2} \{1 - \cos 2\Theta \text{Im}(\langle \Psi^-(t)|\Psi^+(t)\rangle)\}$, i.e., it is completely determined by the Renner-Teller effect alone. This ratio is depicted in Fig. 8 as a function of time for $\Theta = 0$ and the same set of parameters used in Secs. III A and III B. The curve exhibits two types of oscillations. The fast oscillation corresponds to that seen in Fig. 6 and discussed in the preceding subsection. The slow oscillation is due to the excita-
tion from the ground vibronic level to the first excited
Renner-Teller level of the same symmetry. The rate of intensity
(45) is maximally affected by the bending motion at a
time close to the period $2\pi/\omega_b$ of the bending vibration. At
that time the populations of the $g$ and $u$ states are already
strongly damped because of the short lifetime of the core
excited states ($\Gamma=0.14$ eV in CO$_2$). Molecules with longer
lived core states can exhibit a much stronger impact of sym-
metry breaking nonlocalizing modes on the rate of emission.
The presence of modes of this type faster than the slow bend-
ing motion may also intensify this impact. After all, the fac-
tor $\frac{1}{2}\{1-\text{Im}(\langle \Psi^-|\Psi^+(t)\rangle)\}$ shown in Fig. 8 is substantial.

The integral over time of the rate of intensity (45) gives the
x-ray emission intensity at a polarization angle $\Theta$ relative
to that of the exciting light. Figure 9 reproduces the emission
intensity for light with the same polarization as the excita-
tion, i.e., $\Theta=0$, as a function of interstate and intrastate coupling
constants $\lambda$ and $\gamma$ for different inverse lifetimes $\Gamma$. The
values shown are normalized by the sum of emission intensities
from the decaying $|\Pi_g\rangle$ and $|\Pi_u\rangle$ states in the presence of intrastate coupling alone, i.e., for $\lambda=0$. With Fig. 9 we pri-
marily do not intend to study the absolute impact of the
Renner-Teller coupling on the emission intensity itself. We
rather hope to learn about the impact of this coupling on the
dynamical core hole localization. Therefore, we remove that
part of the impact of the Renner-Teller coupling which does
not lead to localization by normalizing the intensity by that
at $\lambda=0$. To avoid confusion we denote the values shown in
Fig. 9 by “normalized intensity.” The picture in the main
frame addresses a fragment of the picture inserted in the right
upper corner. In the latter picture the upper bundle of lines
refers to the normalized emission intensity to a gerade final
state, the lower bundle to that of an ungerade state (see also
Fig. 4). In the main frame the solid lines corresponding to
different lifetimes refer to the normalized emission intensity
for zero intrastate Renner-Teller coupling as a function of
$\lambda/\omega_a$. Accompanying them one can see broken lines which
correspond to nonzero intrastate coupling constants $\gamma$

$$\gamma=0.06 \text{ eV}, \omega_b=0.15 \text{ eV} \text{ (long dashed lines)}$$

$$\gamma=0.23 \text{ eV}, \omega_b=0.5 \text{ eV} \text{ (dotted lines)}$$

For gerade (ungerade) final states one observes at $\Theta=0$ an increase (decrease)
of the normalized x-ray emission intensity by intrastate
Renner-Teller vibronic coupling, which grows with $\gamma$ and $\omega_b$. The vibronic coupling via the bending mode quenches the
effect of the vibronic coupling via the localizing asym-
metric stretching mode. This result points to an apparent in-
fluence on dynamical core hole localization by symmetry
breaking nonlocalizing modes if the emission of only one
polarization is measured. The strength of this influence de-
pends on the lifetime of the intermediate electronic states.

IV. SUMMARY AND CONCLUSIONS

A time-dependent description was presented of the pro-
cess of electronic excitation into a manifold of vibronically
coupled intermediate core excited states which continuously
decay by x-ray emission to final states of appropriate sym-
metry. In symmetric systems two or more atoms are equiva-
ient by symmetry and vibronic coupling among the core ex-
cited states is generic. The photon emission intensity rate
from the decaying manifold to a final state is found to be
proportional to the time-dependent population of the core
excited state of appropriate symmetry. For instance, if the
final state is of gerade (ungerade) symmetry its intensity rate
is proportional to the population of the ungerade (gerade)
core excited state in accordance with the optical dipole se-
lection rules. If the ground state is, for instance, gerade, the
excitation populates the ungerade core excited electronic
state which may emit photons and decay to gerade final
states. In the absence of vibronic coupling the ungerade final
states do not acquire intensity and stay dark. In the presence
of vibronic coupling population flows from the ungerade to
the gerade core excited state as a function of time and un-
gerade final states become bright. Since vibronic coupling
between the core excited decaying states is done by symme-
try breaking nuclear modes, we encounter a dynamical sym-
metry breaking of the molecule and a localization of the electronic core states takes place. This localization is incomplete and depends on the strength of vibronic coupling and on the lifetime of the core states. The picture of \textit{a priori} localized core states gives rise to a substantially wrong result. This result is only approached in the case of infinitely strong vibronic coupling.

Coherence plays an important role in the description of the dynamical symmetry breaking. The populations of the symmetry adapted core states appear in the expressions for the emission rates. If these states are degenerate, the relevant population is that of the coherent superposition of the degenerate components, e.g., $|\Pi_\alpha\rangle$ and $|\Pi_\beta\rangle$, of a state. Expressing the symmetry adapted core states as a linear combination of localized core states as dictated by symmetry, we again encounter a coherent superposition in the equation for the emission rate. The emission rate then depends on the time-dependent overlap $\langle \Psi_f(t)|\Psi_g(t) \rangle$ of the nuclear wave packets corresponding to the localized core excited electronic states. This overlap leads to strong interference effects which are suppressed by vibronic coupling. At infinitely strong vibronic coupling this overlap vanishes, there is no coherence of emission from the localized states left, and the resulting emission intensity is that of \textit{a priori} localized states, i.e., as if the core states were truly localized.

The dynamics of two types of nuclear modes are considered: localizing and symmetry breaking nonlocalizing modes. Distortion of the first type of modes reduces the symmetry of a highly symmetrical molecule and makes atoms initially equivalent by symmetry inequivalent. Consequently, the core component of the core excited molecular state becomes localized on a single atomic site. To symmetry breaking nonlocalizing modes belong modes that break the symmetry of a molecule retaining the equivalence of the atoms. The core component of the core excited state is delocalized over the atoms equivalent by symmetry. The dynamics of these two types of modes involved in the process of x-ray emission is explicitly discussed for a linear symmetric molecule such as, e.g., CO$_2$. In this example the localizing mode is the nondegenerate asymmetric stretching mode, and the doubly degenerate bending mode is the symmetry breaking nonlocalizing mode. The dynamics of the stretching mode is considered first. This model is applicable for instance, for O1$s\rightarrow\sigma^*$ transitions, where the resulting core excited states $|\Sigma_g\rangle$ and $|\Sigma_u\rangle$ are vibronically coupled (interstate vibronic coupling). In the second example we discuss the excitation of the bending mode via the dynamical Renner-Teller effect in the electronic components $|\Pi_\alpha\rangle$ and $|\Pi_\beta\rangle$ of a doubly degenerate core state arising from, e.g., O1$s\rightarrow\pi^*$ transitions (intrastate vibronic coupling). The joint action of both asymmetric stretching and bending modes is considered in the third example for the $|\Pi_\alpha\rangle$ and $|\Pi_\beta\rangle$ cores resulting from the latter mentioned transitions. Here both intrastate and interstate vibronic couplings are active and the coupling among the four states $|\Pi_{\alpha\beta}\rangle,|\Pi_{\alpha\gamma}\rangle,|\Pi_{\beta\gamma}\rangle,|\Pi_{\alpha\gamma}\rangle$ must be considered. The time-dependent evaluation of the nuclear dynamics clarifies that to the leading approximation the populations of the decaying states and hence also the rates of photon emission intensity are products of contributions from each individual nuclear mode. This useful result sheds light on the multimode dynamics in x-ray emission spectra.

For the pure Renner-Teller case (second example) the \textit{coherent} superposition of the nuclear wave packets corresponding to the $|\Pi_\alpha\rangle$ and $|\Pi_\beta\rangle$ electronic states leads to interference effects. This interference is maximal in the absence of intrastate vibronic coupling. Renner-Teller activity reduces the interference. This reduction is dynamical in nature and best described by the dynamical interference term $\langle (\psi_1(t)|\psi_2(t)) - \langle \psi_1(0)|\psi_2(0) e^{-i\Delta E}\rangle$. The situation is formally similar to that encountered in intrastate vibronic coupling, where the dynamics of a localizing mode supresses the interferences. In this case the reduction of interference is governed by $\langle (\psi_1(t)|\psi_2(t)) - \langle \psi_1(0)|\psi_2(0) e^{-i\Delta E}\rangle$. The individual impact of the suppression of coherence by the two types of nuclear modes on observables is, however, very different. Whereas the localizing mode enforces dynamical localization leading to a violation of the electronic optical selection rules, the symmetry breaking nonlocalizing mode changes the polarization of the emitted light. When the simultaneous activity of both modes is considered, we find in addition that intrastate vibronic coupling exerts an apparent impact on the dynamical localization caused by interstate vibronic coupling if the emission of only one polarization is measured.

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**APPENDIX: ANGULAR DEPENDENCE OF THE EMISSION INTENSITY**

In the following we discuss the dependence of the emission intensity on polarization. An intermediate $|\Pi_{\alpha}\rangle$ state is considered and for simplicity of representation we concentrate on linearly polarized light propagating along the molecular axis which is denoted by $z$. The angle between the polarization vector of the exciting and emitted light and the $x$ axis is $\phi$ and $\theta$, respectively.

The column dipole vector $\mu$ has the components $\mu \cos \phi$ and $\mu \sin \phi$ and the row vector of dipole matrix elements between the decaying and the final state is $W = W(\cos \theta, \sin \theta)$. The rate of emission intensity (17) now reads

$$\frac{dI_f(t)}{dt} = \langle \Psi_f(t)|W^\dagger W|\Psi_f(t) \rangle$$

$$= |W|^2|\mu|^2 \left[ \langle 0|\cos \phi, \langle 0|\sin \phi \rangle e^{iH_d t} \right]$$

$$\times \left[ \begin{array}{c} \cos^2 \theta & \sin \theta \cos \theta \\ \sin \theta \cos \theta & \sin^2 \theta \end{array} \right] e^{-iH_d t} \left[ \begin{array}{c} \cos \phi |0\rangle \\ \sin \phi |0\rangle \end{array} \right].$$  

(A1)
VIOLATION OF ELECTRONIC OPTICAL SELECTION . . .

Let us consider a transformation of the initial coordinate system \((x, y, z)\) to the system \((x', y', z)\), the \(x'\) axis of which coincides with polarization vector of exciting light. The transformation matrix reads

\[
\begin{pmatrix}
\cos \phi & \sin \phi \\
-\sin \phi & \cos \phi
\end{pmatrix}.
\]  

(A2)

The wave packet describing the nuclear motion on the potential energy surfaces of a doubly degenerate intermediate state via the bending mode reads (the subscript \(u\) is suppressed)

\[
|\Psi_u(t)\rangle = \begin{pmatrix} |\Psi_x(t)\rangle \\ |\Psi_y(t)\rangle \end{pmatrix} = \mu e^{-i\vec{H}_d t} \begin{pmatrix} \cos \phi |0\rangle \\ \sin \phi |0\rangle \end{pmatrix},
\]  

(A3)

and after the transformation to \((x', y', z)\) coordinate system it gets the following appearance:

\[
|\Psi_u'(t)\rangle = \begin{pmatrix} |\Psi_{x'}(t)\rangle \\ |\Psi_{y'}(t)\rangle \end{pmatrix} = \mu e^{-i\vec{H}_d t} \begin{pmatrix} |0\rangle \\ |0\rangle \end{pmatrix}.
\]  

(A4)

Here, \(\vec{H}_d\) is the Hamiltonian transformed with the transformation (A2). Obviously, in the coordinate system connected with the polarization vector of the exciting light, only the \(|\Pi>\) component of the doubly degenerate state is populated initially. The Hamiltonian \(\vec{H}_d\) couples the nuclear motion on the \(|\Pi\rangle\) and \(|\Pi\rangle\) components and provides a population flow in time from the \(|\Pi>\) to the \(|\Pi>\) component. Expressed in the new coordinates \((x', y')\), this Hamiltonian has the same appearance as \(\vec{H}_d\) in \((x, y)\) coordinates, i.e., the Hamiltonian is invariant to the transformation (A2).

The row vector of dipole matrix elements between the decaying and the final states \(W\) transformed to the \((x', y', z)\) coordinate system reproduces the dependence on the angle between the polarizations of exciting and emitted light, namely,

\[
W' = W(\cos(\theta - \phi), \sin(\theta - \phi)).
\]  

(A5)

Substituting the transformed \(|\Psi_u'(t)\rangle\) and \(W'\) into (A1) leads to

\[
\frac{dI_{\phi}(\theta - \phi, t)}{dt} = |W|^2 \langle \cos(\theta - \phi) \Psi_{x'}(t) + \sin(\theta - \phi) \Psi_{y'}(t) \rangle \times \cos(\theta - \phi) \Psi_{x'}(t) + \sin(\theta - \phi) \Psi_{y'}(t) \rangle.
\]  

(A6)

The rate of photon emission intensity is thus a function of only one angular parameter—the angle between the polarization vectors of the exciting and emitted light. It does not depend on the orientation of the polarization of the excitation which can, therefore, be chosen arbitrarily.


Phys. Rev. Lett. 79, 3371 (1997), and references herein.  
[26] $\lambda/\omega_p$ values between 0.5 and 1 are typical values for $|\Sigma\rangle$ core excited states of CO2 and other small symmetric systems such as C2H4 [see Ref. [4] and N. Dobrodey et al., J. Chem. Phys. (to be published)].  