Quenching of Symmetry Breaking in Resonant Inelastic X-Ray Scattering by Detuned Excitation

P. Skytt,[1] P. Glans,[1,2] J.-H. Guo,[1] K. Gunnelin,[1] C. Såthe,[1] J. Nordgren,[1] F. Kh. Gel'mukhanov,[3]
A. Cesar,[3] and H. Ågren[3]
[1]*Department of Physics, Uppsala University, Box 530, S-75121 Uppsala, Sweden*
[2]*Department of Chemistry, University of Nevada-Las Vegas, Box 454003, Las Vegas, Nevada 89154*
[3]*Institute of Physics and Measurement Technology, Linköping University, S-58183, Linköping, Sweden*
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Observations made in oxygen K emission of CO_2 show that the symmetry selective character of resonant x-ray emission is excitation energy dependent. Electronically dipole forbidden O K emission lines are observed for excitation at the O $1s \rightarrow \pi^*$ resonance, and they are gradually reduced upon detuning the excitation energy below threshold. The occurrence of forbidden transitions is explained in terms of dynamical symmetry breaking due to vibronic coupling, and the observation of quenching of the symmetry breaking upon detuning as due to an effective quenching of this vibronic coupling. Scattering theory applied to a few-level system is shown to account for the energy dependence of the symmetry selection in the limit of narrow bandpass photon excitation. [S0031-9007(96)01834-0]

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The symmetry-selective character of resonant x-ray scattering (RXS) makes resonant x-ray emission (RXE) spectroscopy a powerful tool for electronic structure investigations. The preparation of the intermediate state by the core excitation and the dipole selection rules for the full absorption/emission process restrict the possible symmetries of all involved states. This has made it possible to determine symmetries of unoccupied and occupied orbitals in molecules [1–4]. A complicating factor is the role of vibronic coupling which is expected to lower the symmetry of the system, allowing transitions which are otherwise electronically symmetry forbidden [2,3,5,6]. A correct description of this incoherent contribution is of major importance for understanding the characteristics of RXS in general, for both free molecules and solids [6–10].

Experimental results on homonuclear diatomic molecules firmly established the symmetry-selective character of RXE spectroscopy, as recently demonstrated by measurements on molecular oxygen [4] and nitrogen [11], where the parity selection rule strictly applies. Diatomic molecules only possess a totally symmetric vibrational mode that cannot break the electronic symmetry, and the selection rules therefore operate directly on the electronic symmetry of the states. In order to better understand and quantify the effect of the nontotally symmetric vibrations, we have chosen to investigate a simple system, O K emission of CO_2. As O_2 is a good test case for the demonstration of parity selection in resonant x-ray emission, CO_2 is an equally natural candidate to explore symmetry breaking. The addition of a carbon atom between the two oxygen atoms introduces an antisymmetric stretch mode which can couple the "dark" $1\sigma_u^{-1}2\pi_u$ and the "bright" $1\sigma_g^{-1}2\pi_u$ oxygen core-excited states and, therefore, break the parity selection rule [5]. The intensity of the x-ray emission resulting from the forbidden "dark" state then gives a measure of the magnitude of the symmetry breaking. The main result of the present work is that the symmetry breaking depends strongly on the excitation energy for narrow bandpass excitation. Thus when detuning the excitation energy below the x-ray absorption resonance, the effective vibronic coupling strength is quenched and the symmetry selection rules apply more strictly. In contrast to nonresonant x-ray emission [12] and x-ray absorption [13] the RXE method therefore allows for the possibility to "restore" the dipole selection rules in systems with dynamical vibronic coupling between electronic states of different symmetries.

A very simple illustration of the symmetry breaking problem in CO_2 is given in Fig. 1, with comparison to the

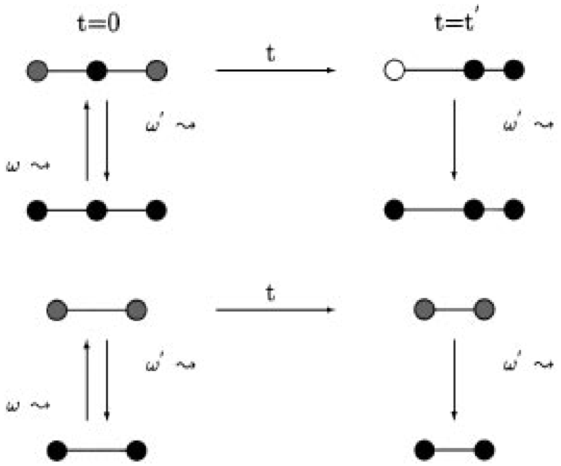

FIG. 1. A simple picture of the symmetry problem for RXS transitions in CO_2 and O_2. White, dashed, and black balls denote 0%, 50%, and 100% occupied core orbital, respectively, where "50%" means superposition of two states with core holes on different oxygen atoms.

O_2 case. At the time of excitation ($t = 0$) the core hole is equally distributed over the two oxygen centers keeping the inversion symmetry, which for both molecules can be described as a superposition of two states with left and right hole localization. The vibronic coupling over the antisymmetric stretch mode between the close lying gerade and ungerade (adiabatic) electronic core hole states of CO_2 leads at time $t = t'$ to an effective shift of the molecular equilibrium with the inversion symmetry broken and to the localization of the core hole to the left or to the right oxygen atom [14]. For the O_2 molecule, the totally symmetric vibrational motion cannot break the electronic symmetry, and the core-excited state remains as a superposition of two hole-states with retained inversion symmetry at all times. We note that "time" here should be considered as the duration time of the RXS process (or correlation time between absorption and emission) which is determined both by the core-excited state lifetime and the inverse of the detuning frequency. The symmetry breaking thus "takes time" and the degree of symmetry breaking therefore critically depends on the vibrational frequency and the duration of the RXS process. If the duration time is much smaller than the vibrational time period, the molecule has no time to execute the antisymmetric vibration that introduces forbidden parity in the electronic wave function through the vibronic coupling.

One can thus introduce a concept of time by regarding the extreme cases of exciting on resonance, respectively, far from resonance (in analogy with resonant and nonresonant photoemission). In the latter case we are dealing with a prompt process (Raman scattering), whereas on resonance the lifetime of the resonant state determines the interaction time (resonant Raman scattering). Tuning away from resonance shortens the duration of the RXS process, and one probes preferentially transitions associated with shorter lifetimes. Thus, vibronic symmetry breaking will be less and less effective.

A qualitative explanation behind the quenching of symmetry breaking can be obtained also from a time-independent picture. We consider the double differential cross section for RXS,

$$\sigma(\omega, \omega') = \sum_f \frac{\omega'}{\omega} |F_f|^2 \Phi(\omega' + \omega_{f0} - \omega, \gamma), \qquad (1)$$

where Φ is the normalized spectral function of the excitation radiation centered at frequency ω and with the width γ. The scattering amplitude F_f is given by the resonant term in the Kramers-Heisenberg formula,

$$F_f = \alpha \omega \omega' \sum_i \frac{\langle f|D'|i\rangle\langle i|D|O\rangle}{\omega' - \omega_{if} + i\Gamma}, \qquad (2)$$

using atomic units and standard notations. This amplitude describes the absorption of the initial and the emission of the final x-ray photons with frequencies ω and ω', respectively. ω_{if} is the resonance energy for transitions between intermediate and final states, and 2Γ is the lifetime width of the intermediate states.

We consider the envelope of excited state vibrational levels $\{i\}$ to have an effective width Δ. We consider also the detuning energy Ω defined as the difference between the excitation photon energy ω and the center of that vibrational envelope. When the detuning energy is much larger than the effective width of the absorption band, $\Omega \gg \Delta$, the denominator can be removed from the sum in the RXS amplitude in Eq. (2). This means that the summation over intermediate vibrational levels $\{i\}$ can be made complete ($\Sigma_i |i\rangle\langle i| = 1$) and the scattering amplitude takes the simple form

$$F_f \propto \langle f|D'D|O\rangle. \qquad (3)$$

It thus becomes independent of (the symmetry broken) intermediate state, and restores the "quadrupole selection rules" of the x-ray scattering tensor [1]. The same operation can be carried out if the lifetime width is large, $\Gamma \gg \Delta$, in which case the resonance x-ray transition thus also will be symmetry purified.

The expression for the scattering amplitude F_f, Eq. (3), can be equally well obtained in a time-dependent representation of the RXS amplitude. The wave packet excited from the ground state at time $t = 0$ decays to the final molecular states at different times ($0 \leq t \leq \infty$). The partial RXS amplitude corresponding to the time t is proportional to the phase factor $\exp(i\Omega t - \Gamma t)$. When the lifetime broadening or the detuning Ω is large, only a partial amplitude (at $t = 0$) of the sudden transition gives significant contributions to F_f. Contributions from decay events at $t \neq 0$ are negligibly small, due to a large damping factor $\exp(-\Gamma t)$ when Γ is large or because the factor $\exp(i\Omega t)$ is oscillating fast when the detuning frequency is large. The quantity $\tau_c = 1/\sqrt{\Omega^2 + \Gamma^2}$ thus characterizes the "suddenness" or "duration" of the RXS process.

Figure 2 shows the detuning spectra referring to resonant excitation to the first unoccupied level, $2\pi_u$, of CO_2 giving the forbidden $|g\rangle = 1\sigma_u^{-1} 2\pi_u\, {}^1\Pi_g$ and allowed $|u\rangle = 1\sigma_g^{-1} 2\pi_u\, {}^1\Pi_u$ core-excited states. The spectra consist of two peaks; the high-energy peak derives from transitions to the forbidden $|f(u)\rangle = |1\pi_g^{-1} 2\pi_u\rangle\, {}^1\Pi_u$ final state and the low-energy peak to the allowed $|f(g)\rangle = 1\pi_u^{-1} 2\pi_u\rangle\, {}^1\Pi_g$ final state (configuration state splitting and contribution from the weak $4\sigma_g$ emission can be neglected [17]). As seen in the figure, the high-energy peak receives significant intensity in violation of the selection rule, and appears quite like the nonresonant x-ray emission spectrum of CO_2 [17]. Thus, the core-excited state cannot be described as a pure $|1\sigma_g^{-1} 2\pi_u\rangle\, {}^1\Pi_u$ state, but must be mixed with the $|1\sigma_u^{-1} 2\pi_u\rangle\, {}^1\Pi_g$ state. By detuning the energy it is clear that the spectrum becomes symmetry purified. The experiments were performed at beam line 7.0 at the Advanced Light Source in Berkeley [15,16], and are described in full in Ref. [17].

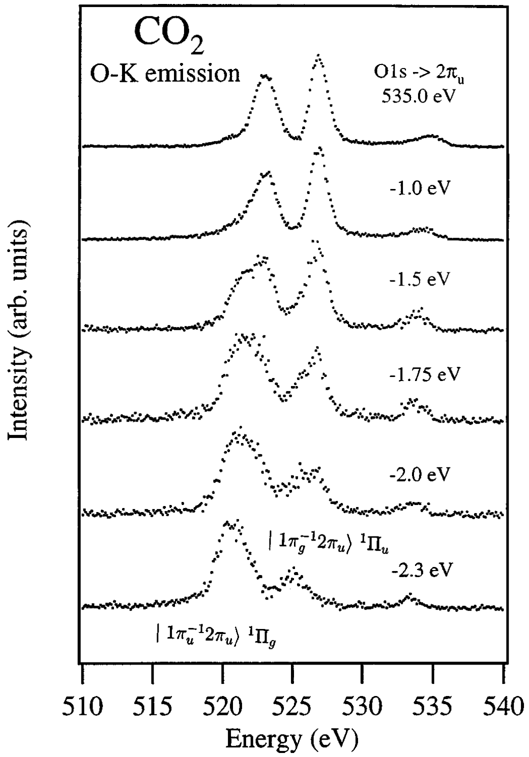

FIG. 2. Oxygen K $2\pi_u$ resonant x-ray emission spectra of CO_2 with different detuning energies below the $2\pi_u$ resonance.

We estimate the resolution of the monochromator and spectrometer in these measurements to be approximately 0.65 and 1.0 eV at full width half maximum, respectively.

We apply a five-level model to the symmetry-breaking problem examining the qualitative difference between broad-band and narrow-band limits for the excitation functions; see Fig. 3. The five-level system considers the O $1s$ transitions to the unoccupied $2\pi_u$ molecular orbital and the following decay transitions to the ungerade and gerade final states, resulting in the high-energy and low-energy peaks, respectively. Initially, the molecule is in the grade ground state. Without vibronic coupling the two intermediate core-excited states, $|g\rangle = |1\sigma_u^{-1}2\pi_u\rangle$ and $|u\rangle = |1\sigma_g^{-1}2\pi_u\rangle$, are eigenstates of the unperturbed electronic Hamiltonian H_0. These two states can be assumed to be degenerate with negligible energy splitting ($\simeq 0.005$ eV). Of the two final states, $|f(u)\rangle = |1\pi_g^{-1}2\pi_u\rangle\,^1\Pi_u$ and $|f(g)\rangle = |1\pi_u^{-1}2\pi_u\rangle\,^1\Pi_g$, only the latter can be reached by dipole transitions because the absorption transition to the dark, gerade, state is forbidden by the dipole selection rules.

In the case of vibronic coupling the two intermediate core-excited states $|g\rangle$ and $|u\rangle$ are mixed by the antisymmetric vibrational mode, with an effective vibronic coupling U. Since the unperturbed intermediate states $|g\rangle$ and $|u\rangle$ are assumed degenerate, the new mixed states, which are eigenfunctions of the total Hamiltonian $H = H_0 + U$, are localized completely to the different oxygen atoms (atoms 1 and 2),

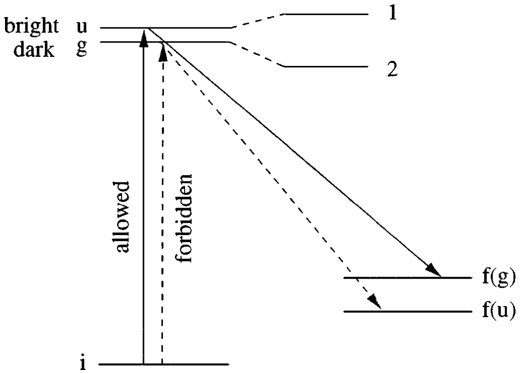

FIG. 3. Five-level system interacting with an exciting field of frequency ω and a scattered field of frequency ω'.

$$|1\rangle = \frac{1}{\sqrt{2}}(|g\rangle + |u\rangle), \quad |2\rangle = \frac{1}{\sqrt{2}}(|g\rangle - |u\rangle). \tag{4}$$

The vibronic coupling U eliminates the degeneracy and leads to that the energy eigenvalues of the new states in Eq. (4) are split by 2λ, where $\lambda = \langle u|U|g\rangle$ is the dynamical vibronic coupling parameter.

The relative intensities of the "forbidden" and "allowed" transitions are given by the ratio of the integral cross section which is proportional to the area of the relevant x-ray emission peak [18]. The broad-band, $\gamma \gg \Delta$, and narrow-band, $\gamma \ll \Delta$, limiting cases for the excitation function have qualitatively different outcomes for the symmetry-breaking problem.

For broad-band excitation, the spectral function Φ [Eq. (1)] can be considered constant, and the intensity ratio of the "forbidden," high-energy peak and the "allowed," low-energy peak is then given by

$$\rho = \frac{d'^2_{f(u)g}}{d'^2_{f(g)u}}\,\chi, \tag{5}$$

where

$$\chi = \frac{(\lambda/\Delta)^2}{2 + (\lambda/\Delta)^2}, \quad 0 \le \chi \le 1. \tag{6}$$

The notations $d'_{f(u)g} = \langle f(u)|D'|g\rangle$ and $d'_{f(g)u} = \langle f(g)|D'|u\rangle$ correspond to the dipole matrix elements for emission. When $\lambda = 0$, i.e., when the dynamical vibronic coupling can be neglected, χ becomes equal to zero. Thus in this limiting case only transitions to the gerade final state are allowed. When $\lambda/\Delta \gg 1$, i.e., when the vibronic coupling is strong, $\chi = 1$ and the ratio only depends on the matrix elements for the emission. We would in this strong dynamical vibronic coupling case expect approximately the same ratio as in the nonresonant spectrum, and the information about the parity of the unoccupied orbital to which the core electron is promoted is thus lost. The result, Eqs. (5) and (6), for the broad-band limit qualitatively agrees with the frequency-independent analysis of Cederbaum [5].

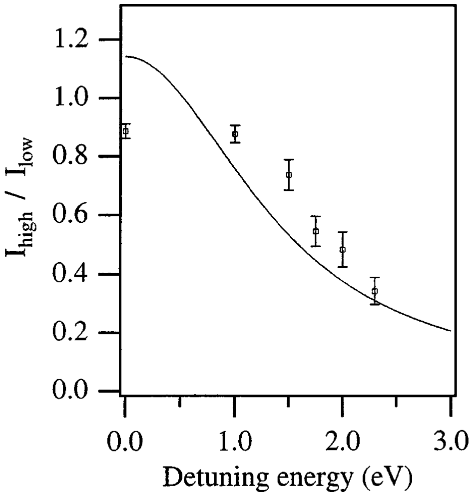

FIG. 4. Ratio between high- and low-energy peaks of the resonant O *K* emission spectra as a function of detuning energy.

For narrow-band excitation ($\gamma \ll \Delta$), on the other hand, the spectral function Φ can be replaced by a δ function in energy. The initial and final photon frequencies then connect through energy conservation, $\omega = \omega' + \omega_{f0}$. The RXS cross section can again be presented in the form of Eq. (5) but with a different value for the parameter χ. The important difference to the case of broad-band excitation, Eq. (6), is that the χ function now depends on the incoming photon frequency,

$$\chi = \frac{\lambda^2}{\Omega^2 + \Delta^2}, \quad 0 \leq \chi \leq \left(\frac{\lambda}{\Delta}\right)^2. \tag{7}$$

One can see from this equation that dynamical vibronic coupling effectively vanishes ($\chi = 0$) in the limit where the detuning is large.

The ratio between experimental intensities of the high-energy and low-energy spectator peaks are plotted versus the detuning energy, measured from the vertical absorption energy, in Fig. 4. We note a gradual decrease in the intensity ratio. The solid line is the prediction based on our simple five-level model assuming an effective broadening 2Δ of 1.4 eV, corresponding to the width of the x-ray absorption vibrational band.

The five-level model thus describes the experimental findings satisfactorily, even though the model effectively takes into account the vibrational structure only via two parameters, λ and Δ. It is relevant here to point out that *ab initio* calculations accounting for the real structure of the dynamical vibronic coupling operator *U*, using many-channel vibronic coupling and multiconfiguration theory also predict the symmetry purification and other vibronically resolved features of the resonant x-ray emission spectrum of CO_2 in a quantitatively correct way [17].

In summary, we have experimentally verified, through observation of "forbidden" peaks in RXE spectra of CO_2, that dynamical vibronic coupling leads to an effective breaking of the inversion symmetry. In particular, we show that the magnitude of this dynamical symmetry breaking is strongly dependent on the excitation energy when a narrow bandpass excitation source is used, and that detuning leads to a quenching of the symmetry breaking making the forbidden peaks weaker. We have applied scattering theory and a simple few-level model system to explain the symmetry purification. The theory shows that the dynamical vibronic coupling effectively vanishes in the limit of large detuning and that in this limit the transitions between the initial ground state and the final states can be regarded as sudden. Dynamical vibronic coupling is of importance for core-excited states in polyatomic molecules and solids. The results presented here are of great significance to resonant x-ray emission studies, and also of relevance to resonant photoemission studies.

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