PHYSICAL REVIEW A VOLUME 56, NUMBER 1 JULY 1997

Collapse of vibrational structure in spectra of resonant x-ray Raman scattering

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(Received 15 November 1996)

Extreme narrowing, or collapse, of electron-vibrational bands is predicted as a new phenomenon in resonant radiative and nonradiative x-ray scattering (RXS) spectra. It is shown that in the inelastic scattering case, that is, when the potential surfaces of ground and final states are different, a considerable narrowing of the vibronic RXS band results from detuning the excitation photon frequency ω away from the absorption resonance. By fine tuning the frequency, this may under special circumstances also occur in the region of strong photoabsorption. In the case of elastic Rayleigh scattering, that is, when the potential surfaces of ground and final states are identical, the narrowing results in a total collapse to a single resonance by detuning the frequency. The theory predicts how the differencies in vibrational structure of resonant and nonresonant photoemission spectra depends on the excitation frequency. The effect of frequency detuning on complex spectral multilevel structures due to multiplet and spin-orbit splittings is discussed qualitatively. It is shown that the notion of duration time for the x-ray scattering process plays a crucial role in the understanding of RXS spectra.
[S1050-2947(97)00707-5]

PACS number(s): 33.20.Rm, 33.20.Tp

I. INTRODUCTION

Due to a rather intense combined experimental and theoretical research effort, many general aspects of radiative and nonradiative resonant x-ray scattering (RXS) have become quite well understood by now [1–16]. At this time, the research direction seems to focus on studies of fine structures, band shapes, and the role of nuclear dynamics in the RXS spectra. In this respect, one can mention works on general vibronic broadening of RXS spectral lines [7,8], vibronic lifetime interference effects [7,8,17–19], nonlinear dispersion of the RXS resonances induced by nuclear motion [20], the implementation of selection rules in nonadiabatic RXS [21,22], and several effects caused by nuclear dynamics on dissociative potential surfaces involved in the x-ray scattering process [9,23,24], as a few out of many examples in the field.

The actual spectral shape of electron-vibrational RXS bands appears, in general, to be quite complicated. The concept of moments [9] of the RXS cross section is therefore helpful to simplify the analysis of observed spectral features. Recently, investigations were carried out on the frequency dispersion for the peak maxima [25] and for the center of gravity [20], i.e., the first moment of the RXS band, for atoms [20,25], and for molecules [20]. Armen and Wang [25] investigated numerically the full width at half maximum (FWHM) for atoms and computed the frequency dependence of the spectral width of atomic RXS in a three-level model. These authors [25] found a nonlinear dependence of the width on the frequency and, for some frequencies, additional broadening caused by the coexistence of two spectral features in RXS, given by the condition for an absorption resonance and the Raman-Stokes law (Stokes doubling effect [5,15,26]).

In this publication, we generalize previous work on spectral moments for RXS [20,25] and present a theory for the second spectral moment of RXS in molecules and solids. We investigate the dependence of the second moment on the frequency of exciting radiation and show that the vibrational structure yields qualitatively new features for the frequency dependence of the width of RXS bands, which are absent for atoms. One intention of the paper is to find precisely how band sharpening can be achieved in resonant x-ray emission of molecules and solids. We show that the detuning of the incoming x-ray photon frequency sufficiently far from the absorption spectral band leads to a narrowing of vibrational structure, or even to a collapse to a single resonance with the spectral shape equal to that of the incoming x-ray radiation.

The paper is organized as follows. A general time-independent description of RXS in the Franck-Condon approximation, also taking into account the temperature of the sample, is given in Sec. II. Section III contains our main result, namely, the general investigation of the narrowing effects in electron-vibrational bands of elastic and inelastic RXS. The time-dependent representation is used in Sec. IV to provide a physical interpretation of the narrowing of the RXS profiles. This interpretation is based on the concept of the duration time for the RXS process introduced in the section. The quantitative characteristics of the narrowing of the spectral profile is given in Sec. V, where the second moment $\Gamma(\omega)$ of RXS bands is investigated analytically and numerically. Here, the analytical expressions for $\Gamma(\omega)$ are obtained for ''fast RXS,'' i.e., for large detuning frequencies and for incoming photon frequencies close to the adiabatic absorption transition (0-0 transition). It is shown how the width of the RXS spectral band is formed by atomiclike and molecularlike contributions. The first contribution, investigated earlier in Ref. [20], depends on the lifetime broadening and the width of the spectral function of incoming radiation, whereas the molecular contribution is expressed through the vibrational frequencies and the equilibrium distances of the states involved in the RXS process. The results of this section dem-

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1050-2947/97/56(1)/256(9)/$10.00

onstrate the strong influence of nuclear dynamics on the asymptotic behavior of the second spectral moment. The possibility of observing narrowing of RXS profiles in other systems, such as solids or atoms with complex multilevel structure, is briefly discussed in Sec. VI. Our findings are summarized in the last section, Sec. VII.

II. THEORY

For ordinary temperatures T, the molecules are in the ground electronic state and distributed over vibrational levels $E_{\boldsymbol{l}}^0$ of this state with the probability

$$\rho_{\boldsymbol{l}}=\frac{\exp(-E_{\boldsymbol{l}}^0/k_BT)}{\Sigma_{\boldsymbol{l}}\exp(-E_{\boldsymbol{l}}^0/k_BT)}, \tag{1}$$

where k_B is Boltzmann's constant. By absorbing incoming x-ray photons with the frequency ω, the molecule is excited to the vibrational levels $E_{\mathbf{m}}^i$ of the intermediate electronic state i. Due to the vacuum fluctuations, this intermediate state decays, emitting x-ray photons with the frequency ω' to the vibrational levels $E_{\mathbf{n}}^f$ of the final electronic state f. Using the harmonic approximation, the vibrational energies of ground $[E_{\boldsymbol{l}}^0=\boldsymbol{\omega}_0(\boldsymbol{l}+\mathbf{1}/2)]$, core-excited $[E_{\mathbf{m}}^i=\boldsymbol{\omega}_i(\mathbf{m}+\mathbf{1}/2)]$, and final $[E_{\mathbf{n}}^f=\boldsymbol{\omega}_f(\mathbf{n}+\mathbf{1}/2)]$ states are expressed through the vectors of vibrational frequencies $\boldsymbol{\omega}_0=(\omega_{01},\omega_{02},\ldots,\omega_{0N})$, $\boldsymbol{\omega}_i=(\omega_{i1},\omega_{i2},\ldots,\omega_{iN})$, $\boldsymbol{\omega}_f=(\omega_{f1},\omega_{f2},\ldots,\omega_{fN})$ and through the vectors of vibrational quantum numbers $\boldsymbol{l}=(l_1,l_2,\ldots,l_N)$, $\mathbf{m}=(m_1,m_2,\ldots,m_N)$, $\mathbf{n}=(n_1,n_2,\ldots,n_N)$, respectively. We will adopt here atomic units and the notation N for the number of vibrational modes and the notation $\mathbf{1}=(1,1,\ldots,1)$. Except for the radiative scattering channel, the core-excited state can decay nonradiatively, emitting an Auger electron with the energy ϵ. A deep connection exists between radiative and nonradiative RXS [6]. The vibrational problem is essentially the same for the two processes and they are both covered by the theory presented below.

The spectral properties of RXS are guided by the double differential cross section [5,6,27]

$$\sigma(\omega',\omega)=\sigma_0\sum_{\boldsymbol{l},\mathbf{n}}\rho_{\boldsymbol{l}}|F_{\boldsymbol{l}\mathbf{n}}|^2\Phi(\Omega'+\omega_{\mathbf{n}\boldsymbol{l}}-\Omega,\gamma), \tag{2}$$

convoluted with the unit-normalized spectral function of the exciting radiation Φ centered at frequency ω and having the width γ. We have collected all nonessential quantities into the constant σ_0 and introduced the detuning $\Omega=\omega-[\mathcal{E}_i(\mathbf{R}_i)-\mathcal{E}_0(\mathbf{R}_0)]$ of the incoming x-ray photon frequency ω, relative to the absorption electronic resonant frequency $\mathcal{E}_i(\mathbf{R}_i)-\mathcal{E}_0(\mathbf{R}_0)$, and the detuning $\Omega'=\omega'-[\mathcal{E}_i(\mathbf{R}_i)-\mathcal{E}_f(\mathbf{R}_f)]$ (or $\Omega'=\epsilon-[\mathcal{E}_i(\mathbf{R}_i)-\mathcal{E}_f(\mathbf{R}_f)]$) of the final x-ray photon frequency ω' (or the Auger electron energy ϵ), relative to the emission electronic resonance frequency $[\mathcal{E}_i(\mathbf{R}_i)-\mathcal{E}_f(\mathbf{R}_f)]$. The electronic energies for the equilibrium geometries $\mathbf{R}_0$, $\mathbf{R}_i$, and $\mathbf{R}_f$ of the ground, intermediate, and final states are denoted here as $\mathcal{E}_0(\mathbf{R}_0)$,$\mathcal{E}_i(\mathbf{R}_i)$ and $\mathcal{E}_f(\mathbf{R}_f)$, respectively, while the difference between vibrational energies of the final and ground states is denoted as $\omega_{\mathbf{n}\boldsymbol{l}}=E_{\mathbf{n}}^f-E_{\boldsymbol{l}}^0$.

The scattering amplitude is given by the Kramers-Heisenberg formula. According to the Franck-Condon (FC) principle, the RXS amplitude can be written as [17,18]

$$F_{\boldsymbol{l}\mathbf{n}}=\sum_{\mathbf{m}}\frac{\langle\mathbf{n}|\mathbf{m}\rangle\langle\mathbf{m}|\boldsymbol{l}\rangle}{\Omega'-\omega_{\mathbf{m}\mathbf{n}}+\imath\Gamma}, \tag{3}$$

where $\omega_{\mathbf{m}\mathbf{n}}=E_{\mathbf{m}}^i-E_{\mathbf{n}}^f$ and Γ is the lifetime broadening (half width at half maximum). The vibrational structure inherent in the RXS cross section formula is formed according to the FC factors, $\langle\mathbf{m}|\boldsymbol{l}\rangle$ and $\langle\mathbf{n}|\mathbf{m}\rangle$, between the vibrational wave functions of ground $|\boldsymbol{l}\rangle$ and core-excited $|\mathbf{m}\rangle$ states, respectively, between the vibrational wave function of core-excited and final $|\mathbf{n}\rangle$ states. The FC factors in turn depend on the equilibria and shapes of the potential surfaces for the ground, intermediate, and final states. According to the normal Franck-Condon principle, vibrational broadening is absent only in the exotic case where the three electronic states involved in the absorption-emission process have the same potential surface. Nevertheless, we show that for elastic RXS it is possible to remove the vibrational broadening completely.

III. NARROWING OF RXS BANDS BY DETUNING THE FREQUENCY

Let us consider the limit of large detuning Ω or large lifetime broadening Γ in comparison with the width of the exciting photon function γ and the effective width Δ of the vibrational band for the considered electronic absorption transition

$$(\Omega^2+\Gamma^2)^{1/2}\gg\Delta,\gamma. \tag{4}$$

We will show in Sec. IV that this limiting case corresponds to a sudden or fast RXS process. The RXS cross section (2) is at maximum when the final photon frequency follows the Raman-Stokes law

$$\Omega'=\Omega-\omega_{\mathbf{n}\boldsymbol{l}}. \tag{5}$$

Because of Eqs. (4) and (5), one can extract the denominator from the sum in Eq. (3):

$$F_{\boldsymbol{l}\mathbf{n}}\simeq\frac{\langle\mathbf{n}|\boldsymbol{l}\rangle}{\Omega+\imath\Gamma}. \tag{6}$$

This expression coincides with the result obtained in the short lifetime limit [18,23], $\Gamma\gg\Delta$. Now the RXS cross section

$$\sigma(\omega',\omega)\simeq\frac{\sigma_0}{\Omega^2+\Gamma^2}\sum_{\boldsymbol{l}\mathbf{n}}\rho_{\boldsymbol{l}}|\langle\mathbf{n}|\boldsymbol{l}\rangle|^2\Phi(\Omega'+\omega_{\mathbf{n}\boldsymbol{l}}-\Omega,\gamma) \tag{7}$$

does not depend on the vibrational structure of the intermediate state. So when $|\Omega|$ or Γ is large, the sum (7) of resonances constitutes the RXS cross section, the spectral shapes of which copy the spectral function of the exciting radiation $\Phi(\Omega,\gamma)$. The strength of a single resonance is defined by the squared overlap integral $|\langle\mathbf{n}|\boldsymbol{l}\rangle|^2$ between vibrational wave functions of the final and ground states. Contrary to the RXS cross section (2), the asymptotic cross section (7) is not

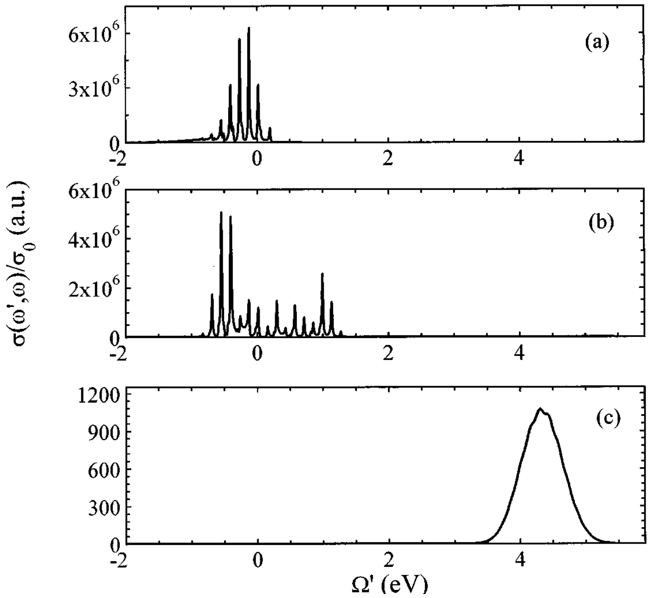

FIG. 1. Narrowing of the vibrational structure in O *K* inelastic RXS of the CO molecule. Inelastic RXS with final state (f): $1\pi^{-1}2\pi^{1}\ {}^{1}\Delta$. Data for O *K* emission of the CO molecule (Table I). The calculation was performed in the harmonic approximation [see Eqs. (2) and (3) and Appendix C] with only the lowest ground-state level populated ($\rho_l=\delta_{l,0}$) and using a Gaussian spectral function (18) with $\gamma=0.1$ eV. $\Gamma=0.01$ eV. (a) $\Omega=-0.05$ eV. (b) $\Omega=1.22$ eV. (c) $\Omega=5.5$ eV.

broadened by the vibrational structure of the core-excited state. The effective width of the fast RXS cross section (7) is given only by the vibrational structure of the final state (and of the ground state if the temperature is sufficiently large). This means that the effective narrowing of the RXS profile takes place for large detuning $|\Omega|$ or for large lifetime broadening Γ (4) [as in Fig. 1(c)]. Figure 1(a) demonstrates narrowing of the vibrational structure for small detuning also, $\Omega=-0.05$ eV. The explanation of this effect will be given in Sec. V A [see Eq. (21) and Fig. 6].

Our main result follows directly from Eq. (7). Indeed, one can see that the vibrational structure of the RXS cross section (7) collapses to a single resonance [see Fig. 2(c)],

$$\sigma(\omega',\omega)\simeq\frac{\sigma_0}{\Omega^2+\Gamma^2}\Phi(\Omega'-\Omega,\gamma), \tag{8}$$

when the potential surfaces of ground and final states coincide: $\langle\mathbf{n}|\boldsymbol{l}\rangle=\delta_{l,\mathbf{n}}$. Here we took into account the condition of completeness $\Sigma|\mathbf{m}\rangle\langle\mathbf{m}|=1$ and the normalization of ρ_l (1) to unity: $\Sigma\rho_l=1$. This effect of narrowing of the electron-vibrational band to a single resonance, with the width equal to the spectral width of incoming radiation γ, occurs strictly for elastic (Rayleigh) RXS. Such a collapse to a single line is, accidentally, possible also for inelastic RXS, for example, when the potential surfaces of ground and final state are similar (see discussion in Sec. VI). It is necessary to mention that the collapse effect is a direct consequence of vibronic lifetime interference [17,18]. Such interference may thus totally remove the contribution of the intermediate vibrational states to the RXS amplitude (6). Equation (8) shows that

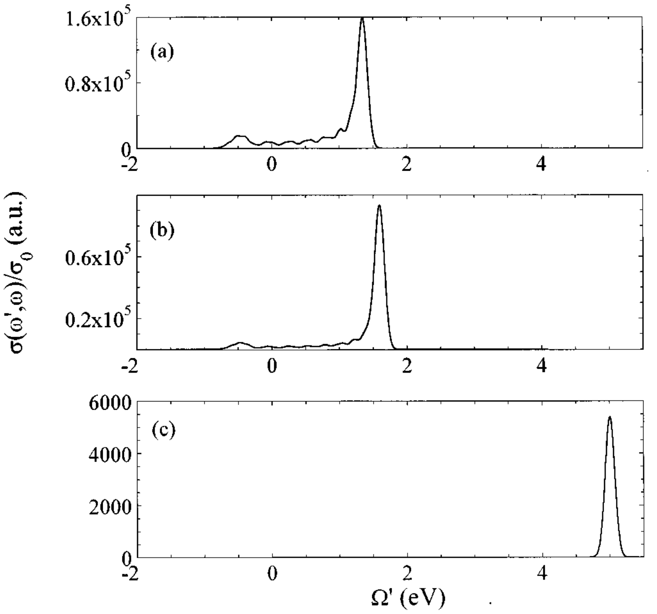

FIG. 2. Collapse of vibrational structure to single resonance in O *K* elastic RXS of the CO molecule (Table I). The calculation was performed in the harmonic approximation [see Eqs. (2) and (3) and Appendix C] with only the lowest ground-state level populated ($\rho_l=\delta_{l,0}$) and using a Gaussian spectral function (18) with $\gamma=0.1$ eV. $\Gamma=0.09$ eV. (a) $\Omega=1.36$ eV. (b) $\Omega=1.6$ eV. (c) $\Omega=5$ eV.

elastic RXS can be used to measure the spectral function of x-ray incident photons (see also [28–31]).

IV. PHYSICAL INTERPRETATION OF THE NARROWING EFFECT

To penetrate more deeply into the physics of the collapse effect discussed here, let us rewrite the scattering amplitude (3):

$$F_{l\mathbf{n}}=\langle\mathbf{n}|\varphi_l\rangle=\int d\mathbf{R}'d\mathbf{R}\varphi_{\mathbf{n}}^{f}(\mathbf{R}')G_E(\mathbf{R}',\mathbf{R})\varphi_l^{0}(\mathbf{R}), \tag{9}$$

in terms of the wave packet $|\varphi_l\rangle$ and the Green's function G_E:

$$|\varphi_l\rangle=G_E|\boldsymbol{l}\rangle,\quad G_E=\frac{1}{E-H_i+\imath\Gamma}=\sum_{\mathbf{m}}\frac{|\mathbf{m}\rangle\langle\mathbf{m}|}{E-E_{\mathbf{m}}^{i}+\imath\Gamma}, \tag{10}$$

with $E=\Omega'+E_{\mathbf{n}}^{f}$, H_i as the nuclear Hamiltonian of the core-excited state, $\varphi_l^0(\mathbf{R})=\langle\mathbf{R}|\boldsymbol{l}\rangle$ and $\varphi_{\mathbf{n}}^{f}(\mathbf{R})=\langle\mathbf{R}|\mathbf{n}\rangle$ as vibrational wave functions $|\boldsymbol{l}\rangle$ and $|\mathbf{n}\rangle$ of the ground and final states in a coordinate representation, and $\mathbf{R}$ as the set of normal molecular coordinates.

The initial vibrational wave packet $\varphi_l^0(\mathbf{R})$ is excited by light from the ground-state potential surface $U_0(\mathbf{R})$ to the intermediate-state potential surface $U_i(\mathbf{R})$ and arrives there as the wave packet $\varphi_l(\mathbf{R}')=\int d\mathbf{R}G_E(\mathbf{R}',\mathbf{R})\varphi_l^0(\mathbf{R})$. The space distribution and spectral composition of this wave packet depend on the detuning Ω' through the Green's function [23]. The stationary lifetime-broadened Green's function $G_E(\mathbf{R}',\mathbf{R})$ describes the propagation of nuclei on a decaying

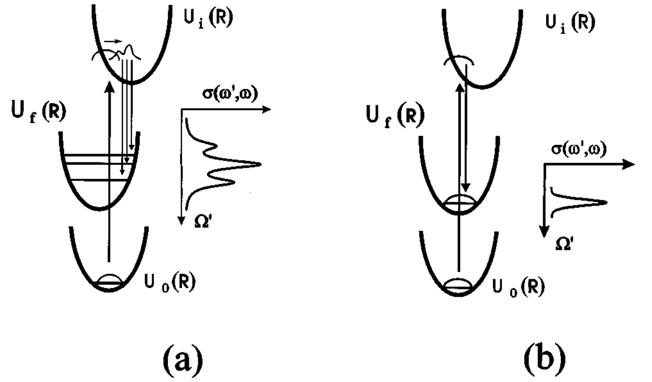

FIG. 3. Qualitative picture for collapse of vibrational structure under off-resonant core excitation (13). $U_f(\mathbf{R})=U_0(\mathbf{R})$. (a) Slow RXS Resonant core excitation: $\tau_c\sim\tau$. The molecule has time to change its geometry ($\mathbf{R}'\neq\mathbf{R}$) so $U_0(\mathbf{R})\neq U_i(\mathbf{R})$, and hence the RXS cross section, has vibrational structure. (b) Fast elastic RXS (13): Since $\tau_c\ll\tau$ and $U_f(\mathbf{R})=U_0(\mathbf{R})$, the molecule has no time to change geometry and the vibrational structure in the RXS cross section $\sigma(\omega',\omega)$ collapses to a single resonance with width $\gamma/\sqrt{2}$.

potential surface $U_i(\mathbf{R})$ from the normal coordinates $\mathbf{R}$, where the molecule was core excited, up to $\mathbf{R}'$, where the emission transition takes place [see Fig. 3(a)]. The wave packet $\varphi_l(\mathbf{R})$ (10) is formed according to two characteristic time scales. The first one is the duration of the RXS process (see Appendix A),

$$\tau_c=(\Omega^2+\Gamma^2)^{-1/2}, \tag{11}$$

while

$$\tau=\Delta^{-1}\sim\left[\omega_0\left(\left|\frac{\Delta R}{R_0}\right|+\left|\frac{\Delta\omega}{\omega_0}\right|\right)\right]^{-1} \tag{12}$$

is the time of deformation of the initial wave packet $\varphi_i^0(\mathbf{R})$ (eigenfunction of the ground-state nuclear Hamiltonian H_0) on the potential surface $U_i(\mathbf{R})$ of the core-excited state (see Appendix B). Here, ω_0 and R_0 denote the vibrational frequency and equilibrium internuclear distances of the ground state, respectively, while $\Delta\omega$ and ΔR denote the characteristic changes of these quantities upon core excitation. The concept of duration time of the RXS process is fundamental in this context; its frequency dependence (see Fig. 4) makes it possible to control it externally (see discussion in Sec. VI).

Let us now consider fast RXS (4):

$$\tau_c\ll\tau, \quad \gamma^{-1} \tag{13}$$

In this limiting case, the denominator in the Green's function (10) can be extracted from the sum over $\mathbf{m}$ [23]:

$$G_E(\mathbf{R}',\mathbf{R})\simeq\frac{\delta(\mathbf{R}'-\mathbf{R})}{\Omega+\imath\Gamma}. \tag{14}$$

Here, Eq. (5) was used. Equation (14) means that the molecule has no time to change its geometry during the RXS process. In other words, the condition (13) [see Fig. 3(b)] implies a sudden or fast RXS process without change of molecular geometry ($\mathbf{R}'=\mathbf{R}$). Hence, the space distribution of the nuclear wave packet $\varphi_l(\mathbf{R})$ (10) coincides with the ground-state vibrational wave function $\varphi_l^0(\mathbf{R})$: $\varphi_l(\mathbf{R})\simeq\varphi_l^0(\mathbf{R})/(\Omega+\imath\Gamma)$. In accordance with this fact, Eq. (9) yields the sudden approximation (6) for the RXS amplitude which leads directly to the collapse effect (8) [see Fig. 2(c) and Fig. 3(b)].

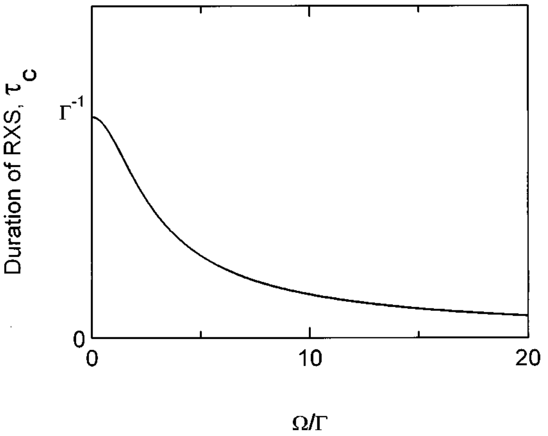

FIG. 4. Spectral dependence of the duration of RXS τ_c [see Eq. (11)].

V. SPECTRAL WIDTH OF ELECTRON-VIBRATIONAL RXS BAND

The quantitative characteristic of the collapse effect is the spectral width $\Gamma(\omega)$ of the RXS band. This width can be introduced in two different ways: first, by defining $\Gamma(\omega)$ as the FWHM of the spectral band [25]; second, as proposed here, as the second moment of the RXS profile:

$$\Gamma(\omega)=\left(\int_{-\infty}^{\infty}d\omega'[\omega'-\epsilon(\omega)]^2\frac{\sigma(\omega',\omega)}{\sigma_0(\omega)}\right)^{1/2}. \tag{15}$$

Here, $\epsilon(\omega)$ is the center of gravity expressed in terms of the first $\sigma_1(\omega)$ and zero $\sigma_0(\omega)$ moments of the RXS cross section:

$$\epsilon(\omega)=\frac{\sigma_1(\omega)}{\sigma_0(\omega)}, \quad \sigma_n(\omega)=\int d\omega'\omega'^n\sigma(\omega',\omega), \quad n=0,1. \tag{16}$$

The spectral features of $\sigma_1(\omega)$ and $\sigma_0(\omega)$ were investigated recently in Refs. [20,32]. The spectral shape of the integral RXS cross section $\sigma_0(\omega)$ coincides with the spectral shape of the x-ray ''absorption'' cross section for a given electron transition:

$$\sigma_0(\omega)=\sigma_0\sum_l \rho_l|\langle\mathbf{m}|\boldsymbol{l}\rangle|^2\int_{-\infty}^{\infty}d\xi\frac{\Phi(\xi,\gamma)}{(\xi+\Omega-\omega_{\mathbf{m}l})^2+\Gamma^2}. \tag{17}$$

This equation generalizes the corresponding expression of $\sigma_0(\omega)$ [20,32] for the case of finite temperatures. The spectral features of $\Gamma(\omega)$, with a Gaussian spectral function normalized to unity

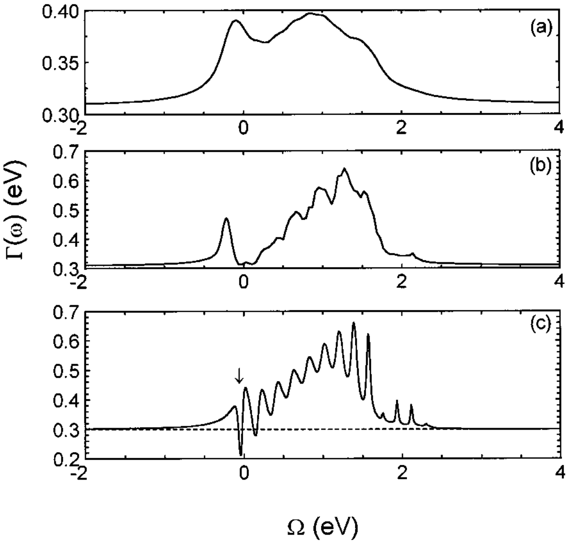

FIG. 5. Spectral width [second moment (15)] of inelastic RXS. Inelastic scattering to the final state (f): $1\pi^{-1}2\pi^{11}\Delta$. Data for O K inelastic RXS of the CO molecule (Table I). (a) $\Gamma=0.09$ eV, $\gamma=0.1$ eV, $\Gamma(\infty)\simeq0.308$ eV. (b) $\Gamma=0.01$ eV, $\gamma=0.1$ eV, $\Gamma(\infty)\simeq0.308$ eV. (c) $\Gamma=0.01$ eV, $\gamma=0.01$ eV, $\Gamma(\infty)\simeq0.3$ eV, $\Gamma(\omega_{00})\simeq0.21$ eV.

$$\Phi(\Omega,\gamma)=\frac{1}{\gamma\sqrt{\pi}}\exp\left[-\left(\frac{\Omega}{\gamma}\right)^2\right], \tag{18}$$

were investigated earlier for the three-level model relevant for atomic RXS [20].

A. Diatomic molecules in the harmonic approximation

As an illustration, we calculate $\Gamma(\omega)$ with a Gaussian spectral function (18) for a diatomic molecule in the harmonic approximation (see Fig. 5 and Fig. 6). These calculations were carried out with the help of Eqs. (15), (C1), and (C3). We assume here temperatures for which only the lowest ground-state vibrational level is populated $(\rho_l=\delta_{l,0})$, which is a good approximation for light molecules at room temperature. To show the dependence of $\Gamma(\omega)$ on the lifetime broadening, we used different values of Γ in our numerical simulations, including the experimental value $\Gamma\simeq0.09$ eV for O K emission of CO.

1. Spectral width of RXS for excitation at the wings of the x-ray absorption band

The one-dimensional harmonic approximation and Eq. (C4) yield an analytical expression for $\Gamma(\omega)$ in the case of fast RXS (4), (13):

$$\Gamma(\infty)\simeq\left[\frac{1}{2}\left\{\gamma^2+\frac{\mu\omega_f^4}{\omega_0}(R_0-R_f)^2+\left(\frac{\omega_0^2-\omega_f^2}{2\omega_0}\right)^2\right\}\right]^{1/2}, \tag{19}$$

where we also used the following asymptotic expression for the center of gravity [20]:

$$\epsilon(\omega)\simeq\omega-\left(\mathcal{E}_f(R_0)-\mathcal{E}_0(R_0)+\frac{\omega_f^2-\omega_0^2}{4\omega_0}\right), \tag{20}$$

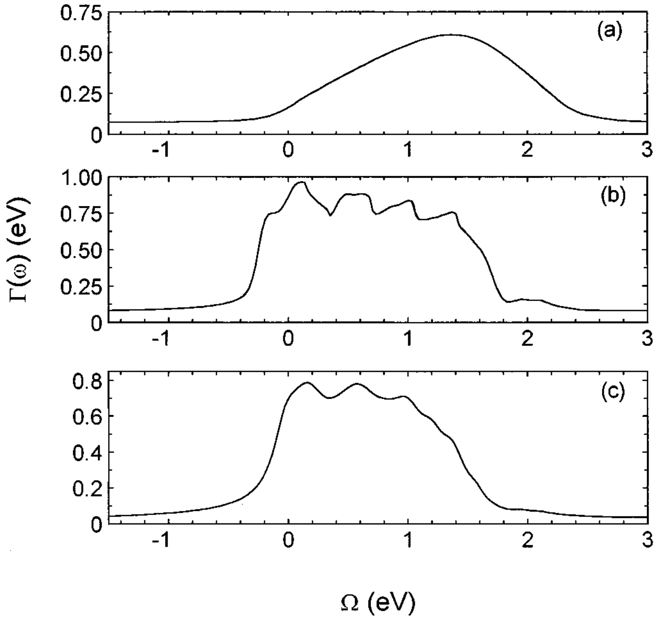

FIG. 6. Spectral width [second moment (15)] of elastic RXS. Data for O K elastic RXS emission of the CO molecule (Table I). (a) $\Gamma=0.09$ eV, $\gamma=0.1$ eV, $\Gamma(\infty)=\gamma/\sqrt{2}\simeq0.071$ eV. (b) $\Gamma=0.01$ eV, $\gamma=0.1$ eV, $\Gamma(\infty)\simeq0.071$ eV. (c) $\Gamma=0.09$ eV, $\gamma=0.01$ eV, $\Gamma(\infty)\simeq0.071$ eV.

with μ denoting the reduced mass of the molecule, and with ω_0, ω_f and R_0, R_f denoting vibrational frequencies and equilibrium internuclear distances of ground (0) and excited (f) states, respectively. Equation (19) confirms the general result of Eq. (8). Indeed, Eq. (19) shows that in the sudden limit (4), (13), the spectral width $\Gamma(\infty)$ is larger than the width $\gamma/\sqrt{2}$ of the spectral function, $\Gamma(\infty)\geqslant\gamma/\sqrt{2}$. The additional broadening (to the width $\gamma/\sqrt{2}$) is caused by vibrational structure. The collapse of this vibrational structure to a single resonance with the width $\Gamma(\infty)=\gamma/\sqrt{2}$ takes place when the interatomic potentials of ground and final states coincide: $\omega_0=\omega_i$, $R_0=R_i$ [see Fig. 6(c)].

2. Spectral width of RXS for adiabatic x-ray absorption

Figure 5 shows that some suppression of the vibrational broadening also takes place for inelastic RXS of the CO molecule. Contrary to elastic RXS (Fig. 6), this suppression is not complete when exciting at the wings of the x-ray absorption profile, since the potential surfaces of ground and final states do not coincide [see Eq. (19) and Table I]. The shape of the second moment $\Gamma(\omega)$ has an additional feature, namely, some suppression of vibrational broadening near the adiabatic 0-0 absorption transition $(l=0\rightarrow m=0)$ for the de-

TABLE I. Vibrational frequencies ω_j, equilibrium internuclear distances R_j $(j=0,i,f)$, and lifetime broadenings Γ for ground (0), core-excited (i), and final (f) states of the CO molecule [41].

State	ω_j (eV)	R_j (Å)	Γ (eV)
ground (0): $X\ ^1\Sigma^+$	0.27	1.128	0
core-excited (i): O $1s^{-1}2\pi^1\ ^1\Pi$	0.18	1.280	0.09
final (f): $1\pi^{-1}2\pi^1\ ^1\Delta$	0.14	1.399	$\simeq 0$

tuning $\Omega=-0.043$ eV [see Fig. 5(c)]. This numerical value falls close to the theoretical prediction of $\Omega=(\omega_i-\omega_0)/2\simeq-0.045$ eV. The numerical experiment [Fig. 5(c)] prompts us to look for a minimum of $\Gamma(\omega)$ for small widths $(\gamma,\Gamma\ll\omega_i)$ and for the 0-0 absorption transition with $\Omega=(\omega_i-\omega_0)/2$. With a small lifetime broadening, the interference between different vibrational levels can be neglected, whereas a small width of the Gaussian spectral function makes it possible to tune exactly to resonance with the 0-0 absorption transition. By means of these two assumptions and by means of Appendix C, we find directly an expression for the RXS second moment $\Gamma(\omega_{00})$ of the 0-0 absorption transition. Likewise, Eq. (19) indicates that this expression can be separated into atomic Γ_{at} and molecular Γ_{mol} contributions:

$$\Gamma(\omega_{00})\simeq[\Gamma_{at}^2(\omega)+\Gamma_{mol}^2]^{1/2}. \tag{21}$$

The RXS second moment of the free atom (without vibrational structure),

$$\Gamma_{at}=\left(\frac{\gamma\Gamma}{\sqrt{\pi}\mathrm{Re}w(z)}-\Gamma^2\right)^{1/2}=\begin{cases}\dfrac{(\gamma\Gamma)^{1/2}}{\pi^{1/4}}, & \text{if}\quad \Gamma\ll\gamma\\[2ex] \dfrac{\gamma}{\sqrt{2}}, & \text{if}\quad \Gamma\gg\gamma\end{cases}, \tag{22}$$

depends only on the interplay between γ and Γ through the parameter $z=\imath\Gamma/\gamma$ and coincides with the corresponding expression of $\Gamma(\omega)$ of the three-level atom given in Ref. [20] (for zero detuning: $\Omega=0$). Here, $w(z)$ is the error function with a complex argument [33]. The molecular contribution caused by vibrational broadening is

$$\Gamma_{mol}=\left[\frac{1}{2}\left\{\frac{\mu\omega_f^4}{\omega_i}(R_i-R_f)^2+\left(\frac{\omega_i^2-\omega_f^2}{2\omega_i}\right)^2\right\}\right]^{1/2}. \tag{23}$$

Contrary to Eq. (19), the vibrational broadening $\Gamma(\omega_{00})$ (21) is defined by the difference of the potential surfaces $U_i(R)$ and $U_f(R)$ of the core-excited and final states. The comparison of this expression with the corresponding molecular contribution for fast RXS (19) indicates that this spectral width refers to a sudden emission transition: $i\rightarrow f$. The physical intuition does not contradict this statement. Indeed, our choice of detuning frequency $\Omega=(\omega_i-\omega_0)/2$ and small γ and Γ leads to core excitation exclusively to the lowest vibrational level $m=0$ of the intermediate state. The accompanying vertical emission transition $i\rightarrow f$ yields the vibronic broadening of Eq. (23). Figure 5(c) shows that the narrowing of the inelastic RXS profile in the region of strong photoabsorption $(\Omega\simeq-0.043$ eV) can be stronger $[\Gamma(\omega_{00})\simeq0.16$ eV for $\gamma,\Gamma\rightarrow0]$ than at the wings of x-ray absorption profile $[\Gamma(\infty)\simeq0.3$ eV]. It is necessary to note that the same decrease of $\Gamma(\omega)$ for small Ω takes place in the elastic case as well [see Figs. 6(b) and 6(c)]. But for elastic RXS, this effect is smaller in comparison with the narrowing $\Gamma(\infty)=\gamma/\sqrt{2}$ obtained by excitation at the wings of the absorption band.

VI. DISCUSSION

The present theory refers to both radiative and nonradiative RXS spectra. In the radiative case, the theory leads to the most conspicuous result, namely, a total collapse of the vibrational structure to a single line for elastic, Rayleigh, scattering. In general, in the inelastic radiative case, there will not be a total collapse, but a distortion that can be quite substantial and which in most cases leads to narrowing. In the nonradiative case the ground and final potential surfaces will in general be different and the collapse will not be complete. In the case of nonradiative participator decay, synonymous with resonant photoemission, the final state is identical with the nonresonant ultraviolet photoemission spectroscopy (UPS) final state, and the present theory describes the frequency-dependent relation between the vibrational band envelopes of these two spectroscopies. Apart from the detuning frequency, the actual narrowing depends on the interplay of the bonding characters of core, unoccupied, and occupied orbitals, and the accompanying shifts in equilibria of the potentials. The first unoccupied levels are mostly antibonding, and the occupied levels bonding, while the core orbital can be both bonding and antibonding, using the traditional definition of a bonding character [34]. An interesting case is given by a nonbonding occupied level, where the nonresonant UPS band shows a single vibrational level, while the corresponding resonant photoemission band shows multilevel structure due to the involvement of the core-state potential. The C $1s^{-1}2\pi^1$ core-excited state of CO, ending at the $X\ ^2\Sigma^+$ state of CO^+ with the nonbonding 5σ orbital as ionized, provides such a case. We can thus expect the multiple structure of the $X\ ^2\Sigma^+$ band [19] to collapse into this single-line feature for large detunings frequencies [35].

Large frequencies can affect the RXS bands not only concerning the vibrational (Franck-Condon) profiles. We have already demonstrated that electronically symmetry-forbidden RXS transitions appearing at resonant excitations are strongly dependent on the excitation frequency when a narrow-bandpass excitation source is used, and that detuning leads to a quenching of the symmetry breaking, making the ''forbidden'' peaks weaker [22]. The detuning effectively quenches the symmetry breaking of vibronic coupling, basically for the same reason it quenches the vibrational excitations demonstrated in this work. The total collapse of vibrational structure in elastic RXS to a single resonance with the spectral shape coinciding with the spectral shape of exciting radiation allows the possibility of actually measuring the spectral shape, even in experiments involving molecules (see also Refs. [28,30]).

Although the main finding of the present work refers to conditions for band narrowing in resonant x-ray scattering, it is relevant to mention that narrowing effects are also observed in the microwave and optical regions, but with completely different physical origins, for example: exchange narrowing of spectral lines in nuclear magnetic resonance of solids [36], pressure narrowing of optical absorption spectral lines in gas phase (Dicke effect [37,38]), collapse of rotational structure and narrowing of spectral lines caused by radiation fields [38]. The narrowing effects in optical spectra of gaseous samples are caused by collisions between atoms or molecules. The collisional broadening of spectral lines in the x-ray region is negligibly small with respect to the lifetime broadening, and so the mechanisms responsible for collapse of spectral lines in the optical region must be considered irrelevant for x-ray spectroscopy.

Our theory also takes into account temperature effects. According to Eq. (7), the finite temperature leads to additional broadening by $\sim k_BT$ of the RXS profile caused by the ground-state vibrational structure (if k_BT is on the order of or larger than ω_0). This temperature broadening takes place for solids and molecules with heavy atoms and for light molecules when the temperature is sufficiently high.

The collapse effect was investigated here under the assumption that the resonant contributions dominate the scattering amplitude. This assumption is valid with high accuracy for radiative inelastic RXS, while the nonresonant contribution (Thomson scattering) can be significant in the case of radiative elastic RXS [10,39]. Numerical simulations of radiative elastic RXS of the CO molecule indicate that the Thomson scattering becomes comparable to the resonant contribution when the incident photon frequency $|\Omega|$ is tuned below the lowest ($1s\rightarrow\pi^*$) transition by about 1.5–2 eV [39]. However, as one can see from Fig. 6, the vibronic profile collapses to a single line much earlier: $|\Omega|\rangle\simeq 0.2$ eV. One can show that the electron-vibrational RXS profile collapses to a single line also if the nonresonant scattering is essential [39]. As is well known from the theory of Fano resonances, the nonresonant scattering (direct photoemission) is more important in the case of nonradiative RXS [11–13,6]. The direct photoemission can change quantitatively (but not qualitatively) the dependence of the spectral width $\Gamma(\Omega)$ on detuning Ω. In the very recent measurements of the resonant C $1s^{-1}2\pi^1$ photoemission spectrum of CO by Sundin *et al.* [35], a collapse phenomenon was demonstrated for detuning at $\simeq 0.3$ eV, i.e., far from the detuning energies for which the direct photoemission becomes significant.

Related narrowing effects of the RXS profiles can be anticipated also for many-level systems, where fine structures may appear due to different types of perturbing interactions, e.g. spin-orbit and open-shell electrostatic interactions leading to spin-sublevel and multiplet splittings. We can thus foresee quenching of such structures as an effect of frequency detuning. To understand this, let us consider the general treatment of RXS with $|0\rangle$, $|i\rangle$, and $|f\rangle$ as the ground, intermediate, and final states, respectively. For complex many-level spectra, the FC factors must be replaced as: $\langle m|l\rangle\rightarrow\langle i|D|0\rangle$ and $\langle n|m\rangle\rightarrow\langle f|Q|i\rangle$. Here, D and Q denote the excitation and deexcitation operators, the latter being the Coulomb operator in the nonradiative cases [6]. As mentioned above, the structure of the scattering amplitude indicates that the effective width $\Gamma(\omega)$ of the RXS band can be decomposed into the spectral widths of absorption (Δ) and emission (Δ_{if}) transitions: $\Gamma(\omega)\sim\Delta+\Delta_{if}$. When the detuning is large (fast RXS: $\tau_c\ll\Delta^{-1}$), the asymptotic Eq. (7) can be replaced by

$$\sigma(\omega',\omega)\simeq\frac{\sigma_0}{\Omega^2+\Gamma^2}\sum_f |\langle f|Q\mathcal{D}|0\rangle|^2\Phi(\omega'+\omega_{f0}-\omega,\gamma). \tag{24}$$

One can see that only the final states contribute to the effective broadening of the RXS profile when $|\Omega|$ is large. As a result, the second moment of the RXS band in general decreases when the magnitude of the detuning $|\Omega|$ increases. This narrowing effect can occur, for example, in solids or in heavy atoms with expanded multiplet structure of core-excited and final states. The narrowing effect can take place for small Ω, too, if γ and Γ are small in comparison with the multiplet splitting. Indeed, only one of the multiplet sublevels is core excited in this case, and the intermediate states will then not contribute to $\Gamma(\omega)$.

We considered here x-ray scattering involving only one intermediate core-excited electronic state. Both ''red'' ($\Omega<0$) and ''blue'' ($\Omega>0$) frequency detunings lead to narrowing of the RXS band in this case. However, a real distribution of core-excited electronic states is inhomogeneous, with the density often rising steeply toward high excitation energies, and lowering toward low excitation energies (being zero in the ''band gap''). The best conditions under which to observe the collapse effect in elastic RXS thus prevails for the detuning on the long wavelength side of the first electronic x-ray absorption resonance, while narrowing of the RXS profile can be absent for blue detuning due to the many overlapping absorption resonances.

VII. SUMMARY

We have presented a theory for the second moment and for vibrational broadening of spectral bands for resonant inelastic and elastic x-ray scattering. The effect on these quantities of detuning the frequency from the absorption resonance was studied in detail. It was shown that the effective spectral width can increase for some frequencies but that it will decrease when the detuning frequency is sufficiently large. The duration of the RXS process τ_c and the time of deformation of the wave packet τ of the core-excited state constitute the important concepts of the investigated problem. It is shown that the RXS duration time τ_c can be monitored by means of detuning the incoming photon frequency from the absorption resonance.

The narrowing of the RXS spectral profiles is shown to qualitatively differ between inelastic and elastic RXS. The width of the RXS band is determined in the general case by the structure of vibrational levels of ground, core-excited, and final states. When the RXS process is fast (large detuning or large lifetime broadening), the molecule has no time to execute vibrations in the intermediate core-excited state, and narrowing of the RXS profile will take place, since the contribution of the core-excited-state potential in forming the RXS band is removed. The RXS profile is then broadened only by vibrational excitations from the direct transition from the ground state to the final optical state. This narrowing effect is typical for inelastic RXS when the potential surfaces of ground and final states differ substantially. The total removal, or collapse, of vibrational broadening takes place if the potential surfaces of ground and final states coincide, as is the case for elastic Rayleigh RXS. Our findings are illustrated by some numerical calculations of RXS spectral profiles and second moments for a diatomic molecule.

ACKNOWLEDGMENT

This work was supported by the Swedish National Science Research council (NFR) and by the Russian Foundation of Fundamental Research (Grant No. 96-0219826).

APPENDIX A: DURATION OF RXS

The RXS process has two characteristic time scales. The first one is the duration time of RXS, τ_c; the second one, τ, characterizes the deformation of the initial wave packet on the potential surface of a core-excited state. The relation between these characteristic time scales strongly influences the RXS spectral shape.

It is natural to introduce a time-dependent representation for the RXS amplitude, Eq. (3), to describe the notion of the duration of RXS:

$$F_{\boldsymbol{l}\mathbf{n}}=\int_0^{\infty} dt F_{\boldsymbol{l}\mathbf{n}}(t), \quad F_{\boldsymbol{l}n}=\imath\sum_{\mathbf{m}} \langle \mathbf{n}|\mathbf{m}\rangle\langle \mathbf{m}|\boldsymbol{l}\rangle \exp[\imath\phi(t)-\Gamma t]. \tag{A1}$$

The phase $\phi(t)=(\Omega'-\omega_{\mathbf{mn}})t$ can be replaced by $\phi(t)=(\Omega-\omega_{\mathbf{m}\boldsymbol{l}})t$ in the case of narrow-band excitation in accordance with Eq. (5). A molecule is core excited due to a photoabsorption at $t=0$. The integral (A1) over emission times t sums all partial RXS amplitudes $F_{\boldsymbol{l}\mathbf{n}}(t)$ to the total RXS amplitude $F_{\boldsymbol{l}\mathbf{n}}$. Apparently, the probability of emission of final x-ray photons is different for different times. The finite lifetime Γ^{-1} of the core-excited state constitutes the primary reason for this strong correlation between times of absorption and emission. Indeed, the delay time between absorption and emission cannot essentially exceed Γ^{-1}, as follows from Eq. (A1). The second reason for the delay of emission relative to absorption is related to the phase difference $\phi(t)$ between the ''sudden'' partial amplitude $F_{\boldsymbol{l}\mathbf{n}}(0)$ and the amplitude $F_{\boldsymbol{l}\mathbf{n}}(t)$ [see Eq. (A1)]. The contribution of $F_{\boldsymbol{l}\mathbf{n}}(t)$ to a total scattering amplitude $F_{\boldsymbol{l}\mathbf{n}}$ is significant only for delay times $t \lesssim |\Omega^{-1}|$ due to the interference of partial RXS amplitudes $F_{\boldsymbol{l}\mathbf{n}}(t)$. It is natural to unite both reasons behind the finite duration of the RXS process and consider τ_c [see Eq. (11)] as the correlation time or duration of the RXS process.

APPENDIX B: CHARACTERISTIC TIME OF DEFORMATION OF THE WAVE PACKET

It is convenient to consider the evolution of the vibrational wave packet $\varphi_{\boldsymbol{l}}$ on the potential surface $U_i(\mathbf{R})$ for the core-excited state in the interaction representation $\varphi_{\boldsymbol{l}}^I=\exp(\imath H_0 t)\varphi_{\boldsymbol{l}}$ [40]. The wave function in this representation is the solution of the equation

$$\imath\frac{\partial}{\partial t}\varphi_{\boldsymbol{l}}^I=V\varphi_{\boldsymbol{l}}^I, \quad V=e^{\imath H_0 t}(H_i-H_0)e^{-\imath H_0 t}. \tag{B1}$$

The dynamics of $\varphi_{\boldsymbol{l}}^I$ is described by the operator V, defined by the difference between the nuclear Hamiltonians H_i and H_0 of the core-excited and ground states, respectively. As follows directly from Eq. (B1) for $\varphi_{\boldsymbol{l}}^I$, the time τ of deformation of the initial wave packet is defined by V^{-1}. One can see that the small perturbation V deforms the initial wave packet quite weakly. The time τ of this deformation can be introduced as [40]

$$\tau^{-1}=\Delta=\left(\sum_{\boldsymbol{l}} (\langle \boldsymbol{l}|V^2|\boldsymbol{l}\rangle-\langle \boldsymbol{l}|V|\boldsymbol{l}\rangle)^2\right)^{1/2}. \tag{B2}$$

The parameter Δ denotes an effective width of the vibrational envelope for the considered electronic x-ray absorption transition. One can see from Eq. (B2) that $\Delta=0$ and $\tau=\infty$ if the potential surfaces of the core-excited and ground states coincide: $V=0$, since $H_i=H_0$. This fact immediately allows us to receive the estimation [Eq. (12)] that is valid for a sufficiently small difference between $U_i(\mathbf{R})$ and $U_0(\mathbf{R})$.

APPENDIX C: RXS SECOND MOMENT IN THE HARMONIC APPROXIMATION

To calculate the second moment of the RXS profile of a diatomic molecule in the harmonic approximation, we use the following formulas. The FC factor between vibrational wave functions $|m\rangle$ and $|n\rangle$ of electronic states i and f,

$$\begin{aligned}\langle n|m\rangle=&(2^n n!2^m m!)^{-1/2}(1-x^2)^{1/4}\exp\left(-\frac{1}{2}f^2(1-x)\right)\\ &\times\sum_{k=0}^{\min(n,m)} \frac{n!m!}{k!}[2(1-x^2)^{1/2}]^k\\ &\times\left(-f\frac{(1-x)}{2^{1/2}}\right)^{n-k}\left[f\left(\frac{1-x^2}{2}\right)^{1/2}\right]^{m-k}\\ &\times h^{n-k}\left(-f\frac{(1-x)}{(-2x)^{1/2}}\right)h_{m-k}\left[f\left(\frac{1-x^2}{2x}\right)^{1/2}\right],\end{aligned} \tag{C1}$$

is expressed in terms of the even function $[h_n(\xi)=h_n(-\xi)]$,

$$h_n(\xi)=\frac{\xi^{-n}}{n!}H_n(\xi),$$

$$h_{n+1}(\xi)=\frac{2}{n+1}\left(h_n(\xi)-\frac{1}{\xi^2}h_{n-1}(\xi)\right), \tag{C2}$$

with $h_0(\xi)=1$, $h_1(\xi)=2$, $h_2(\xi)=2-1/\xi^2$, and $H_n(\xi)$ as Hermite polynomials. The function $h_n(\xi)$ with the recursion formula (C2) is more convenient than $H_n(\xi)$ in numerical calculations of the FC factors, since $h_n(\xi)$ as depending on ξ^2 is well defined in Eq. (C1) for both positive and negative x. The parameters

$$f=\left(\frac{\mu\omega_f}{2}\right)^{1/2}(R_f-R_i), \quad x=\frac{\omega_f-\omega_i}{\omega_f+\omega_i} \tag{C3}$$

in Eq. (C1) depend on the reduced mass μ of the molecule, on the vibrational frequencies (ω_f, ω_i), and on the equilibrium distances (R_f, R_i) of the electronic states f and i, respectively.

To evaluate $\Gamma(\omega)$ in the case of fast RXS [see Eqs. (4) and (13)], the following summations are needed [33]

$$\sum_{n=0}^{\infty} n|\langle n|0\rangle|^2=\frac{1}{2}\left(\mu\omega_f(R_0-R_f)^2+\frac{(\omega_0-\omega_f)^2}{2\omega_0\omega_f}\right), \tag{C4}$$

$$\sum_{n=0}^{\infty} n^2|\langle n|0\rangle|^2=\left(\frac{1}{2}\mu\omega_f(R_0-R_f)^2\right)^2+\frac{\mu(R_0-R_f)^2}{4\omega_0}\times(\omega_0^2+3\omega_f^2-2\omega_0\omega_f)+\left(\frac{\omega_0-\omega_f}{4\omega_0\omega_f}\right)^2\times(3\omega_0^2+3\omega_f^2+2\omega_0\omega_f),$$

where ω_0 and R_0 are the vibrational frequency and equilibrium internuclear distance of the ground state.

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