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Resonant inelastic x-ray scattering with symmetry-selective excitation

Faris Gel'mukhanov*
Institute of Physics, University of Uppsala, S-75121 Uppsala, Sweden

Hans Ågren
Institute of Physics and Measurement Technology, University of Linköping, S-58183 Linköping, Sweden

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We present a theoretical formulation of resonant inelastic x-ray scattering (RIXS) of molecules with an element of symmetry, and study the consequences of this formulation both with respect to short and long lifetimes of the intermediate core-excited scattering states and with respect to localized versus delocalized descriptions for these states. Strong polarization and excitation energy dependencies are predicted. The "core-hole localization" problem is explored also from the point of view of diffractional scattering of an x-ray photon showing that x-ray photons distinguish core holes in the short-wavelength limit only. By analyzing the properties of the x-ray scattering tensor, strict selection rules for the RIXS process are derived. The local decomposition model (one-center approximation) frequently employed in ordinary x-ray emission is generalized for the calculation of intensities and polarization dependence of the RIXS process, assuming either localized or delocalized core holes. It is argued that Stokes doubling should be a commonly observable feature in RIXS spectra. By means of model calculations we demonstrate the crucial role of RIXS selection rules, of channel interferences, of Stokes doubling, and of the form of the excitation frequency function for the appearance of RIXS spectra.

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INTRODUCTION

The development of tunable, narrow-band synchrotron-radiation sources has stimulated studies of inelastic x-ray scattering (IXS) by atoms, molecules, and solids [1–3]. The large interest in spectroscopic studies of IXS processes derives from the potentially rich, but yet largely unexplored, information they provide on electronic structure and scattering dynamics. The achievement in the field of resonant IXS (or resonant x-ray Raman scattering) has spun off from many technical improvements, viz. use of monochromatic x-ray excitation, ability to continuously retune incoming x-ray frequencies near the ionization threshold, use of spectral widths of incoming x-rays smaller than the lifetime broadening of core-excited states leading to resonance narrowing below the lifetime width and to linear dispersions of the resonant IXS (RIXS) lines, possibility for polarization measurements using linearly or circularly polarized radiation, etc. The fact that the width of an x-ray emission line is defined only by the small lifetime broadening of the final optically excited state and by the spectral width of the incoming radiation [4–6] has opened the possibility for superhigh resolution x-ray spectroscopy beyond the resolving power of ten thousand.

The new experimental achievements briefly referred to above has challenged a compatible theoretical progress. Modern formulations of x-ray processes are based on one-step many-channel resonant and off-resonant scattering theory, as introduced by Åberg and co-workers [6]. Using such formulations these authors could establish the sensitive dependence of an x-ray fluorescence spectrum on frequency and spectral shape of the exciting radiation. Studies dating back already to the seventies revealed limitations for the applicability of the so-called two-step model, in which x-ray emission is considered to be independent from the x-ray absorption process. The shortcomings of the two-step model are particularly severe at near-threshold excitation, when the frequency ω of an incoming x-ray photon is close to the ionization threshold for a core electron [6–8], but has also been observed for ω quite far from threshold [4,5,9,10]. In the terminology of the original papers of Refs. [5,7,8] these observations were associated to the effect of *channel interference*, which is not taken into account in conventional theory of x-ray-emission spectra. If the intermediate core-excited states of the RIXS process are coherently excited, the x-ray scattering channels defined by these different core-excited states will interfere when the energy gaps are of the same order of magnitude as the lifetime broadening. The formulation of Refs. [5,7,8] led to a Kramer-Heisenberg-type dispersion formula for the x-ray process, which actually also has been the target for the general scattering formulations [6,9] after appropriate approximations (see, e.g., derivation including nuclear degrees of freedom in Ref. [9]). This common point of departure is reemployed in the present work.

Channel interferences have now been manifested in a number of phenomena, for example, the effect of vibrational-lifetime interference [4,5,9,10], effect of interference between close-lying intermediate core-hole

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*Permanent address: Institute of Automation and Electrometry, 630090 Novosibirsk, Russia.

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electronic states [9], interference in polarization and angular distributions [11]. Of particular interest for the present study is that systems have been identified in which interference between different scattering channels is particularly strong and with sharp dependence of emission spectral shape on the excitation frequency ω and polarization vectors e and e' of initial and final photons. Such systems comprise symmetrical molecules and solids with core-hole states localized or delocalized at different equivalent atoms having the same energies. The interference of scattering channels through the core-hole states localized at different atoms has been studied theoretically for molecules [7] and solids [8] excited by both below and above threshold photons and by electrons [12,13]. As shown in these investigations the RIXS cross section depends very strongly on the symmetry of occupied and unoccupied levels. Strong excitation energy dependence of experimental x-ray fluorescence spectra of diamond [14], fullerene and fullerite (C_{60}) [15] is caused by this interference effect and has been confirmed by some preliminary calculations [15].

Symmetry relations enter in different ways in RIXS spectroscopy; for molecules with multicenter core orbitals delocalized over symmetry related atoms (with the so-called core-hole localization problem entailed), for degenerate core orbitals localized at inversion centers, and for atomic quasidegenerate core orbitals split by molecular fields. As RIXS processes normally are studied for transitions involving penultimate core shells, with resolved valence or Rydberg final states, a dipole character of interaction between molecules and the incoming and scattered radiation is imposed. The RIXS process is constituted by two-photon transitions and the selection rules of this process is, therefore, governed by polarizabilitylike scattering tensors that are similar to those for quadrupole transitions. We will here give formulations of x-ray Raman scattering that are based on localized or delocalized core-hole descriptions. It is demonstrated that the localization problem has particular consequences for channel interference in symmetrical molecules.

In the present work, we explore resonant inelastic x-ray scattering under symmetry selective excitation and give an alternative view of the channel interference effect in this process. The physical reasons for the strong excitation energy dependence of x-ray fluorescence spectra of molecules and solids with an element of symmetry are highlighted. We will show that the selection rules for the x-ray scattering tensor cause a strong dependence of the spectral shape of the RIXS signal on the symmetry of initial and final states and hence on the frequency of the exciting x-ray photons. A demonstration of the theory with respect to symmetry selection, spectral, and polarization effects is given for simplifying models and for the N_2 molecule which represent the common case of symmetry delocalized core-hole states.

The paper is organized as follows. A general theory of the symmetry selective RIXS is given in Sec. I. A qualitative picture of some ideas of this work is presented in the first subsection (Sec. I A). Section II B presents the main relations of RIXS theory with channel interference for randomly oriented molecules. The interference of scattering channels through the core-hole states localized at different atoms is studied in Sec. I C. The delocalized core-hole case is addressed in Sec. I D, followed by an analysis of the notions of localized and delocalized core holes with respect to symmetry selective RIXS and selection rules for the scattering tensor (Sec. I E). In the next subsection (Sec. I F), the problem of x-ray hole localization is analyzed from the point of view of diffractional scattering of x-rays. Section I is concluded by an analysis of Stokes doubling of x-ray emission lines (Sec. I G). Section II presents applications of the theory using simplifying few-state models and the nitrogen molecule as a model system (Secs. II A, II B, and II C). Subsection II B describes the simultaneous action of symmetry selective excitation and Stokes doubling. Our findings are discussed and concluded in the last section, Sec. III.

I. SYMMETRY SELECTIVE RESONANT INELASTIC X-RAY SCATTERING

A. Qualitative picture

Let us consider x-ray fluorescence of a homonuclear diatomic molecule A_2. The process of resonance inelastic scattering of an x-ray photon γ by this molecule can proceed along the following two indistinguishable channels:

$$\gamma+A_2\to\begin{bmatrix}(A^*A)_v\\(AA^*)_v\end{bmatrix}\to(A_2)_{nv}+\gamma' . \tag{1}$$

This process consists of an absorption of a core electron into an unoccupied molecular orbital (MO) ψ_v and the subsequent emission of a final x-ray photon γ' caused by the transition of an electron from the occupied MO ψ_n to the core hole localized at one of the atoms of the molecule. Here, $(A^*A)_v$ and $(AA^*)_v$ denote molecules in intermediate excited states with the core electron promoted from the left and right atoms, respectively, into an unoccupied molecular orbital ψ_v; $(A_2)_{nv}$ denotes the molecule at a final optically excited state $n\to v$. The excited molecules $(A^*A)_v$ and $(AA^*)_v$ have the same energy, therefore, one cannot distinguish between the two channels of the RIXS process in Eq. (1) [the channels (a) and (b) in Fig. 1(I)]. As a result, these channels will interfere, and a phase correlation between them leads to a strong excitation energy dependence for the spectral shape of the fluorescence spectra [7,8,12,13].

Another approach is to assume delocalization of the core holes. In this case, the channel interference will depend on selection rules of the high-symmetry point group (here $D_{\infty h}$). The intermediate core excited states $|1s_1^{-1}\psi_v\rangle$ and $|1s_2^{-1}\psi_v\rangle$ have the same energy, therefore, one can obtain delocalized core-hole wave functions $\psi(1\sigma_g)$ $\psi(1\sigma_u)$ by orthogonal transformations $(1s_1,1s_2\to1\sigma_g,1\sigma_u)$;

$$\psi(1\sigma_{g,u})=\frac{(1s_1\pm1s_2)}{\sqrt{2}} , \tag{2}$$

neglecting for simplicity the vanishing overlap integral between core orbitals $1s_1$ and $1s_2$. In this case, RIXS proceeds through the $1\sigma_g^{-1}\psi_\nu$ or $1\sigma_u^{-1}\psi_\nu$ delocalized core-hole states:

$$\gamma+A_2\rightarrow\begin{bmatrix}(A_2)_{1\sigma_g^{-1}\psi_\nu}\\(A_2)_{1\sigma_u^{-1}\psi_\nu}\end{bmatrix}\rightarrow(A_2)_{n\nu}+\gamma' . \tag{3}$$

Let us consider a symmetry selective excitation of inner-shell electrons by tuning the incoming photon frequency of a strict resonance transition to an unoccupied MO ψ_ν of certain symmetry dictated by dipole selection rules. If the unfilled MO ψ_ν has g or u symmetry only transitions from, respectively, $1\sigma_u$ or $1\sigma_g$ core states are allowed by dipole selection rules and only electrons from occupied MO ψ_n with $g(u)$ symmetry undergo x-ray emission to an inner hole of $u(g)$ symmetry [Fig. 1(II)]. Apparently, dipole emission from an unoccupied MO of u (g) type is forbidden for the same reason. To emphasize the important role of symmetry in this process we address it as symmetry selective RIXS.

Only a part of the MO's assigned in the normal x-ray-emission spectrum generated by broadband excitation can be displayed in symmetry selective RIXS, for which the symmetry of unfilled MO's ψ_ν dictates a one to one correspondence to the symmetry of occupied MO's ψ_n. The symmetry of ψ_ν thus forbids one out of two scattering channels in (3) and, therefore, and opposite to (1), interference between the two inelastic-scattering channels in process (3) will be absent. It is necessary to note that absence of interference of the channels (3) is caused by the particular (high) symmetry of the point group $D_{\infty h}$. The interference of the scattering channels through delocalized core-hole states can of course take place for molecules belonging to other point groups.

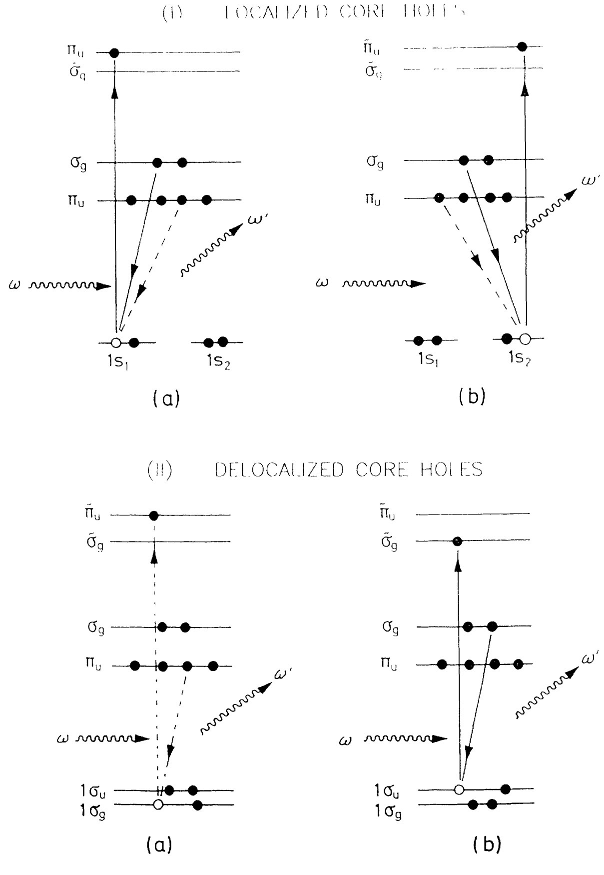

FIG. 1. Qualitative picture of symmetry selective resonance inelastic x-ray scattering. Only the scattering channels with the same final states can interfere. Dashed and solid lines are used to distinguish between scattering channels that lead to different final states.

B. Resonant inelastic x-ray scattering by randomly oriented molecules

The power of contemporary x-ray sources is not sufficient for saturation of the induced radiative transitions and the RIXS process can, therefore, be evaluated in the weak-photon-field limit. Second-order perturbation theory for this two-photon process applies and leads to the Kramers-Heisenberg formula for the resonance x-ray scattering amplitude [4,5,6,16]

$$F_{\nu n}(\omega)=\sum_k f_{\nu n}^k(\omega) , \tag{4}$$

$$f_{\nu n}^k(\omega)=\alpha\omega_{\nu k}\omega_{nk}(\nu)\frac{(\mathbf{e}^*\mathbf{d}_{\nu k})[\mathbf{e}'\mathbf{d}_{kn}(\nu)]}{\omega-\omega_{\nu k}+i\Gamma_{\nu k}} , \tag{5}$$

where $f_{\nu n}^k(\omega)$ denotes the partial or channel amplitude of the RIXS process. The kth channel amplitude $f_{\nu n}^k(\omega)$ describes the two-photon process of absorption of incoming and emission of final x-ray photons, the frequencies, and polarization vectors of which are ω, ω' and $\mathbf{e}$, $\mathbf{e}'$, respectively. The index k enumerates localized or delocalized core orbitals ψ_k. We use atomic units ($\hbar=m=e=1$, $\alpha=\frac{1}{137}$) and the following notations: $\omega_{\nu k}=E(k^{-1}\nu)-E_0$, $\omega_{nk}(\nu)=E(k^{-1}\nu)-E(n^{-1}\nu)$, $\mathbf{d}_{\nu k}=\langle 0|\mathbf{d}|k^{-1}\nu\rangle$, and $\mathbf{d}_{kn}(\nu)=\langle k^{-1}\nu|\mathbf{d}|n^{-1}\nu\rangle$ are resonant frequencies and dipole matrix elements of x-ray-absorption $(k\rightarrow\nu)$ and -emission $(n\rightarrow k)$ transitions, respectively; $\omega_{\nu n}=E(n^{-1}\nu)-E_0$ is a frequency for the optical excitation $n\rightarrow\nu$ and is equal to the difference between energies $E(n^{-1}\nu)$ and E_0 of excited $|n^{-1}\nu\rangle$ and ground $|0\rangle$ molecular states; $\Gamma_{\nu k}$ is the half width at half maximum (HWHM) of the x-ray-absorption line $k\rightarrow\nu$. The electron excited to the vacant MO ψ_ν screens differently the subsequent decay of electrons from various occupied levels n to the inner shell k. This specific screening effect [3] leads to a dependence on ν of the frequencies $\omega_{nk}(\nu)$ and the dipole matrix elements $\mathbf{d}_{kn}(\nu)$.

The spectral and polarization properties of RIXS are guided by the double-differential cross section [4,5]

$$\frac{d^2\sigma}{d\omega' d\Omega}=\sum_\nu\sum_n\frac{\omega'}{\omega}|F_{\nu n}(\omega)|^2\Delta(\omega-\omega'-\omega_{\nu n},\Gamma_{\nu n}) , \tag{6}$$

which takes into account the final-state lifetime broadening $\Gamma_{\nu n}$. The ordinary representation [4,5,6,16] for the double-differential cross section (6) is valid if $\Gamma_{\nu n}=0$.

Here

$$\Delta(\omega,\Gamma)=\frac{\Gamma}{\pi(\omega^2+\Gamma^2)} , \tag{7}$$

$\omega_{\nu n}$ is the resonant frequency of the optical transition $n\rightarrow\nu$ and $d\Omega$ is the solid angle of photon scattering. Formula (6) describes the x-ray fluorescence spectra excited by monochromatic x-ray beams. To describe a realistic experimental situation, we must use the convolution $\sigma(\omega',\omega_0)$

$$\sigma(\omega',\omega_0)=\int d\omega\frac{d^2\sigma}{d\omega' d\Omega}\Phi(\omega-\omega_0) \tag{8}$$

of the RIXS cross section (6) with the incoming photon distribution function $\Phi(\omega-\omega_0)$ centered at frequency ω_0. The lifetime broadening, $\Gamma_{\nu n}$, of the optical transition, $n\rightarrow\nu$ is negligibly small in comparison with the width of x-ray transitions $\Gamma_{\nu k}$. This allows us to use $\Gamma_{\nu n}=0$ and to replace the Δ function (7) in Eq. (6) by the Dirac δ function $\delta(\omega-\omega'-\omega_{\nu n})$. This circumstance is the basis for super-high resolution x-ray spectroscopy and allows the recording of x-ray fluorescence resonances without the x-ray lifetime broadening [4,5,6]. Actually, the width of the convolution lines

$$\sigma(\omega',\omega_0)=\sum_{k'k}\sum_{\nu n}\frac{\omega'}{\omega}f_{\nu n}^{k'}(\omega)f_{\nu n}^{k*}(\omega)\Phi(\omega'+\omega_{\nu n}-\omega_0) \tag{9}$$

is restricted only by the width γ of the spectral function Φ of incoming x rays and, of course, by the instrumental resolution. The frequency ω' of emission x-ray photons has a Raman related shift (Stokes shift) into the long-wave region relative to the frequency ω of the absorbed photon

$$\omega=\omega'+\omega_{\nu n} , \tag{10}$$

in accordance with the energy-conservation law reflected by the $\delta(\omega-\omega'-\omega_{\nu n})$ function.

The line profile (9) for the fluorescence process differs strongly from the pattern that would be formed by a superposition of a set of displaced Lorentzians, characteristic for the ordinary theory of x-ray emission. One finds instead that the shape of emission bands is given by a sum of direct $|f_{\nu n}^{k}|^2$ and interference or cross terms $f_{\nu n}^{k'}(\omega)f_{\nu n}^{k*}(\omega)(k\neq k')$. As seen from Eq. (9) the interference terms have the same order of magnitude as the direct terms when the lifetime broadening is comparable with the energy difference of intermediate core-excited states. Sometimes it is possible to eliminate the interference terms by an appropriate choice of intermediate core-excited states. We shall see below that this is possible for systems of high symmetry when the intermediate states are degenerate. Is it possible to remove the interference in the general case by appropriate transformations of the initial intermediate states? Most probably the answer is negative. The lifetime-vibrational interference effect [4,5,9,10] confirms this partially.

For samples in the gas phase it is necessary to average the cross section (9) over all molecular orientations. This is equivalent to an averaging over the directions of photon propagation under fixed angle θ between the real polarization vectors **e** and **e**′. Denoting averaged quantities by bars and using the formula

$$\begin{aligned}\overline{(e_i'e_j'^{*}e_ke_l^{*})}=\tfrac{1}{6}[&\delta_{ij}\delta_{kl}(1-\cos^2\theta)\\&+\tfrac{1}{5}(\delta_{ij}\delta_{kl}+\delta_{ik}\delta_{jl}+\delta_{il}\delta_{jk})\\&\times(3\cos^2\theta-1)] ,\end{aligned} \tag{11}$$

we get the following invariant expression for the RIXS cross section (9):

$$\sigma(\omega',\omega_0)=\sum_{n\nu}\sum_{kk'}\rho\frac{\Phi(\omega'+\omega_{\nu n}-\omega_0)\Gamma_{\nu k}\zeta_{\nu n}^{kk'}(\theta)}{\pi(\omega-\omega_{\nu k}+i\Gamma_{\nu k})(\omega-\omega_{\nu k'}-i\Gamma_{\nu k'})} . \tag{12}$$

Here, $i,j,k,l=(x,y,z)$; δ_{ij} is the Kronecker δ symbol. $\rho=\pi\alpha^2\omega_{\nu k}\omega_{\nu k'}\omega_{nk}(\nu)\omega_{nk'}(\nu)\omega'/(\omega\Gamma_{\nu k})$ depends only weakly on k, k', n, and ν. In the general case the polarization dependence of the RIXS cross section is described by the function

$$\begin{aligned}\zeta_{\nu n}^{kk'}(\theta)=\tfrac{1}{15}\Bigg[&(\mathbf{d}_{\nu k}\mathbf{d}_{\nu k'})(\mathbf{d}_{kn}(\nu)\mathbf{d}_{k'n}(\nu))(2-\cos^2\theta)\\&+[(\mathbf{d}_{\nu k}\mathbf{d}_{kn}(\nu))(\mathbf{d}_{\nu k'}\mathbf{d}_{k'n}(\nu))\\&+(\mathbf{d}_{\nu k}\mathbf{d}_{k'n}(\nu))(\mathbf{d}_{\nu k'}\mathbf{d}_{kn}(\nu))]\\&\times\left[\frac{3\cos^2\theta-1}{2}\right]\Bigg] .\end{aligned} \tag{13}$$

Due to rotational invariance of this expression we can calculate the scalar product of the dipole matrix elements in any system of reference, for example, in the molecular frame. It is necessary to replace $\cos^2\theta$ in Eq. (13) with $\frac{1}{2}\sin^2\chi$ when the initial x-ray beam is unpolarized or when a summation over the final photon polarization vectors **e**′ is made. In the first case, χ is the angle between **e**′ and the direction **n** of incoming photon propagation, in the second case, χ is the angle between **e** and **n**′, the direction of the outgoing photon propagation.

In the following, we apply the general formulas derived above for the case when core shells of some complex molecule or solid are degenerate. A core hole "is burnt" by light under dipole transitions into an unoccupied MO ψ_ν. The symmetry of the core-hole state or of a certain superposition of core-hole states is defined by the symmetry of ψ_ν due to dipole selection rules. The same selection rules restrict the symmetry of an occupied MO ψ_n from which the emitting transition filling the core hole is allowed. As a result there exists a strong symmetry correlation between unoccupied and occupied MO's which take part in the RIXS process. This symmetry correlation yields the strong frequency and polarization dependencies of x-ray fluorescence spectra in the more general cases too. Below we demonstrate these features for the special case of symmetry selective RIXS when localized, respectively, delocalized core holes are assumed.

C. Localized core holes

In the case of localized core holes we restrict ourselves for simplicity to the common case of K-shell RIXS processes and apply a linear combination of atomic orbital (LCAO) expansion for the molecular orbitals. In the one-center approximation (local symmetry decomposition rule) we then consider molecular orbitals of the form:

$$\psi_i=\sum_k (\mathbf{C}_i^{(k)}\mathbf{p}^{(k)})+\cdots , \tag{14}$$

where the scalar product of the three-dimensional vectors of MO's coefficient $\mathbf{C}_i^{(k)}=(C_i^{(k)}(x), C_i^{(k)}(y), C_i^{(k)}(z))$ and atomic p-wave functions $\mathbf{p}^{(k)}=(p_x^{(k)},p_y^{(k)},p_z^{(k)})$ are introduced. Thus at each center k the atomic p contributions to that center are extracted, since only these atomic orbitals (AO's) are important for a K spectrum. When the general RIXS cross section of Eq. (12) is applied to K fluorescence of localized core holes for molecules with identical atoms the $\zeta_{\nu n}^{kk'}(\theta)$ function of Eq. (13) will have the particular form:

$$\begin{aligned}\zeta_{\nu n}^{kk'}(\theta)=\frac{d^4}{15}\Bigg[&(\mathbf{C}_\nu^{(k)}\mathbf{C}_\nu^{(k')})(\mathbf{C}_n^{(k)}\mathbf{C}_n^{(k')})(2-\cos^2\theta)\\ &+[(\mathbf{C}_\nu^{(k)}\mathbf{C}_n^{(k)})(\mathbf{C}_\nu^{(k')}\mathbf{C}_n^{(k')})\\ &+(\mathbf{C}_\nu^{(k)}\mathbf{C}_n^{(k')})(\mathbf{C}_\nu^{(k')}\mathbf{C}_n^{(k)})]\\ &\times\left[\frac{3\cos^2\theta-1}{2}\right]\Bigg] .\end{aligned} \tag{15}$$

Here, $d=\int d\mathbf{r}\, 1s d_z p_z$ is the atomic dipole matrix element (z is here interchangeable with x or y). Equations (12) and (15) generalize the results obtained in papers from Refs. [7,8,12]. It is sometimes more convenient to represent the RIXS cross section in terms of localized core holes, for example, in the cases of large molecules or molecules with low symmetry when energies of core electrons differ weakly due to a different chemical surroundings (see also Sec. I F). This is exemplified by the applications in Sec. II and is relevant for systems like N_2 adsorbed on a surface or oligomer sequencies, with slightly different core ionization thresholds due to different geometrical positions.

D. Delocalized core holes

Let us apply the general formulas (12) and (13) to RIXS K spectra of systems with delocalized core holes. In this case the ζ function, showing the polarization dependence of RIXS, will depend on the particular point group for the molecule through the particular form or the symmetry adapted LCAO expansions of the molecular orbitals. For systems with periodic boundary conditions (polymers, metals) the ζ functions are derived directly from the Bloch functions of the MO's. Below we consider the most important case, namely, K-shell RIXS of homonuclear diatomics, and restrict the LCAO expansion to atomic s and p orbitals. We thus consider normalized $n\sigma_g$ and $n\sigma_u$ molecular orbitals $\psi(n\sigma_{g,u})$, while doubly degenerate $n\pi_g$ and $n\pi_u$ MO's $\psi(n\pi_{g,u})$ are composed of the normalized p_x and p_y (AO)

$$\begin{aligned}&\psi(n\sigma_{g,u})=C(n\sigma_{g,u})(p_z^{(1)}\pm p_z^{(2)})+\cdots ,\\ &\psi(n\pi_{g,u})=C(n\pi_{g,u})(p_{x(y)}^1\mp p_{x(y)}^2)+\cdots ,\end{aligned} \tag{16}$$

where we have retained only contributions from the p AO's (since we are considering a K spectrum) and where the z axis determines the molecular axis. To begin with we shall use the frozen orbital approximation and calculate the dipole matrix elements

$$\mathbf{d}_{ik}=\int d\mathbf{r}\,\psi(n\sigma_i \text{ or } n\pi_i)\mathbf{d}\psi(1\sigma_k) \tag{17}$$

of the one-electron operator $\mathbf{d}$ between the delocalized K shell ($1\sigma_g$ or $1\sigma_u$) and valence MO's $\psi(n\sigma_i)$ and $\psi(n\pi_i)$. The subscripts i, k indicate here gerade (g) and ungerade (u) states. The dipole matrix element

$$\mathbf{d}_{ik}=\begin{cases}0 , & i=k\\ \sqrt{2}Cd\mathbf{n} , & i\neq k\end{cases} \tag{18}$$

is expressed through the atomic dipole matrix element d defined after Eq. (15) and coefficient $C\equiv C(n\sigma_i)$ or $C(n\pi_i)$ of the MO (16). The unit vector $\mathbf{n}$ is directed along molecular axis z for $\psi=\psi(n\sigma_i)$ and along x or y axes when the π orbital $\psi(n\pi_i)$ has x or y orientation. Formula (18) implies that $g\leftrightarrow u$ transitions are only allowed and that $g\leftrightarrow g$ or $u\leftrightarrow u$ are parity forbidden. The selection rules (18) lead directly to the following expression for the cross section of Eq. (12).

$$\begin{aligned}&\sigma(\omega',\omega_0)=\sum_{\nu n}\sigma_{\nu n}(\omega',\omega_0) ,\\ &\sigma_{\nu n}(\omega',\omega_0)=\rho\Delta(\Omega_n',\Gamma_{\nu k})\Phi(\Omega_\nu-\Omega_n')\zeta_{n\nu}(\theta) ,\end{aligned} \tag{19}$$

where ρ is the frequency dependent factor defined after Eq. (12). To emphasize the resonant character of the cross section (19) the frequency detunings $\Omega_n'=\omega'-\omega_{nk}(\nu)$ and $\Omega_\nu=\omega_0-\omega_{\nu k}$ from the x-ray emission, $\omega_{nk}(\nu)$, and absorption, $\omega_{\nu k}$, resonances are introduced. The subscripts n and ν enumerate all occupied and unoccupied valence MO's, respectively. For brevity we drop the notation n of $n\sigma_i$ and $n\pi_i$ orbitals and implicitly assume summation over $n=(\sigma_i,\pi_i)$ and $\nu=(\tilde\sigma_i,\tilde\pi_i)$ in Eq. (19) over all occupied $(n\sigma_i,n\pi_i)$ and unoccupied $(n\tilde\sigma_i,n\tilde\pi_i)$ orbitals. The symmetry selective interaction is then described by the functions

$$\begin{aligned}&\zeta_{\tilde\pi_j\pi_i}(\theta)=QN_{\pi_i}(C_{\pi_i}\tilde C_{\pi_j})^2(3+\cos^2\theta)\delta_{ij} ,\\ &\zeta_{\tilde\pi_j\sigma_i}(\theta)=2QN_{\sigma_i}(C_{\sigma_i}\tilde C_{\pi_j})^2(2-\cos^2\theta)\delta_{ij} ,\\ &\zeta_{\tilde\sigma_j\pi_i}(\theta)=QN_{\pi_i}(C_{\pi_i}\tilde C_{\sigma_j})^2(2-\cos^2\theta)\delta_{ij} ,\\ &\zeta_{\tilde\sigma_j\sigma_i}(\theta)=QN_{\sigma_i}(C_{\sigma_i}\tilde C_{\sigma_j})^2(1+2\cos^2\theta)\delta_{ij} ,\end{aligned} \tag{20}$$

where $\zeta_{\nu n}(\theta)=\sum_{kk'}\zeta_{\nu n}^{kk'}$; $Q=\frac{2}{15}d^4$, d being the atomic dipole integral defined above, and $i,j=(u,g)$. The population numbers of the ground state can be equal to $N_{\sigma_i}=0$, 1, 2 and $N_{\pi_i}=0,1,2,3,4$ in the general case. Equations (19) and (20) demonstrate directly that only occupied MO's of the $g(u)$ type are represented in the K-emission spectrum when the frequency ω_0 of the incoming photon is tuned into an exact resonance with respect to a vacant MO of $g(u)$ symmetry.

Let us now tune ω_0 to an exact resonance with respect to some Rydberg level $\tilde\nu$. This level is defined by quaside-

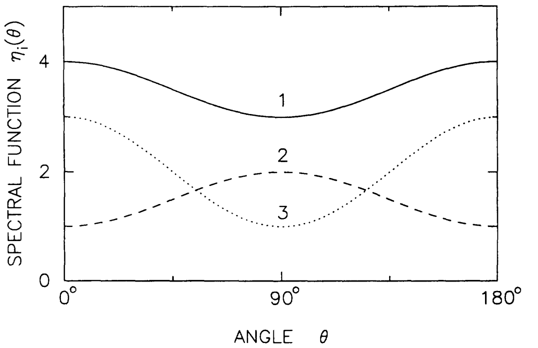

FIG. 2. Polarization dependence [Eq. (20)] of the RIXS cross section. 1: $\eta_1(\theta)=3+\cos^2\theta$, 2: $\eta_2(\theta)=2-\cos^2\theta$, 3: $\eta_3(\theta)=1+2\cos^2\theta$.

generate orbitals of $\tilde{\pi}_{u,g}$, $\tilde{\sigma}_{u,g}$ or higher symmetries, over which the $\zeta_{vn}(\theta)$ functions (20) can be summed. This partial summation over v, $\zeta_{\tilde{v}n}(\theta)=\sum_v \zeta_{vn}(\theta)$, yields one isotropic ζ function only $[n=(\sigma_i,\pi_i)]$.

$$\zeta_{n\tilde{v}}(\theta)=5QN_n(C_n\tilde{C}_{\tilde{v}})^2 , \tag{21}$$

where the $\tilde{C}_{\tilde{v}}$ coefficient refers to the $\tilde{v}p$-atomic orbital in the Rydberg-type MO. The selection rules (20) and (21) for the scattering tensor $\mathbf{F}_{vn}(\omega)$ connected with the scattering amplitude (4), $F_{vn}(\omega)=\mathbf{e}^*\mathbf{F}_{vn}\mathbf{e}'$, makes clear the dependence of the fluorescence spectral shape (19) on the symmetry of the unoccupied MO ψ_v and hence on the frequency of the exciting radiation ω_0. The angular dependence (20) of the x-ray emission spectrum (19) is also symmetry specific (Fig. 2). This effect is caused by the orientation-selective nature of the interaction of x rays with molecules [2,17], when unoccupied MO's mainly oriented along the polarization vector $\mathbf{e}$ are excited. Because the x-ray-excited molecules are partially oriented in space the accompanying emission process will be similar to x-ray emission in oriented crystals.

We note that the results obtained for the delocalized case [Eqs. (19), (20), and (21)] also can be obtained from the localized holes representation, Eq. (15), for the ζ function when the symmetry properties $C_i^{(1)}=\pm C_i^{(2)}$ imposed by the higher point group are considered.

E. Selection rules for the x-ray scattering tensor

Our previous consideration of selection rules was restricted to the one-particle (one-configuration) and frozen orbital approximation. The limitations of this approximation for core excitation processes is well known and will be further dealt with in the next subsection. Here, we consider the bearing of the core-hole localization problem on the symmetry selection of the RIXS process. For example, core localization in the A_2 molecule reduces molecular-orbital symmetries from $D_{\infty h}$ to $C_{\infty v}$. It is natural to ask if the transition between molecular states of opposite parity $u\rightarrow g$ or $g\rightarrow u$ will be strictly forbidden under inelastic x-ray scattering or if this interdiction is valid only in the frozen orbital approximation. Group theory gives a clue to the validity of these selection rules. Let us rewrite the expression (4) for the scattering tensor $\mathbf{F}_{vn}(\omega)$ $[F_{vn}(\omega)=\mathbf{e}^*\mathbf{F}_{vn}(\omega)\mathbf{e}']$:

$$\mathbf{F}_{vn}(\omega)=\langle n^{-1}v|\mathbf{d}\Lambda\mathbf{d}|O\rangle , \tag{22}$$

where the function

$$\Lambda=\sum_k \frac{\alpha\omega_{vk}\omega_{nk}(v)}{\omega-\omega_{vk}+i\Gamma_{vk}}|k^{-1}v\rangle\langle k^{-1}v| \tag{23}$$

is invariant with respect to inversion. This is apparent for the case of delocalized core holes which do not break the symmetry of the $D_{\infty h}$ group. Indeed a real wave function $|k^{-1}v\rangle$ of the $D_{\infty h}$ symmetry can change only sign on inversion. Therefore, on inversion the product $|k^{-1}v\rangle\langle k^{-1}v|$ is invariant. The multiplier $(|1s_1v\rangle\langle 1s_1v|+|1s_2v|)$ is extracted from Eq. (23) for the case of localized core holes, because eigenvalues of the molecular Hamiltonian remain unchanged if the atoms of an A_2 molecule are interchanged. This multiplier and hence Λ is invariant also with respect to inversion. We restrict ourselves to the case when the ground-state wave function $|O\rangle$ is invariant with respect to inversion. It is seen from Eq. (22) that on inversion the wave function $|n^{-1}v\rangle$ can change sign only. The matrix element $\mathbf{F}_{vn}(\omega)$ (22) is the integral over all space for all electrons and is invariant with respect to any transformation of the coordinate system, including any symmetry transformation. Therefore, $\mathbf{F}_{vn}(\omega)\equiv 0$ when $|n^{-1}v\rangle\rightarrow -|n^{-1}v\rangle$ under some transformation. Thus, the selection rules depend on the parity of the final wave function of the optical excited state $|n^{-1}v\rangle$. On inversion the integrand in Eq. (22) changes sign only if $|n^{-1}v\rangle$ changes sign. The RIXS transition will therefore be forbidden if $|n^{-1}v\rangle$ is an odd state. For example, the RIXS transitions are strictly forbidden when occupied (ψ_n) and unoccupied (ψ_v) MO's have opposite parity: ug or gu, and only the final states $|g^{-1}g\rangle$ or $|u^{-1}u\rangle$ can be reached from the ground state $|O\rangle$. So the selection rules for the scattering tensor of the RIXS process are defined for the case of an A_2 molecule by the symmetries of the ground and final optical excited states only.

F. X-ray diffraction scattering and the problem of x-ray hole localization

The problem of symmetry breaking and particle and hole localization has relevance for great many phenomena, but is most conspicuous for core-level spectroscopies for which it has been debated over a long time [18,19]. For example, core-excited states with the hole delocalized or localized at one of the centers of the N_2 molecule differ qualitatively because of relaxation. Hartree-Fock computations show severe instabilities for delocalized, symmetry restricted, solutions. The symmetry broken solutions describing the core hole are thus more stable than the symmetry adapted ones. The symmetry breaking can be seen as a relaxation effect in the lower point group which corresponds to a correlation contribution in the higher point group. The "relaxation" which localizes the core hole thus corresponds to different symmetry adapted (here ungerade and gerade) mixings in the higher-symmetry point group [19,20]. Beyond the one-particle (one-configuration) approximation symmetry adapted and relaxed solutions are easily retained by superposing the (relaxed) configurations with core holes localized at different sites. It is also relevant to point out that in the polyatomic case the symmetry of even the nuclear skeleton will break (and the core holes accordingly localize) due to effective Jahn-Teller interactions between the quasidegenerate delocalized core-hole configurations, CO_2 being the prime example here [21,22]. Nevertheless, to obtain a clue to the problem if the core hole localizes or not during the RIXS process one must, in addition to the pure internal electronic (or vibronic) part of the problem, look at it from the perspective of an electron-photon-field representation. This may be accomplished by analyzing the diffractional scattering of x-rays.

The Kramers-Heisenberg expression for the x-ray scattering amplitude in the form of Eq. (5) is valid only for a soft-x-ray radiation ($\omega,\omega' \ll \alpha^{-1}$), when the wavelength λ of the x-ray photons is larger than the distance $R_{kk'}$ between atoms k and k'. In the general case, the right-hand side of Eq. (5) must be multiplied by the factor $\exp(i\mathbf{q}\mathbf{R}_k)$, where $\mathbf{R}_k$ is the coordinate of the kth atom. The change of the x-ray photon momentum, $\mathbf{q}=\boldsymbol{\kappa}'-\boldsymbol{\kappa}$, during an x-ray scattering can be expressed through the angle φ between momenta of initial $\boldsymbol{\kappa}$ and final $\boldsymbol{\kappa}'$ photons; $q \simeq 2\kappa \sin(\varphi/2)$. As a result the x-ray cross-section formula, Eq. (9) appears with the phase factor

$$\exp(i\mathbf{q}\mathbf{R}_{kk'}) \ , \tag{24}$$

where $\mathbf{R}_{kk'}=\mathbf{R}_k-\mathbf{R}_{k'}$. This quantity describes the diffraction scattering of x rays by atoms in a molecule or a solid. Apparently, only off-diagonal ($k \neq k'$) or interference ζ functions, Eqs. (13) and (15), are modulated by this factor. The original ζ functions are replaced in the general case by the following ζ functions

$$\zeta_{\nu n}^{kk'}(\theta) \rightarrow \zeta_{\nu n}^{kk'}(\theta, qR_{kk'}) \ , \tag{25}$$

which now depend on the ratio of the interatomic distance and the x-ray photon wavelength: $(R_{kk'}/\lambda)$. The explicit expression for this function is quite complex in the case of a K spectrum. However, the limiting dependencies of these functions in terms of the diffractional parameter $qR_{kk'}$ are easily derived:

$$\zeta_{\nu n}^{kk'}(\theta, qR_{kk'}) = \begin{cases} \zeta_{\nu n}^{kk'}(\theta) & \text{if } qR_{kk'} \ll 1 \\ \sim \dfrac{1}{qR_{kk'}} & \text{if } qR_{kk'} \gg 1 \ . \end{cases}$$

The long wave limit is evident because $\exp(i\mathbf{q}\mathbf{R}_{kk'}) \simeq 1$ when $qR_{kk'} \ll 1$. In the opposite limit, $qR_{kk'} \gg 1$, this exponent oscillates strongly as a function of the angle between $\mathbf{q}$ and $\mathbf{R}_{kk'}$. An averaging of the RIXS cross section over molecular orientations yields the factor $1/(qR_{kk'})$, thus decreasing the nondiagonal ζ function by $(qR_{kk'})$ and hence breaking the interference between scattering channels (1). The case of L-spectra with the L electron excited into s orbitals, allows a quite simple expression for the ratio

$$\frac{\zeta_{\nu n}^{kk'}(\theta, qR_{kk'})}{\zeta_{\nu n}^{kk'}(\theta)} = \frac{\sin(qR_{kk'})}{qR_{kk'}} \ , \tag{26}$$

which also exposes directly the diffractional character of the discussed interference terms. This visualizes the so-called "core-hole localization" problem if we also recall Young experiments of light scattered by two slits (here two atoms): Apparently the interference term $\zeta_{\nu n}^{kk'}$ ($k \neq k'$) plays an important role, being nonzero, only when the x-ray photons, in principle, cannot "distinguish" atoms in the molecule, i.e., when the x-ray photon wavelength is comparable or larger than the interatomic distance ($\lambda/R_{kk'} \gtrsim 1$). By contrast, when $\lambda \ll R_{kk'}$ the x-ray photon can "see" an individual atom (slit) and create a core hole in this atom. So only at the short wave region $\lambda \ll R_{kk'}$ the interference of the channels in Eq. (1) is absent and the traditional theory of x-ray emission without the selection rules (20) is valid.

G. Stokes doubling of x-ray emission lines

As it was shown above the spectral shape of x-ray fluorescence spectra is changed strongly when the incoming x-ray photon frequency ω_0 is tuned from one to another x-ray-absorption line. One can see from Eq. (19) that the shape of an x-ray-emission spectrum is changed also when the frequency ω_0 is scanned near one sole absorption line. It is, therefore, relevant to consider the effect of frequency detuning ω_0 from the center of an x-ray absorption line ($1s \rightarrow \psi_\nu$). Considering only one occupied MO ψ_n and one unoccupied MO ψ_ν [(1+1) model] the spectral shape of the RIXS cross section (19) is described only by one function

$$\Xi(\Omega', \Omega) = \Delta(\Omega', \Gamma)\Phi(\Omega - \Omega') \ , \tag{27}$$

where $\Omega=\omega_0-\omega_{\nu k}$ and $\Omega'=\omega'-\omega_{nk}(\nu)$ are the frequency detunings from absorption and emission resonances, respectively. For the sake of simplicity the subscripts n and ν are dropped here. The $\Delta(\Omega', \Gamma)$ function responsible for emission leads to the ordinary condition for an emission resonance:

$$\Omega'=0 \ . \tag{28}$$

The incoming x-rays spectral function $\Phi(\Omega-\Omega')$ has a maximum when the detunings of both incoming and outcoming photons are the same:

$$\Omega'=\Omega \ . \tag{29}$$

This condition, describing the Stokes shift of a scattering line, is equivalent to the energy conservation law (10). The fluorescence spectral line shape (27) described by the $\Xi(\Omega', \Omega)$ function has two resonant features, see Eqs. (28) and (29), when the spectral widths of the $\Delta(\Omega', \Gamma)$ and $\Phi(\Omega-\Omega')$ functions are comparable [23]. We have calculated this function assuming a Lorentz form for the spectral function Φ:

$$\Phi(\Omega-\Omega') = \Delta(\Omega-\Omega', \gamma) \ , \tag{30}$$

with the HWHM being equal to γ. The ordinary emission line (28) is present in all cases shown in Fig. 3, while the Stokes resonance (29) is only seen when $\Omega \neq 0$ (cf. curves 2 and 3 in Fig. 3). The Stokes resonance has a redshift or a blueshift relative to the ordinary emission line (28) if the incoming x-ray photon frequency ω_0 is lower $(\Omega < 0)$ or larger $(\Omega > 0)$ than the resonant frequency ω_{vk}, respectively. This results in a doubling of the x-ray-emission lines, what we can call the "Stokes doubling" effect. The intensity ratio of the Stokes and ordinary emission lines is governed by the width ratio

$$\xi = \frac{\gamma}{\Gamma} \; . \tag{31}$$

as can be seen directly from Eq. (27). The intensity of the Stokes line is smaller than the one of the ordinary emission resonance if the spectral distribution of incoming x rays is broader than the lifetime width Γ, $\xi > 1$ [Fig. 3(a)]. The opposite case takes place when $\xi < 1$ [Fig. 3(c)]. If the lifetime broadening and the spectral width of incoming x-ray photons are the same, $\xi = 1$, the two resonances have the same intensity [Fig. 3(b)].

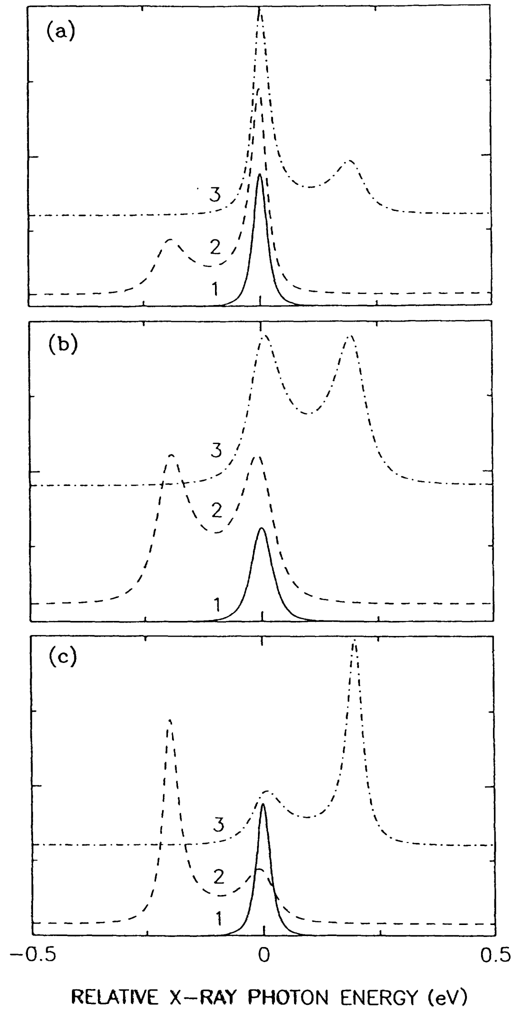

FIG. 3. Stokes doubling in the (1+1) model (27). Dependence of fluorescence intensity on Ω' for different Ω and ξ, see Eq. (31). Ω and Ω' are frequency detunings of incoming and outcoming x-ray photons relative to the corresponding absorption and emission resonances. 1: $\Omega = 0$ (ordinary emission line). The intensity is decreased a factor of 40. 2: $\Omega = -0.2$ eV. 3: $\Omega = 0.2$ eV. (a): $\gamma = 0.04$ eV, $\Gamma = 0.02$ eV $(\xi > 1)$. (b): $\gamma = 0.04$ eV, $\Gamma = 0.04$ eV $(\xi = 1)$. (c): $\gamma = 0.02$ eV, $\Gamma = 0.04$ eV $(\xi < 1)$.

II. APPLICATIONS

We illustrate the formalism presented above by means of model calculations. These include a (2+2) model and the nitrogen molecule. For the (2+2) model we consider the following orbitals in order; (π_u, σ_g) as occupied MO's and $(\tilde{\sigma}_g, \tilde{\pi}_u)$ as unoccupied MO's (Fig. 1). This choice prepares the analysis for the N_2 molecule, the ground state of which has the configuration, $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 ({}^1\Sigma_g^+)$, and first vacant MO's, $1\pi_g$, $4\sigma_g$, $2\pi_u$, and $3\sigma_u$. For experimental x-ray-emission and -absorption studies of N_2 we refer to Refs. [24–27].

A. Symmetry selection in a (2+2) model

In accordance with the selection rules (20) only two partial cross sections, $\sigma_{\tilde{\sigma}_g, \sigma_g}$ and $\sigma_{\tilde{\pi}_u, \pi_u}$, are represented in the RIXS cross section (19)

$$\sigma(\omega', \omega_0) = \sigma_{\tilde{\sigma}_g, \sigma_g}(\omega', \omega_0) + \sigma_{\tilde{\pi}_u, \pi_u}(\omega', \omega_0) \; , \tag{32}$$

the other two partial cross sections $\sigma_{\tilde{\sigma}_g, \pi_u} \sigma_{\tilde{\pi}_u, \sigma_g}$ being equal to zero due to symmetry (20). We assume here closed shells $(N_{\sigma_g} = 2,\ N_{\pi_u} = 4)$ and unit MO coefficients. Two qualitatively different cases exist depending on the ratio

$$\epsilon = \frac{\Delta}{\gamma} \tag{33}$$

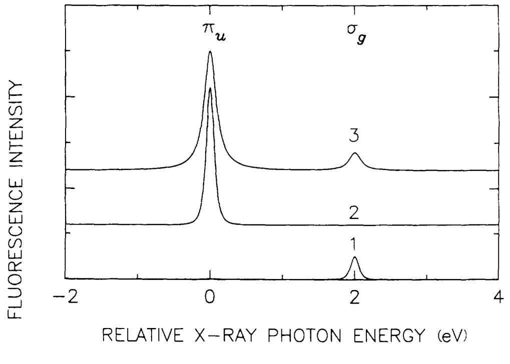

FIG. 4. The K fluorescence of A_2 molecule for the (2+2) model under symmetry selective excitation. The positions of emission lines $\pi \rightarrow 1\sigma_g$ and $\sigma_g \rightarrow 1\sigma_u$ are marked by π_u and σ_g labels. The x-ray emission photon energy is given relative to the $\pi_u \rightarrow 1\sigma_g$ line. $\theta = 90°$. $\Delta = \omega_{\sigma_g 1\sigma_u} - \omega_{\pi_u 1\sigma_g} = 2$ eV. $\Gamma = 0.1$ eV. 1: Excitation of K electron into $\tilde{\sigma}_g$ unfilled MO only $(\gamma = 0.1$ eV). 2: Excitation of K electron into $\tilde{\pi}_u$ unfilled MO only $(\gamma = 0.1$ eV). 3: Broadband excitation of K electron into unoccupied MO's $\tilde{\sigma}_g$ and $\tilde{\pi}_u$ $(\epsilon \ll 1)$.

of the difference between resonance absorption frequencies $\Delta=\omega_{\tilde{\pi}_u k}-\omega_{\tilde{\sigma}_g k}$ and the HWHM γ of the spectral function $\Phi(\omega-\omega_0)$. In the first case, both unoccupied levels, $\tilde{\sigma}_g$ and $\tilde{\pi}_u$, are excited by a broadband light beam ($\epsilon \ll 1$), resulting in an emission spectrum with two lines, $\pi_u \rightarrow 1s$, $\sigma_g \rightarrow 1s$ (line 3, Fig. 4). The same spectral shape is observed by "tail excitation" with ω_0 quite far from the K-ionization threshold. In the opposite limit of narrow band excitation, $\epsilon \gg 1$, individual absorption lines can be resonantly (and exclusively) populated; $1s \rightarrow \tilde{\sigma}_g$ or with $1s \rightarrow \tilde{\pi}_u$ (lines 1 and 2, respectively, Fig. 4). That only one resonance emission band is obtained in any of these two cases can be seen as an effect of the symmetry selection rules for the scattering tensor in the delocalized core-hole case or as due to interference of the scattering channels (1) in the localized core-hole case.

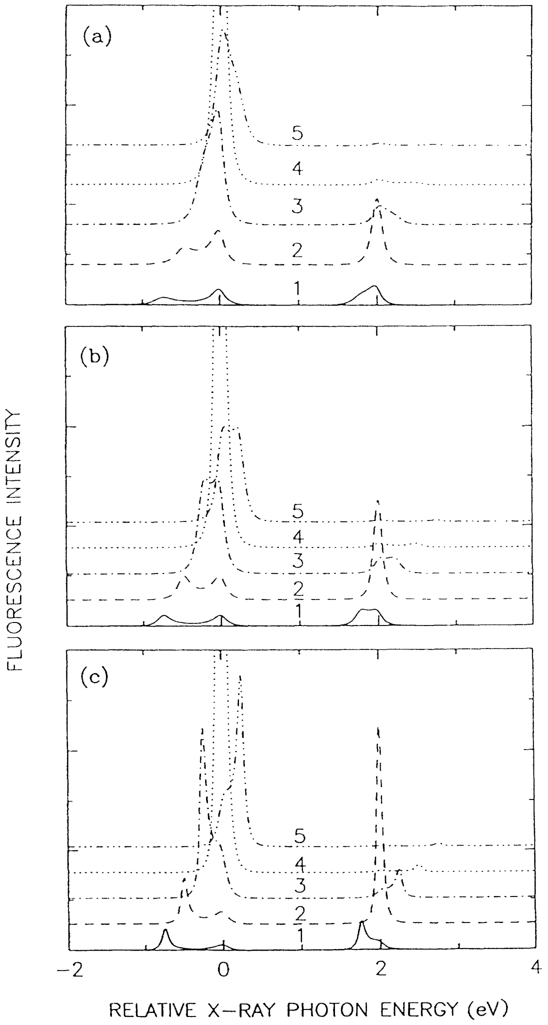

FIG. 5. Dependence of fluorescence intensity on emission frequency detuning $(\omega'-\omega_{\pi_u k})$ relative to $\pi_u \rightarrow 1s$ emission frequency. The order and values of energy levels are same as in Fig. 4. $\omega_{\tilde{\pi}_u k}-\omega_{\tilde{\sigma}_g k}=0.5$ eV, $\Gamma=0.1$ eV, $\theta=90°$. The curves 1, 2, 3, 4, and 5 correspond, respectively, to the following values of absorption photon detuning; $\omega_0-\omega_{\tilde{\sigma}_g k}=-0.25$, 0, 0.25, 0.5, and 0.75 eV. (a) $\gamma=0.15$ eV. (b) $\gamma=0.1$ eV. (c) $\gamma=0.05$ eV. The intensity of the left single resonance in curve 4 is 6.5 times larger than the right single resonance of curve 2.

B. Simultaneous action of symmetry selective excitation and Stokes doubling

The (2+2) model is capable of demonstrating the simultaneous action of symmetry selective excitation and Stokes doubling. The following parameters are assumed: $\Gamma=0.1$ eV; the energy difference between emission transitions from σ_g and π_u MO's is 2 eV and the energy difference between absorption transitions into $\tilde{\pi}_u$ and $\tilde{\sigma}_g$ is 0.5 eV. The curves 2 and 4 of Fig. 5 correspond to the cases when the carrying frequency ω_0 of the spectral distribution $\Phi(\omega-\omega_0)$ is tuned into strict resonance for the transitions $1s \rightarrow \tilde{\sigma}_g$ and $1s \rightarrow \tilde{\pi}_u$, respectively. The width of the Φ distribution (30) is in our calculations comparable with the energy difference between the $\tilde{\pi}_u$ and $\tilde{\sigma}_g$ vacant MO's. Therefore, the tail of the Φ distribution "excites" also partially the $\tilde{\sigma}_g$ level, when ω_0 is strictly equal to the frequency of the $1s \rightarrow \tilde{\pi}_u$ transition. As a result, additional x-ray-emission lines (in this case, near the transitions from the π_u MO) will be observed. Apparently, tail excitation of x-ray fluorescence acts like a broadband excitation. Therefore, the curves 1, 2, 3, and 4 in Fig. 5 are similar to the curve 3 in Fig. 4 generated by broadband excitation. The tail excitation of $\tilde{\sigma}_g$ is evidently weaker than the excitation of the $\tilde{\pi}_u$ level. This causes the absence of significant fluorescence near 2 eV (curve 5, Fig. 5), and here we can observe the effect of symmetry selective excitation. The Stokes doubling effect is clearly seen near -1 to 0 eV for curves 1, 2, 3, and 5 and near 2 eV for curves 1 and 3 (Fig. 5). The ordinary resonance emission lines are situated strictly at 0 and 2 eV (Fig. 5). The Stokes resonance is shifted either to the left or to the right side relative to the corresponding emission line. The sign of the Stokes shift (29) is defined by the sign of the detuning of the incoming x-ray photon frequency ω_0 relative to the corresponding absorption resonance. Let us consider the evolution of the Stokes resonance situated near 0 eV (Fig. 5) while ω_0 is scanned from the "red" to the "blue" side of the $1s \rightarrow \tilde{\pi}_u$ absorption line. When the detuning $\Omega=\omega_0-\Omega_{\tilde{\pi}_u k}$ increases from -0.25 eV (curve 3, Fig. 5) to 0.25 eV (curve 5, Fig. 5) the Stokes resonance is shifted from $\Omega'=\omega'-\omega_{\pi_u k}=-0.25$ eV (curve 1) to $\Omega'=0.25$ eV (curve 5). The intensity ratio of the Stokes and ordinary emission lines is governed by the parameter ξ (31). One can see from Fig. 5 that the Stokes resonance is weaker than the ordinary emission when $\xi > 1$, but stronger if $\xi < 1$.

C. X-ray fluorescence near the *K* edge of the nitrogen molecule

We give further illustrations of the findings described above by computing the RIXS cross section for the nitrogen molecule. The calculation of the spectral shape of

TABLE I. Transition energies (eV) and relative intensities of x-ray absorption and emission of N_2.

	x-ray-emission data				x-ray-absorption data			
Quantity \ MO	$2\sigma_g$	$2\sigma_u$	$1\pi_u$	$3\sigma_g$	$1\pi_g$	$4\sigma_g$	$2\pi_u$	$3\sigma_u$
Energy[a]	372.1	391.33	393.34	394.40	400.87	406.15	407.12	408.35
Intensity[a]	0.075	0.09	1.00	0.47	27.3	1.00	2.3	1.16
Energy[b]	371.73	391.4	393.32	394.8				
Intensity[b]	0.08	0.10	1.00	0.43				

[a] Calculation in Ref. [26].

[b] Calculation in Ref. [27].

the RIXS cross section (19) and (20) of nitrogen requires as input transition frequencies and relative intensities for both emission and absorption K spectra. We have for simplicity not accounted for vibrational fine structure, and treated only the "electronic part" of the problem. In the calculations of nitrogen K fluorescence we used both experimental and theoretical data; molecular nitrogen has been the subject of several K-emission [24,25] and K-absorption [29,30] studies. The assignment of the nitrogen K-absorption spectrum can be found, e.g., in Ref. [29]. The energy positions of the line spectrum were obtained from x-ray absorption [30] and emission data [25], and the relative absorption line intensities were taken from the experiment [30]. For emission lines and intensities computational data are required as input. The *ab initio* configuration interaction (CI) calculations reported in Ref. [27] were used for a definition of relative emission line intensities I_i. Older one-particle results by Ransil [26] are confirmed by these, when the relation $[I_i \propto N_i (C_i^k)^2]$ between I_i and MO coefficients C_i^k is used. We point out that these N_2 calculations are model calculations in so far as the emission data are taken from the normal x-ray emission from the bare core-hole state. In the case of resonant radiationless transitions (autoionization) it is known that the decay of core-valence states,

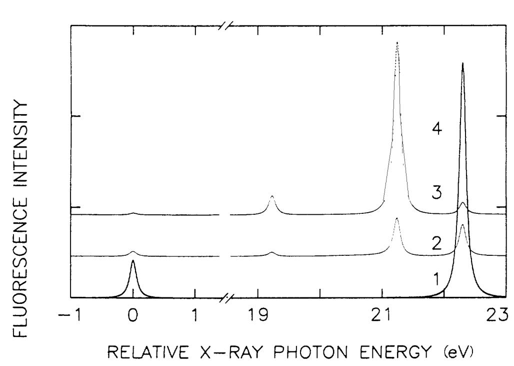

FIG. 6. The K fluorescence of the N_2 molecule as a function of $\omega' - \omega_{2\sigma_g k}$. $\gamma = 0.5$ eV, $\Gamma = 0.066$ eV. Lines 1, 2, and 3 correspond to resonant excitation of K electrons into the unoccupied MO's $1\pi_g$, $4\sigma_g$, and $2\pi_u$ MO's, respectively. Spectrum 4 is the ordinary K-emission spectrum of N_2. The intensity of spectrum 1 is reduced by a factor of 5. $\theta = 90°$.

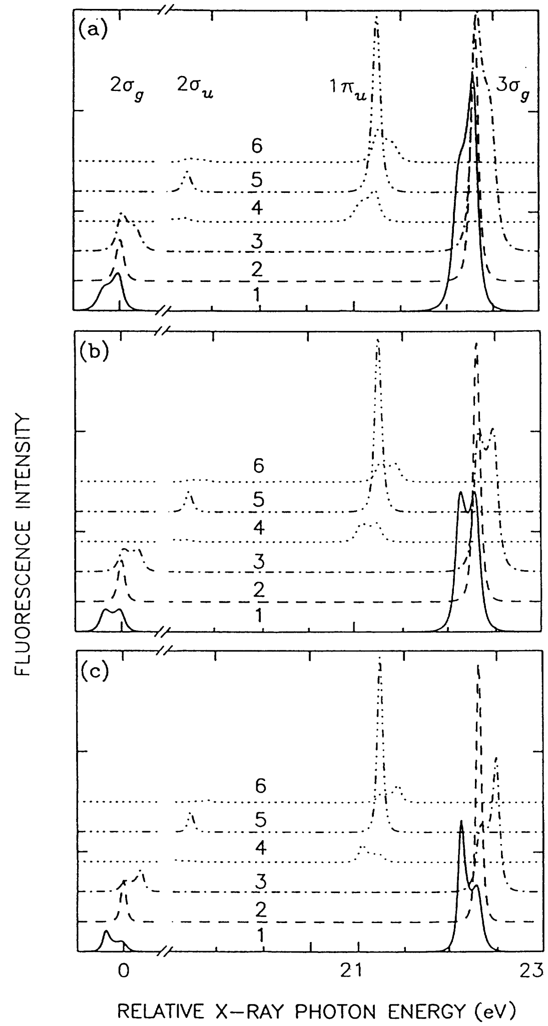

FIG. 7. The K fluorescence of the N_2 molecule as a function of $\omega' - \omega_{2\sigma_g k}$. $\Gamma = 0.066$ eV. Spectra 1, 2, 3 and 4, 5, 6 correspond to excitations of K electrons into $1\pi_s$ and $2\pi_u$ unoccupied MO's, respectively. The absorption frequency detuning, $\omega_0 - \omega_{1\pi_g k}$, relative to the $1s \rightarrow 1\pi_g$ absorption line is equal to -0.2, 0, and $+0.2$ eV for spectra 1, 2, and 3, respectively. The detuning $\omega_0 - \omega_{2\pi_s}$ relative to the $1s \rightarrow 2\pi_u$ line is equal -0.2, 0, and $+0.2$ eV for spectra 4, 5, and 6, respectively. (a) $\gamma = 0.099$ eV. (b) $\gamma = 0.066$ eV. (c) $\gamma = 0.044$ eV. The intensity of spectra 2 is reduced by a factor of 5. $\theta = 90°$.

e.g., the $1s^{-1}1\pi_g^1$ state of N_2, produce spectra that are quite different from the normal bare core-hole (Auger) spectrum, while decay from resonantly excited core-Rydberg states largely repeat the Auger structure [28]. Resonant radiative and radiationless processes are not directly comparable because of the different selection rules, but the experimental finding referred to above nevertheless indicates that the model for N_2 is appropriate for core-Rydberg states, while quite crude for the core-valence excited states for which the bound electronic structure is screened by the excited electrons. This screening emerges in CI calculations in Ref. [27] with a rather substantial correlation effect, and model calculations using a strict MO picture is limited, also, from that point of view.

Table I collects all data used to calculate the spectral shape of the RISX cross section of N_2. The lifetime broadening differs slightly for different lines [30]. We used the observed minimal value: $\Gamma=0.066$ eV. Figure 6 shows a change of spectral shape of the nitrogen x-ray fluorescence under tuning of the absorption photon frequency ω_0 in exact resonance with transitions into unoccupied MO's of different symmetry. In accordance with the general theory outlined above emission from the occupied $1\pi_u$ and $2\sigma_u$ MO's is forbidden when the K electron is excited into the vacant $1\pi_g$ MO (curve 1, Fig. 6). At first sight K excitation into the vacant $4\sigma_g$ MO leads to the same spectrum with two lines. However, spectra with four lines are observed in Fig. 6 (curves 2 and 3). It is caused by the large spectral width ($\gamma=0.5$ eV) which is comparable to the energy distance (~ 1 eV) between frequencies of transitions into unoccupied $4\sigma_g$, $2\pi_u$, and $3\sigma_u$ MO's. Indeed, the vacant $2\pi_u$ and $3\sigma_u$ MO's are also partially populated by the tail of the spectral function (30) even when ω_0 is strictly equal to the frequency of the $1s\rightarrow 4\sigma_g$ transition. This "tail" excitation is removed by a narrowing of the spectral function for the excited radiation (see Fig. 7). The effect of these selection rules (20) for the scattering tensor is demonstrated by Fig. 7. One can also see in Fig. 7 the effect of Stokes doubling. The transference of the Stokes component (29) from the left to the right side of the ordinary emission line (28) takes place if the detuning Ω changes sign (compare curves 1, 3, 4, and 6 in Fig. 7). A comparison of Fig. 7(a), 7(b), and 7(c) shows the strong dependence of the intensities of the Stokes component on the ratio (31) of the spectral distribution width and lifetime broadening.

CONCLUSIONS

We have presented a theory of interference effects in resonant inelastic x-ray scattering, emphasizing the effect of symmetry selective excitation. The treatment of the excitation and the subsequent decay of the excited state as a single quantum-mechanical process reveals the strong dependence of x-ray emission spectra on the frequency and spectral shape of the exciting radiation. Several, qualitatively different, points of view for x-ray scattering by symmetrical molecules have been explored. The selection rules of the RIXS process are clearly manifested for the case of resonant excitation of single core-excited states of certain symmetries for which a one-to-one correspondence between symmetries of unoccupied and occupied levels involved in the RIXS process can be obtained. For broadband excitation or excitations to close-lying Rydberg levels, these selection rules are differently manifested in the RIXS spectrum. A change of the spectral shape of the incoming x rays or a change of the excitation energy implicates by virtue of these selection rules sharp changes in the spectral appearance. This sharp dependence gives additional possibilities to assign symmetries of the involved electronic states. The analysis of the x-ray scattering tensor displays the symmetry properties of the RIXS process, for instance, it was shown here that representations of localized and delocalized core holes lead to the same result with respect to selection rules for the x-ray scattering tensor.

The symmetry selective character of the RIXS process was investigated in conjunction with hole localization for the common case of multicenter core orbitals delocalized over symmetry related atoms. The present analysis can evidently also be applied to other cases, such as degenerate core orbitals localized at inversion centers, or quasidegenerate core orbitals split by molecular fields. The latter case is quite common for L spectra of second row compounds. The symmetry selective excitation into an unoccupied MO ψ_ν of certain symmetry "burns" a hole in the degenerate (or quasidegenerate) $2p$ shell. The spatial orientation and symmetry of this hole are defined by the symmetry of ψ_ν. The probability of emission from this spatially oriented core-hole state depends on its orientation relative to the corresponding occupied MO ψ_n. As a result the resonant value of the RIXS cross section depends on a relation between symmetries of occupied ψ_n and unoccupied ψ_ν MO's. Hence the spectral shape of the RIXS signal will depend strongly on the excitation energy which selects the transition $2p\rightarrow\psi_\nu$. Let us note that this effect differs qualitatively from those effects considered earlier [17].

The diffractional nature of RIXS may become important in the hard-x-ray region, and a diffractional term added to the Kramers-Heisenberg scattering cross section may be used to extract information about geometrical structure of molecules when using hard-x-ray excitation. This is in close resemblance with diffraction theory in the conventional extended x-ray absorption fine-structure case [3]. It is shown that the effect of Stokes doubling will be important in high-resolution RIXS studies, and will lead to the appearance of additional fine structure in x-ray fluorescence spectra, when the spectral width of radiation is comparable with the lifetime broadening. The Stokes doubling effect can be distinguished by its specific dependence on the detuning frequency and spectral shape of excitational radiation.

Screening effects and particular effects due to electron correlation is important for RIXS involving valencelike core-excited levels, and must be accounted for in an electronic structure calculation [27], while for core-Rydberg levels this effect (and the differential screening effect) presumably is small. Vibronic structure [25,30] and vibrational-lifetime interference effects [4,5,9,10] are outside the scope of the present study. Such effects have been thoroughly studied in ordinary x-ray emission spectra [25], and will surely be relevant also in high-resolution studies of RIXS with symmetry selective excitation.

In conclusion, we have explored the symmetry selective character of the RIXS process and shown that resonant inelastic x-ray scattering of a narrow-band and polarized photon beam can be used for very-high-resolution and symmetry-sensitive studies of molecular electronic structures for ground and excited states. In future work, we will explore the consequences of the present analysis for orientational probing of surface adsorbates.

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