Comment on "Nondipole Resonant X-Ray Raman Spectroscopy: Polarized Inelastic Scattering at the *K* Edge of Cl_2"

Recently, Mills *et al.* [1] obtained experimental evidence of the violation of the quadrupole selection rules for the resonant x-ray scattering (RXS) tensor at the *K* edge of Cl_2. Together with corresponding results obtained in the soft x-ray region [2], the novel experimental results of Ref. [1] concerning selection rules in the hard x-ray region relate to the core hole state symmetry and localization dilemma. There seems to be complete consensus [1–3] that the x-ray scattering tensor is invariant [3] with respect to localized (L) or delocalized (DL) representations for the core hole or to any orthogonal transformations between these representations. However, we cannot agree with Mills *et al.* [1] that this fact implies that "arguments involving localization or delocalization mechanisms are irrelevant to interpretations of resonant x-ray Raman emission measurements on homonuclear diatomic molecules" [1].

The violation of the quadrupole selection rules for hard x rays, predicted in [3] and observed in [1], is caused by interference scattering of x-ray photons and motivates a consideration of selection rules of the x-ray scattering process in terms of the classical Young's double-slit experiment (YDSE). In a localized representation the RXS amplitude, $F = F_1 + F_2$, contains partial amplitudes $F_n = f_n e^{i\mathbf{q}\mathbf{R}_n}$ expressed with the phase factor $\exp(i\mathbf{q}\mathbf{R}_n)$ [3] and which describes scattering through the core-excited state $|n\rangle$ with the core hole in the nth atom at the site $\mathbf{R}_n$. Here $f_n \propto (\mathbf{e}'\mathbf{D}_{fn})(\mathbf{e}\mathbf{D}_{no})$, and $\mathbf{q} = \mathbf{k}' - \mathbf{k}$ denotes the change of the photon momentum. The RXS cross section ($\sigma \propto \langle |F|^2 \rangle$) is naturally divided into two contributions typical for quantum mechanics,

$$\sigma = \sigma_{\mathrm{dir}} + \sigma_{\mathrm{int}}^{12}, \qquad \sigma_{\mathrm{dir}} = \sigma_1 + \sigma_2\,, \tag{1}$$

referring to the direct or "localized" term σ_{dir} and the interference contribution $\sigma_{\mathrm{int}}^{12}$ which provides a natural structure information [3] and forms a "bridge" between classical and wave mechanics. Here $\sigma_{\mathrm{int}}^{12} \propto 2\,\mathrm{Re}\langle (f_1^* f_2 e^{i\mathbf{q}\mathbf{R}}) \rangle$, $\mathbf{R} = \mathbf{R_2} - \mathbf{R_1}$, and brackets denote the averaging over molecular orientations. The meaning of $\sigma_n \propto \langle |f_n|^2 \rangle$ as the cross section with core excitation only of the nth atom is very close to the meaning of the intensity I_1 in the YDSE: "I_1 is the intensity of the wave from hole 1 (which we find by measuring when hole 2 is blocked off)" (see [4], pp. 1–3). The coherence, $\sigma_{\mathrm{int}}^{12}$, between scattering channels defined by the interference parameter qR can be experimentally varied by means of the scattering angle and the wavelength [3].

Despite the equivalence of the L and DL representations for σ [3], statements can be made about RXS through L or DL core-excited states in reconciliation with the well-known paradigm of quantum physics that the measurement selects the appropriate physical representation. The measurement thus projects an undetermined quantum state into some measurement eigenstate and acts as a *filtering process* (Ref. [4], pp. 5–8).

Indeed, Eq. (1) shows that σ_{dir} can be measured if the coherence between scattering channels 1 and 2 is absent: $\sigma_{\mathrm{int}}^{12} \propto 1/(qR) \to 0$ [3]. This is *the limit of hard x rays* ($qR \gg 1$) when a short wave x-ray photon can "see" an individual atom (slit) because of the orientational dephasing of the scattering channels 1 and 2 [3]. Because of the independent scattering through the L core-excited states ($\sigma = \sigma_1 + \sigma_2$) the parity selection rules for the RXS tensor are violated [3], as experimentally confirmed in [1].

In the opposite limit of *soft x-ray or forward scattering* ($qR \ll 1$), the orientational dephasing is strongly suppressed and both scattering channels 1 and 2 are coherent ($\sigma \propto \langle |f_1 + f_2|^2 \rangle \neq \sigma_1 + \sigma_2$). Hence, the photon "cannot distinguish" atoms (slits) and one cannot say that scattering through the L states $|1\rangle$ and $|2\rangle$ are independent events. Contrary to the total cross section σ (1), the interference contribution and hence the notion of coherence is not invariant. Moreover, it is possible to suppress the coherence $\sigma_{\mathrm{int}}^{\alpha\beta}$ between scattering channels α and β by an appropriate orthogonal transformation to the new intermediate states $|\alpha\rangle$ and $|\beta\rangle$ [3]. A transformation to the DL gerade $|g\rangle$ and ungerade $|u\rangle$ states makes the scattering channels totally independent, since they do not interfere ($\sigma_{\mathrm{int}}^{gu} = 0$) [3], and leads directly to the strict parity selection rules for RXS [3]. The measurable quantities are now direct DL contributions $\sigma = \sigma_g$ or $\sigma = \sigma_u$ [2,3]. The experimental evidence of these parity selection rules for O_2 shows that soft-x-ray photons scatter through DL independent channels. With resonant x-ray scattering of diatomics we thus have an example, not uncommon in quantum physics, that the measurement selects the appropriate physical representation ([4], pp. 5–8).

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