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Reply to Comment on 'Nondipole Resonant X-ray-Raman Spectroscopy: Polarized Inelastic Scattering at the K Edge of Cl2,'

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Mills *et al.* Reply: In their Comment on our Letter [1], Gel'mukhanov and Ågren [2] reiterate recent assertions [3] based on their earlier theoretical studies [4]. The primary purpose of their Comment is apparently to refute our stated conclusion that core-excited-state localization/delocalization mechanisms are irrelevant to interpretations of reported Raman scattering experiments on homonuclear diatomic molecules.

Our theoretical predictions are invariant to the use of localized, delocalized, or any other orthogonally equivalent representation of the core-excited states [1]. The invariance can be seen most simply by expressing the cross section in terms of the intermediate-state projector $\hat{P} = |K_g\rangle\langle K_g| + |K_u\rangle\langle K_u|$, which is itself invariant to orthogonal transformation of K_g/K_u. Although Eqs. (2) and (3) of [1] do not describe the most general orthogonal transformation, possibly obscuring rather than clarifying the development, the cross-sectional invariance is generally agreed upon in any event [4,5]. It is on the basis of this invariance we assert that localization/delocalization mechanisms are irrelevant to interpretations of our x-ray Raman scattering experiments [1]; all such states give the same Kramers-Heisenberg cross section.

Nevertheless, Gel'mukhanov and Ågren argue in their Comment, and elsewhere [3–5], that measured Raman scattering data, interpreted with the Kramers-Heisenberg expression, can directly elucidate the degree of localization/delocalization of core-excited resonance states. Their line of reasoning seems to be that use of delocalized states in O_2 (and by inference in F_2) gives rise to dipole selection rules ($g \rightarrow u \rightarrow g$), so experimental observations of scattering intensities that are in agreement with dipole selection rules are, accordingly, tantamount to experimental observations of delocalized core-excited states. Similarly, in the hard x-ray limit their reasoning seems to be that use of localized states gives rise to finite nondipole scattering intensities ($g \rightarrow u \rightarrow u$ or $g \rightarrow g \rightarrow u$), experimental observations of which imply detection of localized core-excited states. They dismiss the incompatibility of these assertions with the invariance of the Kramers-Heisenberg expression by decomposing the cross section into representation-dependent "direct" and "interference" terms that individually are not invariant to the choice of degenerate core-excited states, and by implying that such terms can be measured under appropriately selected but largely unspecified experimental conditions, or through selection of a particular intermediate-state representation by an unspecified measurement process.

The line of reasoning advanced by Gel'mukhanov and Ågren is obviously incorrect. Specifically, although delocalized states do indeed give dipole selection rules in the Raman cross section of O_2, localized states also give rise to such dipole selection rules in this case. That is, use of delocalized states is a *sufficient* condition for the prediction of dipole selection rules in the case of O_2, but it is not a *necessary* condition. Accordingly, the converse proposition that observations of scattering intensities in accord with dipole selection rules imply detection of delocalized states in the case of O_2 is logically false. A similar counter argument applies to their assertion that localized states can be detected in the hard-x-ray limit. Simply put, there is, in general, no connection between scattering intensities predicted by the Kramers-Heisenberg expression (i.e., selection rules) and a particular choice of degenerate-state representation, because the cross sectional values are invariant to this choice.

The direct and interference terms as defined by Gel'mukhanov and Ågren [4,5] are not individually measured in our scattering experiments, nor do our measurements select a particular intermediate-state representation, since these states appear only in the invariant projector $\hat{P}$. Rather, our measurements detect photons associated with coherent transitions between initial and final states, and provide the representation-independent cross sections we have reported in Eq. (4) and in Figs. 2(b) and 3 of our Letter [1].

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[1] J. D. Mills, J. A. Sheehy, T. A. Ferrett, S. H. Southworth, R. Mayer, D. W. Lindle, and P. W. Langhoff, Phys. Rev. Lett. **79**, 383 (1997).
[2] F. Gel'mukhanov and H. Ågren, preceding Comment, Phys. Rev. Lett. **82**, 666 (1999).
[3] P. Glans, K. Gunnelin, P. Skytt, J.-H. Guo, N. Wassdahl, J. Nordgren, H. Ågren, F. Gel'mukhanov, T. Warwick, and E. Rotenberg, Phys. Rev. Lett. **76**, 2448 (1996).
[4] F. Gel'mukhanov and H. Ågren, Phys. Rev. A **49**, 4378 (1994).
[5] F. Gel'mukhanov and H. Ågren, J. Electron Spectrosc. Relat. Phenom. **93**, 31 (1998).

