Comparative Study of the Valence Electronic Excitations of N_2 by Inelastic X-Ray and Electron Scattering

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Bound-state, valence electronic excitation spectra of N_2 are probed by nonresonant inelastic x-ray and electron scattering. Within usual theoretical treatments, dynamical structure factors derived from the two probes should be identical. However, we find strong disagreements outside the dipole scattering limit, even at high probe energies. This suggests an unexpectedly important contribution from intramolecular multiple scattering of the probe electron from core electrons or the nucleus. These effects should grow progressively stronger as the atomic number of the target species increases.

The inelastic scattering of electrons, as in electron energy loss spectroscopy (EELS), provides a valuable tool to study both dipole-allowed and dipole-forbidden electronic excitations. This has proven central to numerous scientific and technical disciplines, including fundamental molecular physics and chemistry [1,2], optical properties of terrestrial and planetary atmospheres [3], and numerous branches of energy science [4]. While the simplest theoretical treatments dating to the earliest days of quantum scattering theory have proven to be a valuable starting point in essentially all cases, there is steadily growing evidence that such treatments are often, and perhaps in general, fundamentally inadequate [5–9]. There would be great value in having an alternative experimental technique that probes the same kinematic parameter space as inelastic electron scattering but whose scattering dynamics unequivocally obey the lowest-order theoretical approaches. Nonresonant inelastic x-ray scattering (NRIXS or NIXS) using hard x rays provides this approach [10].

In this Letter, we compare bound-state valence electron excitations of molecular N_2 using inelastic scattering by electrons and by hard x rays. The electron and photon scattering results disagree upon leaving the low momentum transfer limit, with gross qualitative and quantitative deviations at high momentum transfer. We discuss these results in the context of multiple intramolecular scattering, wherein the probe electron transfers significant energy and limited momentum to the electronic degrees of freedom along with large momentum and little energy transfer to the core electrons and nucleus of the target species. If this explanation is correct, the observed phenomenon should scale strongly with Z and become progressively more pronounced for heavier elements.

Under the simplest scattering approximations, NIXS and EELS are equivalent probes of target electronic structure,

with double-differential cross sections (DDCS) given by

$$\left(\frac{d^2\sigma}{d\Omega d\omega}\right)_{\gamma,e} = \left(\frac{d\sigma}{d\omega}\right)_{Th,Ru} S(\mathbf{q}, \omega), \qquad (1)$$

where γ, e refer to photon and electron scattering, respectively, and Th, Ru refer to Thomson and Rutherford differential cross sections. The variable q refers to momentum transfer, ω is probe particle energy loss, and Ω is detection solid angle. The quantity $S(q, \omega)$ is known as the material's *dynamic structure factor.* For inelastic photon scattering (NIXS), Eq. (1) is derived directly from first order perturbation in the $\vec{A} \cdot \vec{A}$ electron-photon interaction Hamiltonian. Extensive evidence demonstrates that Eq. (1) holds with considerable certainty for NIXS [10]. For EELS, however, the conclusion relies on a weak probe-target electron interaction [the first Born approximation (FBA)], the purely binary interaction between the probe electron and the quantum electronic excitations of the target [the binary encounter approximation (BEA)], and the negligible influence of the internal structure of the target on the asymptotic form of the probe wave function [the plane-wave impulse approximation (PWIA)] [8]. Here, we label the experimentally determined $S(\mathbf{q}, \omega)$ as $S_\gamma(\mathbf{q}, \omega)$ when it is derived from NIXS and as $S_e(\mathbf{q}, \omega)$ when it is derived from EELS.

To explain the large differences we will demonstrate between $S_\gamma(\mathbf{q}, \omega)$ and $S_e(\mathbf{q}, \omega)$, it is important to briefly review the expected behavior of $S(\mathbf{q}, \omega)$ [11]. To begin,

$$S(\mathbf{q}, \omega) = \sum_f |\langle u_f | e^{i\mathbf{q}\cdot\mathbf{r}} | u_i \rangle|^2 \delta(E_f - E_i - \hbar\omega), \quad (2)$$

where u_i and u_f represent target initial and final electronic states with energies E_i and E_f. In the momentum basis,

$$\langle u_f | e^{i\mathbf{q}\cdot\mathbf{r}} | u_i \rangle = \int d^3 p \cdot u_f^*(\mathbf{p}) u_i(\mathbf{p} + \mathbf{q}), \qquad (3)$$

where $u_{f,i}(\mathbf{p})$ are the momentum-space final and initial wave functions, respectively. Note that the transferred momentum causes a relative shift of the arguments for the momentum-space wave functions, but otherwise Eq. (3) is simply an overlap integral. A large enough shift (i.e., momentum transfer in the scattering event) will render the overlap nil. For bound final states, $S(\mathbf{q}, \omega)$ should rapidly vanish as q grows large compared to the widths of the momentum-space wave functions. Below, we will discuss the explicit dependence of $S(\mathbf{q}, \omega)$ on q, but the effective valence shell size of $d_{\text{eff}} \sim 4$ a.u. leads to a general momentum transfer scale of $2\pi/d_{\text{eff}} \sim 1.5$ a.u. above which the overlap integral should be expected to decay rapidly.

The dependence of $S(\mathbf{q}, \omega)$ on the relevant selection rule for a bound-state excitation follows from expanding the exponential operator of Eq. (2) in spherical harmonics and performing the average over orientations (or equivalently, over the direction of momentum transfer) appropriate for polycrystalline or gaseous samples,

$$|\langle u_f | e^{i\mathbf{q}\cdot\mathbf{r}} | u_i \rangle|^2 = \sum_{l,m} |4\pi i^l \langle u_f | j_l(qr) Y_{l,m}(\hat{\mathbf{r}}) | u_i \rangle|^2. \qquad (4)$$

The q dependence is entirely in the spherical Bessel function. Since $j_l(qr) \rightarrow 0$ at order $(qr)^l$ as $qr \rightarrow 0$, we can make the following general statements: At low q, $S(q, \omega)$ shows dipole-allowed transitions exclusively. As q grows, the dipole transitions fade away, and quadrupole transitions dominate $S(q, \omega)$. As q continues to grow, this process repeats at higher and higher multipoles: quadrupole transitions fading and octupole transitions rising, and so on [11]. This behavior is commonly termed q-dependent *multipole selection rules*. For N_2 gas, we will demonstrate that these selection rules break down for EELS-derived $S_e(q, \omega)$, while they remain intact for NIXS-derived $S_\gamma(q, \omega)$.

All NIXS measurements were performed with the lower-energy resolution inelastic x-ray scattering (LERIX) spectrometer [12] at sector 20-ID-B of the Advanced Photon Source. To obtain the spectra, incident photon energy was scanned between 9896 and 9910 eV. The beamline monochromator was operated with either a double Si (111) or a double Si (311) configuration for 1.4 or 0.9 eV net energy resolution, respectively. Allowing for the differing energy resolutions in the two studies (1.4 eV versus 0.9 eV), the spectra were mutually consistent. The lowest q (0.42 a.u.) analyzer was misaligned for the high-resolution data collection, so the 1.4 eV resolution data is used. Otherwise, all data are from the 0.9 eV resolution measurements. A NIXS-compatible gas-phase pressure cell [13] was used to collect data at 1.0 MPa pressure, with a total integration time of 120 sec per incident energy. Spectra were verified to be independent of gas pressure. After correction for known systematic effects, $S_\gamma(q, \omega)$ was converted to units

of (eV molecule)$^{-1}$ by application of the Bethe f-sum rule [10,14]. The NIXS normalization to absolute units is estimated correct to within 10% [15].

EELS measurements were performed with two different instruments. Initial measurements were performed with an EELS spectrometer [16] at McMaster University using an incident electron energy of 2.25 keV. Spectra were verified to be independent of gas pressure. The quantity $S_e(q, \omega)$ was normalized to the published N_2 elastic cross-section [17]. The McMaster EELS measurements were performed with 0.7 eV energy resolution, but have been broadened to 0.9 eV final resolution for ease of comparison with NIXS spectra. Additional measurements were performed with an EELS spectrometer at the Australian National University (ANU) [18]. The incident energies used in the ANU EELS measurements ranged from 0.6 to 6.0 keV and the energy resolution was 0.6 eV.

In Fig. 1, we compare $S_\gamma(q, \omega)$ and $S_e(q, \omega)$ for the low-energy (valence) electronic excitations of N_2 gas. When the present EELS results are compared to prior studies [19] (and references therein) of the dipole-forbidden, quadrupole-allowed Lyman-Birge-Hopfield (LBH) band at ~ 9 eV, they agree favorably [15]. Figure 1 shows that, within the combined uncertainty in the EELS and NIXS normalizations, the lowest-q EELS and NIXS data are in agreement. In the limit $q \rightarrow 0$, it is well established that both $S_\gamma(q, \omega)$ and $S_e(q, \omega)$ become proportional to the optical absorption spectrum, so this result is expected and it verifies our current methodology [10,20].

At higher q, however, $S_e(q, \omega)$ and $S_\gamma(q, \omega)$ rapidly diverge from one another. $S_\gamma(q, \omega)$ behaves as expected: First, there is an overall decrease in intensity as q grows larger than the momentum-space width of the valence-state wave function. Second, $S_\gamma(q, \omega)$ exhibits the expected multipole selection rules in the q-dependent transition intensities. For example, the lowest energy excitation of N_2 (largely the $a\,^1\Pi_g$ feature) is known to be dipole forbidden and quadrupole allowed, and indeed, for NIXS at low q this feature is strongly damped, rises for midrange q, and then falls away at high q. On the other hand, $S_e(q, \omega)$ displays markedly different q dependence. In the inelastic electron scattering results, spectral features rise up, but they do not fade away at higher q. Note that similar analysis applies to all features in the spectra; the NIXS spectra give insight into the appropriate rate of decay of the dipole channel with rising q. The illustrated breakdown of the selection rules, when coupled with the firmer footing of the approximations leading to Eq. (1) in the NIXS case, is experimental evidence for the failure of one or more of the approximations leading to Eq. (1) for EELS.

The consistency of features in $S_e(q, \omega)$ as q grows has an important consequence: Since the energy transfer is known to be entirely due to the electronic degree of freedom at low q, this must extend to high q, even though $S_e(q, \omega)$ and $S_\gamma(q, \omega)$ disagree. With this in mind, the unexpectedly high transition amplitudes in $S_e(q, \omega)$ at high q are a key
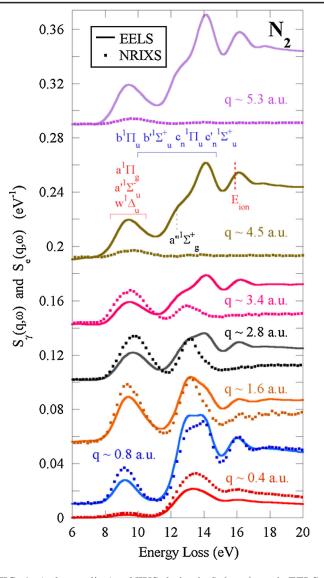
FIG. 1 (color online).   NIXS-derived $S_\gamma(q, \omega)$ and EELS-derived $S_e(q, \omega)$ from nitrogen gas with symmetry designations labeled for bound final states. Values of q are for the NIXS experiment. The EELS data were taken with the McMaster spectrometer using an initial electron energy of 2250 eV and have been broadened to match the NIXS energy resolution. (dashed line) EELS scattering angles are 2°, 4°, 7°, 12°, 16°, 20°, 24°, with corresponding q-values of 0.4, 0.9, 1.6, 2.6, 4.5, and 5.3 a.u. Curves are offset for clarity.

detail. Valence electronic excitations in a single scattering event are not equipped to take up the momentum transfer, even though they are known to take up the energy transfer. This suggests multiple scattering, though multiple intermolecular scattering is ruled out by the independence of the EELS spectra on N$_2$ gas density. Instead, we propose that the inelastic electron scattering results are due to multiple *intramolecular* scattering, in which nearly all the energy transfer occurs in a scattering event between the electron probe and the valence electron configuration, but some (possibly large) fraction of the momentum trans-

fer occurs via (quasi)elastic scattering between the probe electron and the target's core electrons or nucleus.

This model is supported by both contemporary work on electron or heavy ion-impact ionization [2,21] and also by older work on the lower-energy excitations to bound states [5,7,22,23]. In the former case, the key experimental observation has been the discovery of a significant momentum transfer to the residual ion, which was most convincingly explained by making corrections to the plane-wave approximation that reflect the gradually decreased screening of the nuclear charge at small classical impact parameters [2]. In the latter case, early examples of FBA violations were found in He bound-state excitations by Opal and Beaty [24] and Dillon and Lassettre [25]. Experiments yielding similar results were performed on Hg by Hanne, Kessler, Lassettre, and Skerbele [26]. There were related theoretical explanations put forth by Huo [27], and Hidalgo and Geltman [28], which include a dominant effect from nuclear scattering at high q, and also by Bonham [9] and Kelsey [7], using a somewhat unconventional second Born approximation—one scattering event from an electronic potential and a second from the nuclear potential or other electronic degrees of freedom. The various theoretical approaches are complementary treatments of the same problem: a direct sensitivity of the probe electron to the detailed internal structure of the target, in violation of some subset of the FBA, PWIA, or BEA. The same issues are not measurable for NIXS due to the suppression by $1/m^2$ for x-ray scattering from the nucleus and also the weakness of both the elastic and inelastic channels with respect to photoelectric effects (i.e., absorption).

A subtlety arises out of this discussion. While it is well known that the FBA is violated at low incident electron energy in EELS, here we have found evidence for a violation of Eq. (1) at high incident electron energies. Similar considerations arose in some of the earliest treatments leading to distorted-wave Born approximations, and predicted asymptotic violations of the FBA [22]. In Fig. 2, we further explore this by presenting EELS spectra at higher incident energy and higher q, obtained with the ANU spectrometer, along with the unbroadened 5.3 a.u. McMaster spectrum, for comparison. Note that the 6 keV, 45° and the 1 keV, 135° measurement [curves (a) and (b), respectively] differ sharply in terms of one spectral feature (∼13 eV), but are otherwise similar throughout the rest of this range of energy loss. The momentum transfer in these two measurements is quite close; consequently, the EELS DDCS is not a function of q and ω only. Furthermore, note that comparisons between the McMaster $q = 5.3$ a.u. data and the ANU $q = 5.1$ or 6.6 a.u. data alone could easily lead to the erroneous conclusion that Eqn. (1) is satisfied, since the spectra would seem to be independent of incident energy.

In summary, the bound-state electronic excitation spectra for N$_2$ exhibit profound qualitative and quantitative differences when they result from inelastic electron as opposed to inelastic x-ray scattering, even at very similar
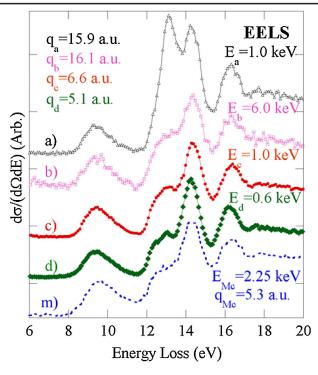
FIG. 2 (color online). (a),(b),(c),(d) The N_2 EELS scattering cross-section at various incident electron energies (E_0), and q-values taken at the Australian National University. For (a), the scattering angle was 135°, while it was 45° for the others. (m) The bottom curve (dashed) is the unbroadened McMaster EELS data displayed uppermost in Fig. 1, for comparison. Curves are offset for clarity.

momentum transfers. This behavior is consistent with intramolecular multiple scattering of electrons, giving additional sensitivity to the internal structure of the target and especially to the presence of the nuclear charge. The ratio of such effects to the traditional first Born approximation contribution to the double-differential cross section are expected to grow progressively stronger with increasing Z [7]. Hence, this behavior may have far-reaching consequences for inelastic electron scattering from bound-state excitations, especially for heavier target species.

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[1] G. Cooper, A. P. Hitchcock, and C. A. Chatzidimitriou-Dreismann, Phys. Rev. Lett. **100**, 043204 (2008); A. P. Hitchcock, J. Electron Spectrosc. Relat. Phenom. **112**, 9 (2000); M. S. Schoffler *et al.*, Science **320**, 920 (2008).
[2] M. Foster *et al.*, Phys. Rev. Lett. **97**, 093202 (2006).
[3] P. V. Johnson *et al.*, J. Geophys. Res. **110**, A11 311 (2005); M. A. Khakoo *et al.*, Phys. Rev. A **71**, 062703 (2005).
[4] G. Katumba *et al.*, Solar Energy Mater. Sol. Cells **92**, 1285 (2008); I. Kuchiwaki *et al.*, Solar Energy Mater. Sol. Cells **92**, 71 (2008); K. T. Moore and G. van der Laan, Rev. Mod. Phys. **81**, 235 (2009); G. Yang, R. F. Klie, and Q. Ramasse, Phys. Rev. B **78**, 153109 (2008); K. T. Moore, Micron **41**, 336 (2010).
[5] D. Eimerl, Phys. Rev. A **14**, 2061 (1976).
[6] T. Giannerini *et al.*, Phys. Rev. A **75**, 012706 (2007); M. Inokuti, Rev. Mod. Phys. **43**, 297 (1971); D. H. Madison *et al.*, Phys. Rev. Lett. **91**, 253201 (2003); N. V. Maydanyuk *et al.*, Phys. Rev. Lett. **94**, 243201 (2005); C. W. McCurdy *et al.*, J. Phys. B **37**, R137 (2004); T. N. Rescigno *et al.*, Science **286**, 2474 (1999); T. G. Wong *et al.*, Eur. J. Phys. **30**, 447 (2009).
[7] E. J. Kelsey, Ann. Phys. (N.Y.) **98**, 462 (1976); E. J. Kelsey, Ann. Phys. (N.Y.) **322**, 1925 (2007).
[8] I. E. McCarthy and E. Weigold, Rep. Prog. Phys. **54**, 789 (1991).
[9] R. A. Bonham, J. Electron Spectrosc. Relat. Phenom. **3**, 85 (1974).
[10] W. Schuelke, *Electron Dynamics by Inelastic Scattering* (Oxford University Press, New York, 2007).
[11] J. A. Soininen *et al.*, Phys. Rev. B **72**, 045136 (2005).
[12] T. T. Fister *et al.*, Rev. Sci. Instrum. **77**, 063901 (2006).
[13] M. Minzer *et al.*, Rev. Sci. Instrum. **79**, 086101 (2008).
[14] M. Inokuti *et al.*, Rev. Mod. Phys. **50**, 23 (1978).
[15] J. A. Bradley *et al.* (to be published).
[16] I. G. Eustatiu *et al.*, Chem. Phys. **257**, 235 (2000).
[17] R. H. J. Jansen *et al.*, J. Phys. B **9**, 185 (1976).
[18] M. Vos *et al.*, J. Phys. B **41**, 135204 (2008).
[19] K. T. Leung, J. Electron Spectrosc. Relat. Phenom. **100**, 237 (1999); T. C. Wong *et al.*, J. Chem. Phys. **63**, 1538 (1975); R. A. Bonham, in *Electron Spectroscopy* (Academic, New York, 1979), Vol. 3, p. 127.
[20] E. N. Lassettre, J. Chem. Phys. **42**, 2971 (1965).
[21] O. Al-Hagan *et al.*, Nature Phys. **5**, 59 (2009); M. Schulz *et al.*, Nature (London) **422**, 48 (2003); R. W. van Boeyen *et al.*, Phys. Rev. A **73**, 032703 (2006); M. R. Went and M. Vos, J. Electron Spectrosc. Relat. Phenom. **169**, 35 (2009).
[22] S. Geltman and M. B. Hidalgo, J. Phys. B **4**, 1299 (1971).
[23] J. F. Williams, J. Phys. B **8**, 2191 (1975).
[24] C. B. Opal and E. C. Beaty, J. Phys. B **5**, 627 (1972).
[25] M. A. Dillon and E. N. Lassettre, J. Chem. Phys. **62**, 4240 (1975).
[26] F. Hanne and J. Kessler, Phys. Rev. A **5**, 2457 (1972); A. Skerbele and E. N. Lassettre, J. Chem. Phys. **52**, 2708 (1970); A. Skerbele and E. N. Lassettre, J. Chem. Phys. **58**, 2887 (1973).
[27] W. M. Huo, J. Chem. Phys. **57**, 4800 (1972).
[28] M. B. Hidalgo and S. Geltman, J. Phys. B **5**, 617 (1972).
[29] B. P. Xia *et al.*, arXiv:0906.3210.