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Low-Energy Nondipole Effects in Molecular Nitrogen Valence-Shell Photoionization

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Observations are reported for the first time of significant nondipole effects in the photoionization of the *outer-valence orbitals* of diatomic molecules. Measured nondipole angular-distribution parameters for the $3\sigma_g$, $1\pi_u$, and $2\sigma_u$ shells of N_2 exhibit spectral variations with incident photon energies from thresholds to ~ 200 eV which are attributed via concomitant calculations to particular final-state symmetry waves arising from $(E1) \otimes (M1, E2)$ radiation-matter interactions first-order in photon momentum. Comparisons with previously reported *K*-edge studies in N_2 verify linear scaling with photon momentum, accounting in part for the significantly enhanced nondipole behavior observed in inner-shell ionization at correspondingly higher momentum values in this molecule.

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Continuing interest over the past four decades has been attached to measurements of the angular distributions of electrons photoejected from molecules and other atomic aggregates [1–8]. The atomic and molecular line and continuum light sources employed in earlier studies [1] have been supplemented with synchrotron-radiation sources [2,3], making possible systematic investigations of partial-channel cross sections and associated angular distributions over broad photon energy ranges [4] and providing a wealth of information on the bound and continuum states of molecules [5]. The angular-distribution patterns and their spectral variations have been found to be particularly sensitive to attributes of the molecules studied and to the dynamical aspects of the photoionization process more generally [6–8].

With few exceptions [9–13], measured photoelectron angular distributions have been commonly interpreted employing the so-called dipole or uniform-electric-field approximation to the interactions between radiation and matter, in which case symmetry considerations [14] limit the nature of the possible distributions to a well-known analytical form for both atoms and free molecules [15,16]. Considerable recent evidence indicates, however, that this approximation can be inadequate for interpretations of atomic photoelectron angular distributions at surprisingly low photon energies. Specifically, nondipole effects first-order in photon momentum have been observed in the 1–3 keV photon energy region in Ar and Kr [17,18], in the hundreds-of-eV range and below in Ne and Xe [19–21], and as low as 13 eV in the case of Cd [22], behaviors largely confirmed by theory [23–29]. The measured and calculated angular distributions exhibit considerable sensi-

tivity to the presence of Cooper minima, to the nature of the potential more generally, and to electronic channel coupling in certain cases, effects which all give rise to prominent features in the angular asymmetry parameters at relatively low photon energies.

In this Letter, we report the first observations of nondipole effects in the valence-shell photoionization of molecules, employing the $3\sigma_g$, $1\pi_u$, and $2\sigma_u$ channels of N_2 as prototypical examples. Significant nondipole behaviors are observed over the entire (~ 200 eV) spectral range studied which are attributable in these cases to interference between electric-dipole ($E1$) and electric-quadrupole—magnetic-dipole ($E2$, $M1$) terms in the angular distributions [23–29] (see Fig. 1)

$$\frac{d\sigma}{d\Omega}(\theta, \phi) = \frac{\sigma}{4\pi} \{1 + \beta P_2(\cos\theta) + (\delta + \gamma \cos^2\theta) \sin\theta \cos\phi\}. \quad (1)$$

Here σ is the partial-channel cross section, β is the dipole anisotropy parameter, $P_2(\cos\theta) = (3\cos^2\theta - 1)/2$ is the second-degree Legendre polynomial, and δ and γ are the nondipole parameters of interest. The present investigation complements our earlier *K*-shell studies performed at higher photon energy and momentum [30–33] and provides an opportunity to compare the nondipole behaviors of the more spatially extended valence orbitals in N_2 with those of the nearly degenerate compact $1\sigma_g/1\sigma_u$ orbitals.

Two independent sets of experiments were carried out over distinct but overlapping incident photon energy intervals at Wisconsin's Synchrotron Radiation Center (SRC) and at the Advanced Light Source (ALS) of the Lawrence

FIG. 1. Geometry applicable to photoelectron angular-distribution measurements using linearly polarized light.

Berkeley National Laboratory. The 26–100 eV photon energy range was studied at the SRC on the Undulator 071 beam line. First-order linearly polarized radiation from the undulator at SRC was monochromatized with a plane grating monochromator that provides a bandpass that varies from 8 to 60 meV for photon energies from 26 to 100 eV, respectively. The beam enters a doubly μ -metal-shielded vacuum chamber housing four parallel plate electron analyzers which are described elsewhere [34]. The electron analyzers were operated at sufficient resolution to fully separate the three outer-valence ($3\sigma_g$, $1\pi_u$, $2\sigma_u$) N_2 peaks. To check for systematic errors in the SRC experiment, the asymmetries of several Xe $N_{4,5}$ -OO Auger-electron lines in the 3–33 eV kinetic energy range were measured. An average asymmetry of $\gamma + 3\delta = 0.004(34)$ was measured for the Auger electrons, which is consistent with zero first-order nondipole asymmetries adopting a two-step interpretive model [35].

Measurements over the 80–200 eV photon energy range were made at the ALS on undulator beam line 8.0.1 during several two-bunch periods, which provide the timing mode crucial to the time-of-flight (TOF) spectrometer employed in the ALS experiment. The monochromator employed houses three interchangeable spherical gratings, which provide an approximately constant relative photon energy resolution of $(\Delta E/E) \approx 10^{-4}$ over the entire spectral range studied. The detection chamber contains five electron TOF analyzers in a CoNetic-shielded housing for gas-phase measurements, as previously described [36]. The TOF method employed can measure photoelectron peaks at many kinetic energies and at multiple emission angles simultaneously, eliminating several sources of experimental uncertainty in measurements of electron angular distributions. The helium 1s photoline was used to calibrate the analyzers employing the known dipole and nondipole contributions to the He 1s angular distributions [37] and to determine the degree of linear polarization of the synchrotron light ($> 99.9\%$).

In both experiments, electron analyzers were positioned at judiciously chosen sets of angles that provide sensitivity to different combinations of β , δ , and γ [see Eq. (1)],

so that ratios of the measured photoelectron intensities yielded values of $\gamma + 3\delta = \zeta$ [30]. The experimental data so obtained for the three valence channels in N_2 are shown in Fig. 2, where ζ is seen to have values close to zero near threshold for all three valence lines and to take on values between -0.2 and $+0.2$ over the photon energy range studied. The relatively larger error bars and scatter of the ALS data shown in the figure are consequences of the lower photon flux in the two-bunch mode of operation and the smaller photoionization cross sections at higher energies.

Theoretical studies have been performed in order to verify the magnitudes and to interpret the spectral variations of the experimentally determined nondipole parameters reported in Fig. 2. The formalism adopted for this purpose is based on density-matrix considerations for the interactions between radiation and matter employing familiar irreducible-tensor representations of the photon-electron interaction operators [38,39]. Following previous developments for atoms [23–29], it is convenient in con-

FIG. 2. N_2 $3\sigma_g$, $1\pi_u$, and $2\sigma_u$ nondipole asymmetry parameters $\zeta = \gamma + 3\delta$ measured at the SRC (solid symbols) and the ALS (open symbols) compared with calculations (ζ , solid curve; δ , dashed curve; γ , dotted curve). The measured $1\pi_u$ - and $2\sigma_u$ -channel data are also compared with experimental $2p$ and $2s$ Ne values (triangles [45]) and with corresponding calculations (dotted-dashed curve) [19,29], as discussed further in the text.

structuring theoretical expressions which are first-order in photon momentum for the nondipole parameters δ and γ for molecules to separate them into their electric-dipole—magnetic-dipole ($E1 \otimes M1$) and electric-dipole—electric-quadrupole ($E1 \otimes E2$) contributions.

Calculations of the initial- and final-state molecular wave functions and transition matrix elements employ familiar (ℓ, m) -wave representations [40,41] and a previously described Lippmann-Schwinger method implemented in the so-called single-channel static-exchange approximation [42]. This approach, in which the final-state scattering functions describing the ionized electrons ($\ell_{\max} \approx 10$) are determined in the frozen hole-state potentials obtained by deleting one electron from a selected occupied ($3\sigma_g, 1\pi_u, 2\sigma_u$) orbital ($\ell_{\max} \approx 40$), has been found to provide useful first approximations to the dipole photoionization cross sections of the outer-valence-shell orbitals of many molecules [4]. Although a significant number of individual terms arise in the (ℓ, m) -wave density-matrix approach to calculations of the molecular δ and γ parameters [38,39], these can be summed over and grouped in terms of the axial *body-frame* projection quantum numbers of the contributing final-state scattering orbitals ($k\sigma, k\pi, k\delta, \dots$) [32,33]. After completion of our work, density-functional theory calculations have been reported for the N_2 channels of interest here which are in general accord with the present results [43].

The measured and calculated nondipole parameters for the $3\sigma_g$ channel reported in Fig. 2 are in very good accord, except for a distinct feature at threshold in the calculations. This peak is a consequence of a well-known spurious π^* contribution to $k\pi_u$ final-state continuum orbitals which can arise in static-exchange calculations [4] and can be ignored in the present context. The spectral variation of the measured and calculated $3\sigma_g$ nondipole parameter is highly similar to that of the previously reported ($1\sigma_g, 1\sigma_u$) K -shell nondipole parameter in N_2 [30], although the peak magnitude in the latter profile is a factor of ≈ 5 larger than that of the $3\sigma_g$ result in Fig. 2, and the spectral positions of the peaks and troughs in the two profiles occur at slightly different kinetic energies. The difference in peak heights is accounted for largely by the ratio of the different values of photon momenta for the two peaks ($k_{1s}/k_{3\sigma_g} \approx 0.12/0.024 = 5.0$). In contrast, however, a recent study reports an entirely null K -edge ζ value in N_2 [44], in disagreement with our previous results [30] and with independently determined values [31]. The origins of this discrepancy have yet to be identified.

The calculated polarization-symmetry components (not shown) of the $E1 \otimes E2$ and $E1 \otimes M1$ contributions to the δ and γ nondipole parameters of Fig. 2 show that the maximum at ≈ 90 eV in the $3\sigma_g$ channel includes large $k\pi_u \otimes k\delta_g$ final-orbital symmetry terms, where $k\pi_u$ refers to the dipole ($E1$) term and $k\delta_g$ to the electric-quadrupole ($E2$) term in the ($E1 \otimes E2$) interaction first-order in photon momentum. A similar situation is found in the K -shell

nondipole parameter [30], although there are also strong contributions from $k\sigma_u \otimes k\delta_g$ and $k\sigma_u \otimes k\pi_g$ terms in the $3\sigma_g$ channel. Moreover, the high-energy behavior of the $3\sigma_g$ parameter includes $k\pi_u \otimes k\delta_g$ dipole-quadrupole terms, as in the K -shell study, and also non-negligible $k\sigma_u \otimes k\sigma_g$ and $k\pi_u \otimes k\pi_g$ contributions, presumably a consequence of the more complex atomic $2p_z$ orbital character of the $3\sigma_g$ molecular orbital. The δ parameter for the $3\sigma_g$ channel is seen to be generally small but not negligible relative to γ , particularly at the 90 eV maximum and at the 140 eV local minimum in Fig. 2, where its contribution is required for quantitative agreement with experiment. All calculated $3\sigma_g$ -channel symmetry contributions to δ and γ are found to exhibit oscillations over the entire photon energy range studied, accounting for the significant spectral variation in the nondipole parameter ζ .

In the absence of a theoretical determination of the N_2 $1\pi_u$ -channel asymmetry parameter, a consequence of the higher-symmetry waves required in this case, experimental [45] and previously reported theoretical Ne $2p$ -channel parameters [19,29] are shown in Fig. 2 for comparison (see also [43]). The Ne $2p$ -channel values are in satisfactory accord in both magnitude and spectral variation with the present $1\pi_u$ -channel data at higher photon energy, whereas a small but distinct molecular resonancelike feature in the latter values at ≈ 50 to 100 eV is not present in the atomic Ne values [19,29]. The N_2 $1\pi_u$ molecular orbital, composed approximately of two in-phase $2p_N$ atomic orbitals perpendicular to the molecular axis, apparently gives rise to a nondipole asymmetry parameter that behaves similarly to that of an atomic $2p_{Ne}$ orbital at sufficiently high photon energies.

The $2\sigma_u$ -channel results reported in Fig. 2 show general accord between theory and experiment, and with independent calculations [43], although agreement is unsatisfactory at higher photon energy. This discrepancy between theory and experiment can possibly be attributed to coupling with deeper-lying inner-valence-shell ionic channels neglected in the calculations, suggesting that additional more refined calculations may be required in order to resolve the discrepancy in this channel. The negative values observed at higher photon energies are similar to the measured [45] and calculated Ne $2s$ -channel asymmetry parameter [19,29] also shown in Fig. 2, in accord with the largely $2s$ antibonding character of the $2\sigma_u$ orbital.

The sensitivity of the asymmetry parameters of Fig. 2 to the orbital ionized indicates that further nondipole measurements in molecules may reveal additional novel behaviors and that the oscillatory behaviors of the large numbers of ℓ -wave contributions to the calculated parameters may require additional theoretical study in order to gain a complete quantitative understanding of molecular nondipole phenomena. In spite of these complications, the present Letter clearly contradicts a pervasive notion that nondipole effects occur only at very high photon energy in atoms and molecules. It can be expected, rather, that such

considerations should apply to atoms, molecules, clusters, surfaces, and solids quite generally.

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- [1] T. Carlson, *Auger and Photoelectron Spectroscopy* (Academic, New York, 1975).
 - [2] J. Berkowitz, *Photoabsorption, Photoionization, and Photoelectron Spectroscopy* (Academic, New York, 1979).
 - [3] *Synchrotron Radiation Research*, edited by H. Winnick and S. Doniach (Plenum, New York, 1980).
 - [4] J. W. Gallagher, C. E. Brion, J. A. R. Samson, and P. W. Langhoff, *J. Phys. Chem. Ref. Data* **17**, 9 (1988).
 - [5] *VUV and Soft X-Ray Photoionization*, edited by U. Becker and D. A. Shirley (Plenum, New York, 1996).
 - [6] P. W. Langhoff, J. C. Arce, and J. A. Sheehy, *J. Electron Spectrosc. Relat. Phenom.* **123**, 117 (2002).
 - [7] T. Seideman, *Annu. Rev. Phys. Chem.* **53**, 41 (2002).
 - [8] K. L. Reid, *Annu. Rev. Phys. Chem.* **54**, 397 (2003).
 - [9] M. O. Krause, *Phys. Rev.* **177**, 151 (1969).
 - [10] J. W. Cooper and S. T. Manson, *Phys. Rev.* **177**, 157 (1969).
 - [11] M. Ya. Amusia, P. U. Arifov, A. S. Baltenkov, A. A. Grinberg, and S. G. Shapiro, *Phys. Lett.* **47A**, 66 (1974).
 - [12] A. Ron, R. H. Pratt, and H. K. Tseng, *Chem. Phys. Lett.* **47**, 377 (1977).
 - [13] G. Leuchs, S. J. Smith, S. N. Dixit, and P. Lambropoulos, *Phys. Rev. Lett.* **56**, 708 (1986).
 - [14] C. N. Yang, *Phys. Rev.* **74**, 764 (1948).
 - [15] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1958), p. 248ff.
 - [16] J. Cooper and R. N. Zare, *J. Chem. Phys.* **48**, 942 (1968).
 - [17] B. Krässig, M. Jung, D. S. Gemmell, E. P. Kanter, T. LeBrun, S. H. Southworth, and L. Young, *Phys. Rev. Lett.* **75**, 4736 (1995).
 - [18] M. Jung, B. Krässig, D. S. Gemmell, E. P. Kanter, T. LeBrun, S. H. Southworth, and L. Young, *Phys. Rev. A* **54**, 2127 (1996).
 - [19] O. Hemmers, G. Fisher, P. Glans, D. L. Hansen, H. Wang, S. B. Whitfield, R. Wehlitz, J. C. Levin, I. A. Sellin, R. C. C. Perera, E. W. B. Dias, H. S. Chakraborty, P. C. Deshmukh, S. T. Manson, and D. W. Lindle, *J. Phys. B* **30**, L727 (1997).
 - [20] O. Hemmers, R. Guillemin, E. P. Kanter, B. Krässig, D. W. Lindle, S. H. Southworth, R. Wehlitz, J. Baker, A. Hudson, M. Lotrakul, D. Rolles, W. C. Stolte, I. C. Tran, A. Wolska, S. W. Yu, M. Ya. Amusia, K. T. Cheng, L. V. Chernysheva, W. R. Johnson, and S. T. Manson, *Phys. Rev. Lett.* **91**, 053002 (2003).
 - [21] S. Ricz, R. Sankari, À. Kövèr, M. Jurvansuu, D. Varga, J. Nikkinen, T. Ricsoka, H. Aksela, and S. Aksela, *Phys. Rev. A* **67**, 012712 (2003).
 - [22] N. L. S. Martin, D. B. Thompson, R. P. Bauman, C. D. Caldwell, M. O. Krause, S. P. Frigo, and M. Wilson, *Phys. Rev. Lett.* **81**, 1199 (1998).
 - [23] M. Peshkin, *Adv. Chem. Phys.* **18**, 1 (1970).
 - [24] M. Ya. Amusia and V. K. Dolmatov, *Sov. Phys. JETP* **52**, 840 (1980).
 - [25] A. Bechler and R. H. Pratt, *Phys. Rev. A* **39**, 1774 (1989); **42**, 6400 (1990).
 - [26] J. W. Cooper, *Phys. Rev. A* **42**, 6942 (1990); **45**, 3362(E) (1992); **47**, 1841 (1993).
 - [27] V. K. Dolmatov and S. T. Manson, *Phys. Rev. Lett.* **83**, 939 (1999).
 - [28] M. Ya. Amusia, A. S. Baltenkov, Z. Felfli, and A. Z. Msezane, *Phys. Rev. A* **59**, R2544 (1999).
 - [29] W. R. Johnson, A. Derevianko, K. T. Cheng, V. K. Dolmatov, and S. T. Manson, *Phys. Rev. A* **59**, 3609 (1999).
 - [30] O. Hemmers, H. Wang, P. Focke, I. A. Sellin, D. W. Lindle, J. C. Arce, J. A. Sheehy, and P. W. Langhoff, *Phys. Rev. Lett.* **87**, 273003 (2001).
 - [31] R. Guillemin, O. Hemmers, D. W. Lindle, E. Shigemasa, K. Le Guen, D. Ceolin, C. Miron, N. Leclercq, P. Morin, M. Simon, and P. W. Langhoff, *Phys. Rev. Lett.* **89**, 033002 (2002).
 - [32] J. C. Arce, J. A. Sheehy, P. W. Langhoff, O. Hemmers, H. Wang, P. Focke, I. A. Sellin, and D. W. Lindle, *Chem. Phys. Lett.* **346**, 341 (2001); **349**, 349 (2001).
 - [33] P. W. Langhoff, J. C. Arce, J. A. Sheehy, O. Hemmers, H. Wang, P. Focke, I. A. Sellin, and D. W. Lindle, *J. Electron Spectrosc. Relat. Phenom.* **114–116**, 23 (2001).
 - [34] B. Krässig, J.-C. Bilheux, R. W. Dunford, D. S. Gemmell, S. Hasegawa, E. P. Kanter, S. H. Southworth, L. Young, L. A. LaJohn, and R. H. Pratt, *Phys. Rev. A* **67**, 022707 (2003).
 - [35] N. M. Kabachnik and I. P. Sazhina, *J. Phys. B* **29**, L515 (1996).
 - [36] O. Hemmers, S. B. Whitfield, P. Glans, H. Wang, D. W. Lindle, R. Wehlitz, and I. A. Sellin, *Rev. Sci. Instrum.* **69**, 3809 (1998).
 - [37] E. P. Kanter, B. Krässig, S. H. Southworth, R. Guillemin, O. Hemmers, D. W. Lindle, R. Wehlitz, M. Ya. Amusia, L. V. Chernysheva, and N. L. S. Martin, *Phys. Rev. A* **68**, 012714 (2003).
 - [38] B. Zimmermann, in *Studies of Vacuum Ultraviolet and X-Ray Processes*, edited by U. Becker (Wissenschaft and Technik Verlag, Berlin, 2000), Vol. 13.
 - [39] A. N. Grum-Grzhimailo, *J. Phys. B* **36**, 2385 (2003).
 - [40] J. C. Tully, R. S. Berry, and B. J. Dalton, *Phys. Rev.* **176**, 95 (1968).
 - [41] D. Dill and J. L. Dehmer, *J. Chem. Phys.* **61**, 692 (1974).
 - [42] R. R. Lucchese, G. Raseev, and V. McKoy, *Phys. Rev. A* **25**, 2572 (1982).
 - [43] D. Toffoli and P. Decleva, *J. Phys. B* **39**, 2681 (2006).
 - [44] K. Hosaka, J. Adachi, A. V. Golovin, M. Takahashi, T. Teramoto, N. Watanabe, A. Yagishita, S. K. Semenov, and N. A. Cherepkov, *J. Phys. B* **39**, L25 (2006).
 - [45] O. Hemmers *et al.* (unpublished).