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Nondipole effects in molecular nitrogen valence shell photoionization

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Abstract

Nondipole photoelectron parameters ζ have been obtained experimentally for the outer-valence $3\sigma_g$, $1\pi_u$ and $2\sigma_u$ shells in molecular nitrogen from threshold to ~200 eV photon energy. Significant nondipole effects are observed even in the immediate threshold regions of these valence-shell distributions. The results of preliminary calculations for the $3\sigma_g$ and $2\sigma_u$ clarify the origins of the observed features in terms of contributing molecular symmetry channels. Theory and experiment are in excellent accord, suggesting that the large nondipole effects previously observed in atoms and the K-shells of molecules can also appear at low photon energies in the outer-valence shells of molecules.

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There has been great interest in molecular photoelectron angular distributions for over three decades. Systematic studies over broad energy ranges began in the late 1970s [1,2] and continued through the 1980s [3] and 1990s [4]. These studies provided a wealth of information for probing the electronic structure of small molecules both for gas-phase and molecules on surfaces. All studies focused on dipole dependent differential cross-sections and most studies focused on interchannel coupling and shape-resonance effects near the ionization thresholds of the molecular valence lines. The extension of these studies to nondipolar effects in the threshold region of small molecules is clearly long overdue.

Two different sets of measurements of the nondipole asymmetries of the three outer molecular valence orbitals of N_2 were made with quite different methods. Experiments were carried out over the 26–100 eV photon energy range at Wisconsin's Synchrotron Radiation Center (SRC) on the PGM Undulator 071 beamline. The first-order linearly polarized radiation from the undulator was monochromatized with a plane grating monochromator using 255-μm entrance and 150-μm exit slits giving a bandpass between 8 and 60 meV for 26 and 100 eV, respectively. The beam then entered a doubly μ-metal-shielded vacuum chamber housing four parallel plate electron analyzers (PPAs) which are described in [5].

Measurements over the 80–200 eV photon energy range were made at the Advanced Light Source (ALS) of the Lawrence Berkeley National Laboratory on undulator beamline 8.0.1 during several 2-bunch periods, which provide only two electron bunches in the synchrotron ring and about 10% of the photon flux of normal operation. Nevertheless, this mode is crucial for time-of-flight (TOF) spectroscopy. The spherical grating monochromator (SGM) houses three interchangeable gratings with the lowest energy of 78 eV at 1.9 GeV ring energy. The entrance and exit slits were set to 20 and 40 μm, respectively, and the bandpass was between

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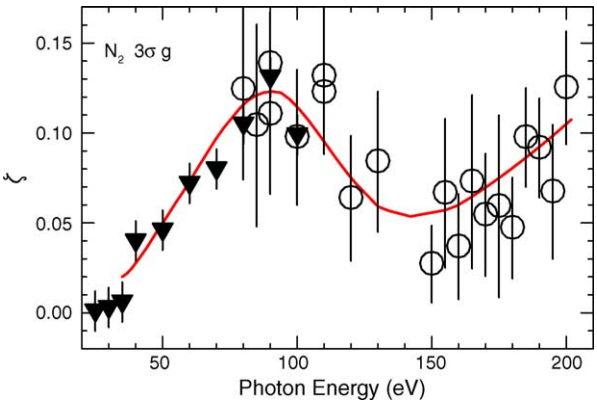

Fig. 1. Experimental data (triangles, SRC and circles, ALS) of the N_2 $3\sigma_g$ nondipole anisotropy parameter ζ in comparison to FCHF calculations.

25 and 80 meV for 80 and 200 eV, respectively. The experimental chamber consists of five electron TOF-analyzers in a CoNetic shielded chamber for gas-phase measurements, which is described in [6].

In both sets of measurements, electron analyzers were positioned at sets of angles that are sensitive to different combinations of the dipole parameter, β, and the nondipole parameters δ, and γ [7]. These nondipole parameters arise from cross terms of electric-dipole with electric-quadrupole and magnetic-dipole photoionization amplitudes. Linear combinations of the measured photoelectron intensities yielded values of $\gamma + 3\delta = \zeta$.

The photoionization transition amplitudes are calculated using the Frozen-Core Hartree-Fock (FCHF) approximation. The molecular ground-state wave function has been derived in a self-consistent-field approximation. The ionized molecular state is then obtained by removing one electronic charge out of the orbital that is to be ionized. The molecule is not allowed to relax ('frozen core'). The photoelectron orbitals were obtained using an iterative procedure to solve the Lippmann–Schwinger equation associated with the one-electron Schrödinger equation which these orbitals satisfy (for further details see [8]). Details to the calculations of nondipolar angular distributions will be published elsewhere [9].

As an example we present in Fig. 1 the N_2 $3\sigma_g$ results which are clearly dominated by a resonance-like structure with a maximum near a photon energy of 90 eV. This structure is not related to the extensively studied $3\sigma_g \rightarrow \sigma_u^*$ shape resonance which has its maximum near 29 eV. Here, at 29 eV the nondipole parameter goes through a minimum for the $3\sigma_g$. The solid line represents our preliminary theoretical results and is comprised of the sum of interference terms between dipole (first term) and nondipole (second term) contributions. Based on the individual interference terms (not shown) it was determined that the overall increase of ζ for the $3\sigma_g$ is mainly due to the interaction of the $\sigma\sigma$, $\pi\pi$, and $\pi\delta$ interference terms and the maximum near 90 eV is created by $\pi\pi$ and to some extent by $\sigma\pi$ and $\pi\delta$ interference terms.

In summary, measurements of the nondipole parameter ζ for the three outer-valence lines in molecular nitrogen have been made over a broad energy range. Significant nondipole effects are found even close to threshold and for the $3\sigma_g$ have been described with a newly developed formalism within the Frozen-Core Hartree-Fock (FCHF) approximation. The experimental and preliminary theoretical data for the $3\sigma_g$ show excellent agreement, and through the combination of theory and experiment, results certainly contradict the prior notion that nondipole effects occur only at high energy. The complete data set for the three outer-valence states in N_2 will be published elsewhere once the calculations are finished. Of additional importance is that the nondipole effects in low-energy photoionization observed here are not unique to molecular nitrogen; it is expected that such effects will show up in many molecules and these considerations should apply to surfaces, clusters and solids as well.

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