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Shape-resonance effects mediated by channel interaction: Angular distributions of N_2 $2\sigma_u$ photoelectrons

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We show that photoelectron angular distributions in the $2\sigma_u$ channel of N_2 are significantly distorted by continuum-continuum coupling with the f-wave ($l=3$) shape resonance in the $3\sigma_g$ photoionization channel. This distortion is clearly seen in measured $2\sigma_u$ angular distributions. The effect is demonstrated using K-matrix methods to couple the one-electron $2\sigma_u\epsilon\sigma_g$ and $3\sigma_g\epsilon\sigma_u$ $^1\Sigma_u^+$ channels. Non-Franck-Condon N_2^+ $B\,^2\Sigma_u^+$ vibrational branching ratios and vibrationally dependent $2\sigma_u\epsilon\sigma_g$ photoelectron asymmetry parameters are predicted as additional effects.

Coupling between molecular photoelectrons and residual electrons is typically weak, because continuum electrons are so diffuse[1] that they have negligible amplitude in the molecular interior where strong interaction can take place. By the same token, prominent structure in photoionization spectra can signal special dynamical circumstances which enhance electronic amplitude in the core region, and which thereby may amplify many-electron effects. We have proposed[2] that the marked deviations from one-electron predictions seen in the 29–35-eV photon energy range in the photoionization spectra of the $2\sigma_u$ level of N_2 reflect just such amplification. The deviations coincide with the shape-resonant enhancement of $3\sigma_g\epsilon\sigma_u$ f-wave ($l=3$) photoelectrons in the molecular core,[3–5] and they are particularly striking in the photoelectron asymmetry parameter β. This correlation in energy with the shape resonance together with strong angular distortion characteristic of high orbital momenta is the basis of our surmise that a significant portion of the measured distortion in the $2\sigma_u$ spectrum is due to electronic continuum configuration mixing with the $3\sigma_g\epsilon\sigma_u$ f-wave shape resonance. The purpose of this Rapid Communication is to report the results of an *ab initio* K-matrix study which show directly that this mechanism is an important part of N_2 $2\sigma_u$ photoionization dynamics.

Shape-resonance-enhanced interchannel coupling has been known for many years in atomic photoionization. For example, one-electron (Herman-Skillman and Hartree-Fock) rare-gas s-subshell photoionization cross sections and angular distributions may be substantially modified by interchannel coupling with strong, shape-resonant amplitude in other photoionization channels.[6,7] Shape-resonant enhancement mediated by continuum-continuum coupling has also been proposed recently to account for resonant activity seen in SF_6 photoionization channels that do not themselves support shape resonances.[8] What we are including in the present description is the probability amplitude of forming a quasibound excited complex composed predominantly of an electron excited out of the $3\sigma_g$ subshell into the $\epsilon\sigma_u$ continuum. Within this complex, the $\epsilon\sigma_u$ electron may collide with an electron in the $2\sigma_u$ subshell. Thereby a $2\sigma_u$ electron may be ejected by simultaneous deexcitation of the $\epsilon\sigma_u$ electron back into the $3\sigma_g$ subshell. The $2\sigma_u$ orbital is more compact than the outer valence levels, and for an electron ejected from the outermost $3\sigma_g$ orbital to experience close collision with this inner-shell electron with significant probability, and with observable consequences, an amplification mechanism must exist. The mechanism here is the molecular shape resonance, in which electronic amplitude in the $3\sigma_g\epsilon\sigma_u$ channel penetrates a potential barrier in the molecular field over a narrow electron kinetic energy range. Thereby the $\epsilon\sigma_u$ electron becomes quasibound with large amplitude in the core region,[1,3] and hence provides favorable conditions for electronic collision.

The calculations have been performed by adapting the K-matrix expansion methods, developed by Fano and coworkers[9] in the context of atomic photoionization, to the molecular photoelectron continuum, using multiple-scattering model (MSM)[10] one-electron orbitals. The details of implementing K-matrix methods in the MSM framework will be reported elsewhere.[11] The exact, final-state, incoming-wave normalized continuum eigenfunction of total energy E is written as the expansion[6,7,9,11]

$$|\gamma LE\rangle^{(-)}=\sum_{\gamma' L'}\left[|\gamma' L' E'\rangle+\sum_{\gamma'' L''}\mathrm{P}\int dE''\frac{|\gamma'' L'' E''\rangle\langle\gamma'' L'' E''|K|\gamma' L' E'\rangle}{E-E''}\right]C^{(-)}_{\gamma' L',\gamma L}(E)\ . \tag{1}$$

Here, γ specifies the state of the ion core and the symmetry of the photoelectron wave function, and $L=(l,m)$ designates a particular partial-wave component of the ejected photoelectron. The states $|\gamma LE\rangle$ are determinants constructed from bound and standing-wave normalized continuum one-electron eigenfunctions of the MSM model Hamiltonian. The coefficient $C^{(-)}_{\gamma' L',\gamma L}(E)$ enforces incoming-wave boundary conditions appropriate for photoionization for the many-electron, coupled-channel state. The K matrix in Eq. (1) satisfies the integral equation[6,7,9,11]

$$\langle\gamma' L' E'|K|\gamma LE\rangle=\langle\gamma' L' E'|V_{\mathrm{res}}|\gamma LE\rangle+\sum_{\gamma'' L''}\mathrm{P}\int dE''\frac{\langle\gamma' L' E'|V_{\mathrm{res}}|\gamma'' L'' E''\rangle\langle\gamma'' L'' E''|K|\gamma LE\rangle}{E-E''}\ . \tag{2}$$

In the above formulas P indicates that principal-part integration is performed, and the integrals over E also include summation over discrete excited states in the channels γ. The residual interaction V_{res} is the difference between the exact (fixed-

nuclei) electronic Hamiltonian H and the model Hamiltonian H_{MSM} defined in terms of the MSM one-electron, self-consistent-field potential V_{MSM}. The methods used in evaluating this operator in the MSM coordinates are given elsewhere.[11,12]

For actual calculations the complete set expansions must be truncated to a finite number of interacting channels, to yield a finite-size matrix V. The MSM accounts well for the orbital momentum coupling at the one-electron level, but there will be recoupling by the residual intra- and interchannel interactions. For this prototype study we have solved a minimum, two-channel problem involving the dominant orbital momentum components in each channel: $l=0(s)$ for $2\sigma_u\epsilon\sigma_g$ and $l=3(f)$ for $3\sigma_g\epsilon'\sigma_u$. The interchannel interaction of the $2\sigma_u\epsilon\pi_g$ channel with both the $2\sigma_u\epsilon\sigma_g$ channel and the shape-resonant $3\sigma_g\epsilon'\sigma_u$ channel vanishes by symmetry, and we have also neglected all intrachannel coupling within the $2\sigma_u\epsilon\pi_g$ channel. In this way we include *limited* intra- and interchannel coupling in the final-state wave function chosen to incorporate the dominant interactions. The many-electron channels for the present calculation are thus the determinantal states

$$|2\sigma_u\epsilon\sigma_g\rangle = |N_2^+\ B\,^2\Sigma_u^+, \epsilon s\sigma_g; {}^1\Sigma_u^+\rangle\ ,$$

$$|3\sigma_g\epsilon'\sigma_u\rangle = |N_2^+\ X\,^2\Sigma_g^+, \epsilon' f\sigma_u; {}^1\Sigma_u^+\rangle\ ,$$

with channel $|2\sigma_u\epsilon\sigma_g\rangle$ corresponding to the observation channel. Using these determinants the residual interaction matrix is reduced to sums of one- and two-electron integrals over the single-particle orbitals using the Slater-Condon rules.[13]

The MSM one-electron orbitals were computed using symmetry allowed partial waves up to $l=5$ about the molecular center and $l=2$ about the nitrogens for orbitals of σ_u, π_u, and σ_g symmetry. These orbitals yielded matrix elements converged to approximately 1%–5% change upon addition of more partial waves, for an energy range extending to kinetic energy $\epsilon=1.9$ Ry in channel $|2\sigma_u\epsilon\sigma_g\rangle$ and $\epsilon'=2.2$ Ry in channel $|3\sigma_g\epsilon'\sigma_u\rangle$. These were taken to be the high-energy cutoffs in solving Eq. (2) for the two-channel K matrix, using an algorithm which reduces the integral equations to a inhomogeneous linear system of equations.[14] A total of 18 explicit configurations (distinguished by the electronic excitation energy ϵ) were used for channel $|2\sigma_u\epsilon\sigma_g\rangle$ and 20 configurations (different energies ϵ') were used for channel $|3\sigma_g\epsilon'\sigma_u\rangle$. There was thus required the inversion of a 38×38 matrix at each total energy E of the observation channel. Several discrete Rydberg states were included in each channel, but these had little effect on the present results.

In Fig. 1 we examine the s-wave dipole amplitude component for production of the $2\sigma_u\epsilon\sigma_g$ final state, which we have coupled to the shape resonance. Curve a shows the combined effect of the intra- and interchannel interaction on the length-form, ingoing-wave normalized dipole amplitude. The enhancement due to the $3\sigma_g\epsilon'\sigma_u$ shape resonance is clearly seen. In curve b we show the dipole amplitude taking into account only the $2\sigma_u\epsilon\sigma_g$ intrachannel interaction. No coupling to the $3\sigma_g\epsilon'\sigma_u$ is possible and so there is no resonance, but the intrachannel interaction does increase the coupled dipole amplitude over the whole energy range. This behavior is correct, reflecting the fact that the K-matrix calculation must approach Hartree-Fock results.[6] Comparison of these curves shows that interchannel coupling is highly localized in the kinetic energy region $\epsilon\approx0.9$–1.2 Ry. The rapid rise in curve a beyond $\epsilon\approx1.3$ Ry is due to breakdown of the intrachannel expansion in the $2\sigma_u\epsilon\sigma_g$ channel. This inaccurate intrachannel component was removed beyond this energy when computing the angular distribution presented here.

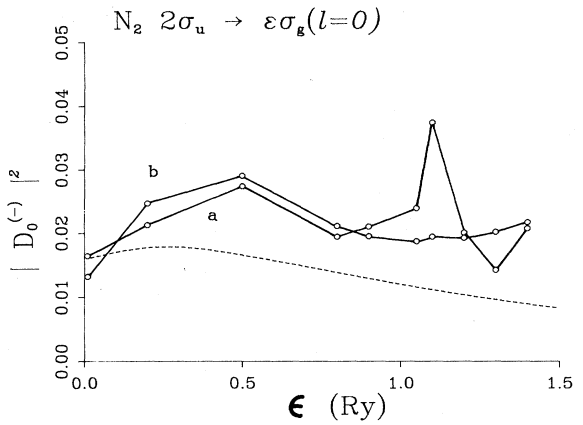

FIG. 1. N_2 $2\sigma_u$ K-matrix length-form dipole strengths $|D_0^{(-)}|^2$, for $2\sigma_u\epsilon\sigma_g$ $l=0$ (s) channel, in units of a_0^2/Ry. Circles are calculated points, which have been connected to guide the eye. Curve a is for full intra- and interchannel coupling. Curve b is for intrachannel coupling only. Dash curve is one-electron MSM dipole strength.

In Fig. 2 we show the calculated K-matrix asymmetry parameter, the MSM one-electron result of Wallace, Dill, and Dehmer[15] and the Hartree-Fock (with initial-state correlation) result of Lucchese, Raseev, and McKoy.[16] Included also are the original measurements of Marr, Morten, Holmes, and McCoy,[17] and very recent measurements of Adam, Morin, Lablanquie, and Nenner.[18] The experimental data clearly show a minimum, perhaps two, in the photon energy range $h\nu\approx28$–35 eV. The K-matrix calculation begins to dip at $h\nu\approx31$ eV, rapidly falls to a minimum value $\beta\approx0.7$ at $h\nu\approx34$ eV, and then undergoes a rapid rise and oscillation beyond the resonance. The minimum value of β attained is in general good agreement with experimental

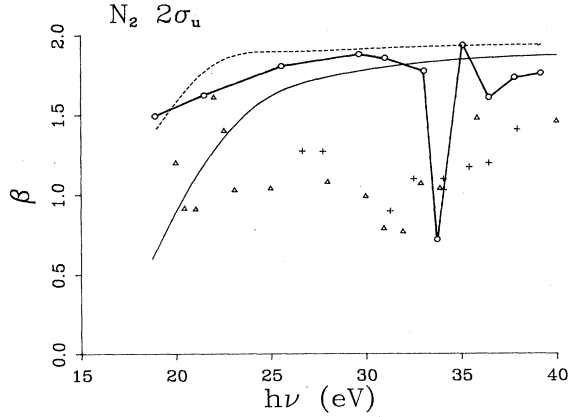

FIG. 2. N_2 $2\sigma_u$ K-matrix length-form asymmetry parameters β. Solid curve: theoretical result of Lucchese *et al.* (Ref. 16); dash curve: one-electron MSM result of Wallace *et al.* (Ref. 15); Δ: experimental result of Marr *et al.* (Ref. 17); +: experimental result of Adam *et al.* (Ref. 18).

values in this region, although the energy of the calculated minimum appears approximately 3 eV too high compared with the experimental minimum. (This reflects the placement of the $3\sigma_g\epsilon'\sigma_u$ shape resonance at too high an energy, a known deficiency of our MSM treatment.) The existence of this variation, compared with the nearly constant one-electron results in this region, is the main result of this calculation. From threshold up to the resonance, the lower K-matrix asymmetry parameter values relative to the MSM calculation are due mainly to the intrachannel interaction, and are an improvement over the one-electron results. Indeed, the K-matrix calculation approaches the values of Lucchese *et al.*,[16] which should contain the full intrachannel interaction exactly. The other features observed in the data near $h\nu \approx 23$ eV, which are also quite sparse, have been qualitatively ascribed[19,20] to interaction of doubly excited states with the underlying continuum.

In assessing our K-matrix results the following concluding points are relevant, and should be considered in future work on the $2\sigma_u$ level of N_2. *First,* we stress that these are approximate, prototype calculations, in that we have neglected residual electrostatic coupling between other angular components of the final state. We do not expect these additional couplings to change the qualitative features of the present results. *Second,* we have neglected vibrational effects. While vibrational averaging over the ground-state nuclear motion has negligible effect on the one-electron $2\sigma_u \rightarrow \epsilon\sigma_g, \epsilon\pi_g$ cross sections,[21] such averaging significantly diminishes and broadens the $3\sigma_g \rightarrow \epsilon\sigma_u$ shape resonance compared with calculations at fixed (equilibrium) internuclear distance, and also causes the maximum of the resonance to shift approximately 1–2 eV towards the $3\sigma_g$ threshold.[22] Since the $\epsilon\sigma_u$ shape resonance plays a fundamental role in the interchannel coupling mechanism implemented here, we anticipate that this type of vibrational dependence may have significant effects. These may include non-Franck-Condon N_2^+ $B\,^2\Sigma_u^+$ vibrational branching ratios and vibrationally dependent $2\sigma_u\epsilon\sigma_g$ photoelectron asymmetry parameters. *Third,* we cannot discard the possible role of a competing dissociation process and/or configuration interaction with the excited C $^2\Sigma_u^+$ state of the ion.[18,20,23,24] Weak enhancements in the photoionization cross section, near 31-eV photon energy, have been observed in the electron energy-loss measurements of Hamnett, Stoll, and Brion,[23] and in the fluorescence excitation data of Lee.[24] Recent work by Tabche-Fouhaile *et al.*[20] and Lablanquie[25] confirm these results, and these authors further discuss the possible role of the C $^2\Sigma_u^+$ state. If these effects exist there will likely be complex interplay with the purely electronic mode of excitation studied here.

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