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## Shape-Resonance-Enhanced Nuclear-Motion Effects in Molecular Photoionization

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Shape resonances in molecular photoionization are shown to induce strong coupling between vibrational and electronic motion over a spectral range several times broader than the resonances half-width. This coupling is manifested by large deviations from Franck-Condon intensity distributions and strong dependence of photoelectron angular distributions on the vibrational state of the residual ion. These effects are illustrated for the  $3\sigma_g$  photoionization channel of  $N_2$ .

Molecular photoionization at wavelengths unaffected by autoionization, predissociation, or ionic thresholds is generally believed to produce Franck-Condon (FC) vibrational intensity distributions and  $v$ -independent photoelectron angular distributions. In this Letter, we predict that the shape resonances being identified<sup>1-7</sup> in the spectra of a growing, diverse collection of molecules represent an important class of exceptions to this picture. In particular, the temporary trapping of the photoelectron by a centrifugal barrier enhances the coupling between electronic and vibrational motion, leading to striking non-FC intensities and strongly  $v$ -dependent asymmetry parameters over a broad spectral range encompassing the resonance. We illustrate these ideas with a calculation of the  $3\sigma_g$  photoionization channel of  $N_2$ , which exhibits the well-known  $\sigma_u$ ,  $f$ -wave shape resonance.<sup>2,4-6,8-18</sup> In addition to predicting non-FC vibrational branching ratios, we account for the long unexplained observation<sup>19</sup> that the  $\beta$  values for production  $N_2^+ X^2\Sigma_g^+(v=0, 1)$  differ significantly at 584 Å (and other wavelengths), where

none of the more traditional mechanisms mentioned above apply. We believe that this illustration for  $N_2$  is merely the first of many examples of shape-resonance-enhanced nuclear-motion effects which have hitherto gone undetected only because vibrationally resolved photoelectron studies have not been carried out systematically through molecular shape resonances, as is now possible with synchrotron-radiation sources.

The breakdown of the FC principle arises from the quasibound nature of the shape resonance, which is localized in a spatial region of molecular dimensions by a centrifugal barrier. This barrier and, hence, the energy and lifetime (width) of the resonance are sensitive functions of internuclear separation  $R$  and vary significantly over a range of  $R$  corresponding to the ground-state vibrational motion. This is illustrated in the upper portion of Fig. 1 where the dashed curves represent separate, fixed- $R$  calculations of the partial cross section and asymmetry parameter for  $N_2$   $3\sigma_g$  photoionization over the range  $1.824a_0 \leq R \leq 2.324a_0$ , which spans the  $N_2$  ground-

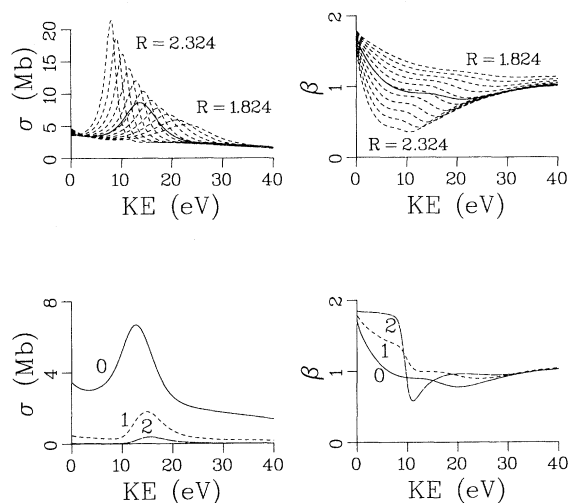


FIG. 1. Cross sections  $\sigma$  and asymmetry parameters  $\beta$  for photoionization of the  $3\sigma_g$  ( $v_i=0$ ) level of  $N_2$ . Top: fixed- $R$  (dashed curve) and  $R$ -averaged, vibrationally unresolved (solid curve) results. Bottom: results for resolved final-state vibrational levels,  $v_f=0-2$ .

state vibrational wave function. The calculations were carried out as described elsewhere,<sup>4</sup> only using the Schwarz value<sup>20</sup> ( $\alpha=0.751$ ) of the exchange coefficient. The peak in the  $3\sigma_g$  partial-cross-section curves is caused by the well-known shape resonance in the  $\sigma_u$  ionization channel. This resonance has been studied extensively in inner-shell (Refs. 2, 4, 6, 8, 11, 12, and 14-16), valence-shell (Refs. 5, 9, 10, 13, 15, 17, and 18), and oriented-molecule<sup>5, 8, 16</sup> contexts and is known to result from a centrifugal barrier acting on the  $f$ -wave ( $l=3$ ) component of the  $\sigma_u$  final-state wave function.

Of central importance in Fig. 1 is the clear demonstration that resonance positions, strengths, and widths are sensitive functions of  $R$ . In particular, for larger separations, the effective potential acting on the  $l=3$  component of the  $\sigma_u$  wave function is more attractive and the shape resonance shifts to lower kinetic energy, becoming narrower and higher. Conversely, for lower values of  $R$ , the resonance is pushed to higher kinetic energy and is weakened. This indicates that nuclear motion exercises great leverage on the spectral behavior of shape resonances, since small variations in  $R$  can significantly shift the delicate balance between attractive (mainly Coulomb) and repulsive (mainly centrifugal) forces which combine to form the barrier. In the present case, variations in  $R$ , corresponding to the

ground-state vibration in  $N_2$ , produce significant resonant behavior over a spectral range several times the full width at half maximum of the resonance calculated at  $R=R_e$ . By contrast, nonresonant channels are relatively insensitive to such variation in  $R$ , as will be shown by our results on the  $1\pi_u$  and  $2\sigma_u$  photoionization channels in  $N_2$ , to be published elsewhere.<sup>15, 21</sup>

Thus, in the vicinity of a shape resonance, the electronic transition moment varies rapidly with  $R$ , indicating strong coupling between electronic and vibrational motion. We have estimated this coupling in the adiabatic-nuclei approximation<sup>22</sup> by computing the net transition moment for a particular vibrational channel as an average of the  $R$ -dependent dipole amplitude, weighted by the product of the initial- and final-state vibrational wave function at each  $R$ :

$$D_{v_f v_i}^- = \int dR \chi_{v_f}^+(R) D^-(R) \chi_{v_i}(R). \quad (1)$$

The vibrational wave functions were approximated by harmonic-oscillator functions and the superscript minus denotes<sup>16, 23</sup> that incoming-wave boundary conditions have been applied and that the transition moment is complex. Note that even when the final vibrational levels  $v_f$  of the ion are unresolved (summed over), vibrational motion within the initial state  $v_i=0$  causes the above equation to yield results significantly different from the  $R=R_e$  result, because the  $R$  dependence of the shape resonance is highly asymmetric. This gross effect of  $R$  averaging can be seen in the upper half of Fig. 1 by comparing the solid line ( $R$ -averaged result, summed over  $v_f$ ) and the middle dashed line ( $R=R_e$ ). Hence, even for the calculation of gross properties of the whole, unresolved electron band, it is necessary to take into account vibrational-motion effects in channels exhibiting shape resonances. As we stated earlier, this is generally not a critical issue in nonresonant channels.

Effects of nuclear motion on individual vibrational levels are shown in the bottom half of Fig. 1. Looking first at the partial cross sections, we see that the resonance position varies over a few volts depending on the final vibrational state, and that higher levels are relatively more enhanced at their resonance position than is  $v_f=0$ . This sensitivity to  $v_f$  arises because transitions to alternative final vibrational states preferentially sample different regions of  $R$ . In particular,  $v_f=1, 2$  sample successively smaller  $R$ , governed by the maximum overlap with the ground vibrational state, causing the resonance in those vi-

brational channels to peak at higher energy than that for  $v_f=0$ . The impact of these effects on branching ratios is clearly seen in Fig. 2, where the ratio of the higher  $v_f$  intensities to that of  $v_f=0$  is plotted in the resonance region. There we see that the ratios are slightly above the FC factors<sup>24</sup> (9.3%,  $v_f=1$ ; 0.6%,  $v_f=2$ ) at zero kinetic energy, go through a minimum just below the resonance energy in  $v_f=0$ , then increase to a maximum as individual  $v_f>0$  vibrational intensities peak, and finally approach the FC factors again at high kinetic energy. Note the maximum enhancement over the FC factors is progressively more pronounced for higher  $v_f$ , i.e., 340% and 1300% for  $v_f=1, 2$ , respectively. Gardner and Samson<sup>25</sup> have systematically measured vibrational intensity distributions in  $N_2$ ; however, the discrete wavelengths utilized in that study did not cover the critical kinetic-energy range between 10 and 25 eV. Their data show non-FC effects but these were believed to be due mainly to autoionization. It may be significant that their 584- and 537-Å ( $v=1/v_f=0$ ) ratios were 6.9%, i.e., lower than the FC factors, and that the 304 Å ratio was 13.1%, i.e., higher than the FC factors; however, this is not conclusive. A systematic mapping of the critical region in Fig. 2 using synchrotron radiation is needed to test the prediction given here.

Equally dramatic are the effects on  $\beta(v_f)$  shown in the lower right-hand portion of Fig. 1. Especially at and below the resonance position, the  $\beta$ 's vary greatly for different final vibrational levels. The  $v_f=0$  curve agrees well with the solid curve in the upper half, since the gross be-

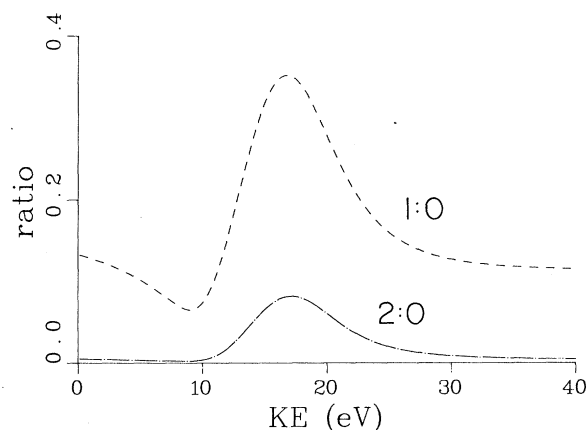


FIG. 2. Vibrational-state branching ratios  $\sigma(v_f)/\sigma(v_f=0)$  for photoionization of the  $3\sigma_g$  level of  $N_2$ .

havior of the vibrationally unresolved electronic band will be governed by the  $\beta$  of the most intense component. The  $R=R_e$  curve has been found to agree well with recent wavelength-dependent measurements,<sup>17,18</sup> and the agreement is improved by the slight damping caused by  $R$  averaging. More significant for the present purposes is the  $v_f$  dependence of  $\beta$ . Carlson first observed (Refs. 19a, 19b) that, at 584 Å, the  $v_f=1$  level in the  $3\sigma_g$  channel of  $N_2$  had a much larger  $\beta$  than the  $v_f=0$  level even though there was no apparent autoionizing state at that wavelength. This has been studied in the meantime by several workers<sup>19c-19f</sup> with the same general conclusions, i.e.,  $\beta(v_f=0)\sim 0.7$  and  $\beta(v_f=1)\sim 1.4$ . This is in semiquantitative agreement with the present calculation which gives  $\beta(v_f=0)\sim 1.0$  and  $\beta(v_f=1)\sim 1.5$ . Although the agreement is not exact, we feel this demonstrates the "anomalous"  $v_f$  dependence of  $\beta$  in  $N_2$  stems mainly from the  $\sigma_u$  shape resonance which acts over a range of the spectrum many times its own  $\sim 5$  eV width. The underlying cause of this effect is the shape-resonance-enhanced  $R$  dependence of the dipole amplitude, just as for the vibrational partial cross sections. In the case of  $\beta(v_f)$ , however, both the  $R$  dependence of the phase and of the magnitude of the complex dipole amplitude play a crucial role, whereas the partial cross sections depend only on the magnitude.

This prototype study has demonstrated several aspects of photoionization channels exhibiting shape resonances: First, the time delay in photoelectron escape associated with a shape resonance enhances the coupling between nuclear motion and electronic motion, invalidating the FC factorization of the two modes. In time-independent language, the great asymmetric and non-monotonic sensitivity of the transition amplitude to internuclear separation requires folding of the transition amplitude with the vibrational motion of the molecule, at the very least in an adiabatic scheme. When resonance lifetimes and the vibrational period are comparable, nonadiabatic effects (analogous to those observed<sup>26</sup> for the 2.4-eV  $\pi_g$  resonance in  $e-N_2$  scattering) are likely to be important as well. Second, the effects are large in both vibrational intensities and angular distributions, but have heretofore been largely overlooked because shape-resonance effects tend to lie in an inconvenient wavelength range for laboratory light sources. Synchrotron radiation will be most useful for this purpose, and we expect this to be a major theme in vibrationally re-

solved photoelectron measurements using this broad-range continuum source. Third, it is significant to note that the effects of the shape resonance described above act over tens of volts of the spectrum, several times the half-width of the resonance, and that  $\sigma$  and  $\beta$  probe the effects differently, i.e., have maximal effects in different energy regions. This underscores the well-known differences of the dynamical information contained in the two physical observables. Fourth, a long-standing "anomalous"  $v_f$  dependence in the photoelectron angular distributions of the  $3\sigma_g$  channel of  $N_2$  has been resolved. Finally, the phenomena described here for one channel of  $N_2$  should be very widespread, as shape resonances now appear to affect one or more inner- and outer-shell channels in most (nonhydride) molecules.

Experimental verification of shape-resonance-induced non-FC vibrational intensity distributions has been recently reported for the  $5\sigma$  channel of CO by Stockbauer *et al.*<sup>27</sup>

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