THEORETICAL PREDICTION OF SHAPE-RESONANCE-ENHANCED NUCLEAR MOTION EFFECTS IN MOLECULAR PHOTOIONIZATION*

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Shape resonances in molecular photoionization are predicted to induce strong non-Franck-Condon effects over a spectral range several times broader than the resonance half-width. This is manifested by large deviations from Franck-Condon vibrational 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 in Figures 1 and 2, using the multiple-scattering model and the adiabatic nuclei approximation.

Of central importance in Figure 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 $\ell = 3$ components of the σ_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 resonance, 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 FWHM of the resonance calculated at $R = R_e$.

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*Summary of both a paper appearing in Phys. Rev. Letters 43, 1005 (1979) and part of a paper presented at the XIth ICPEAC, Kyoto, Japan, Aug. 29-Sept. 5, 1979 [J. L. Dehmer and Dan Dill, Electronic and Atomic Collisions, N. Oda and K. Takayanagi, Eds., North-Holland Publ. Co., Amsterdam, pp. 195-208 (1980)].

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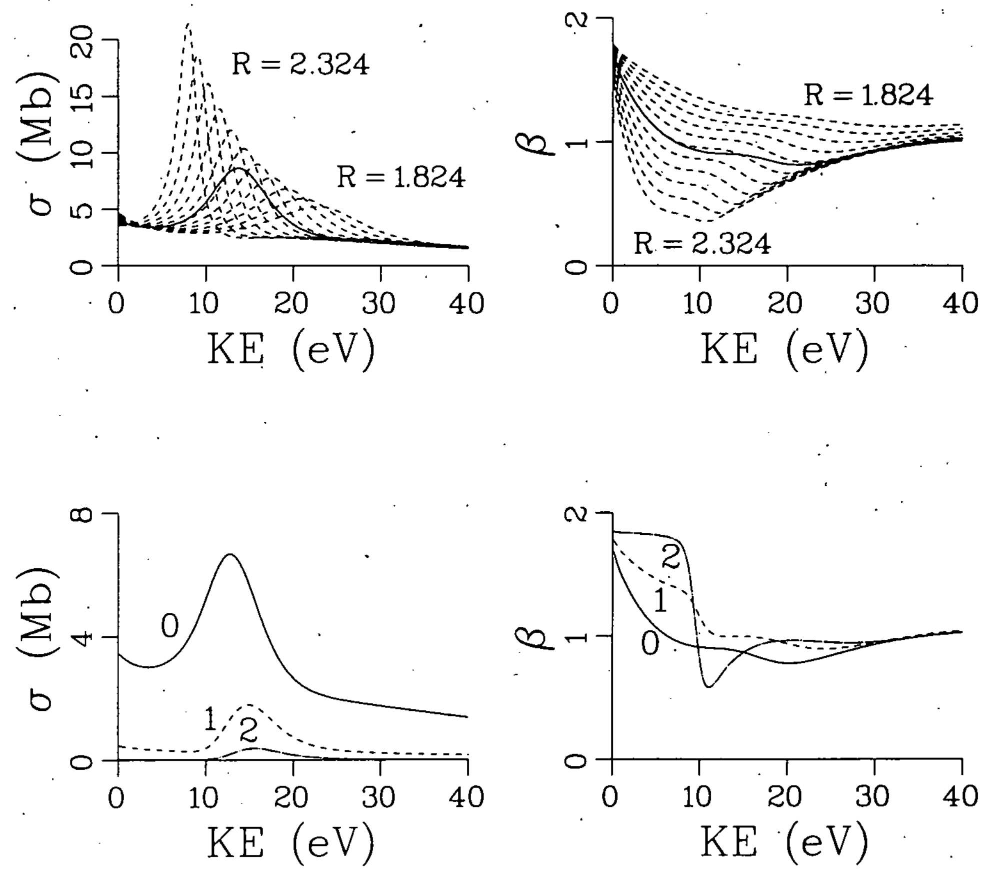

FIG. 1.--Cross sections σ and asymmetry parameters β for photoionization of the $3\sigma_g$ (v_i = 0) level of N_2. Top, fixed R (----) and R-averaged, vibrationally unresolved (——) results. Bottom, results for resolved final-state vibrational levels, v_f = 0-2.

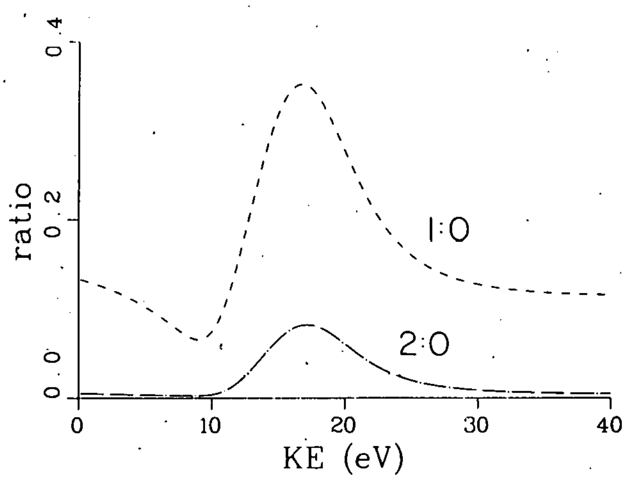

FIG. 2.--Vibrational state branching ratios $\sigma(v_f)/\sigma(v_f = 0)$ for photoionization of the $3\sigma_g$ level of N_2.

Effects of nuclear motion on individual vibrational levels are shown in the bottom half of Figure 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 vibrational channels to peak at higher energy than that for $v_f = 0$. The impact of these effects on branching ratios is clearly seen in Figure 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 the ratios are slightly above the FC factors[1] (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, finally approaching the FC factors again at high kinetic energy. Note the maximum enhancement over the FCF's is progressively more pronounced for higher v_f, i.e., 340% and 1300% for $v_f = 1,2$, respectively.

Equally dramatic are the effects on $\beta(v_f)$ shown in the lower right-hand portion of Figure 1. Especially at and below the resonance position, the β'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 behavior of the virationally unresolved electronic band will be governed by the β of the most intense component.

Reference

1. D. L. Albritton, private communication.