MEASUREMENT OF THE EFFECTS OF SHAPE RESONANCES ON VIBRATIONAL INTENSITY DISTRIBUTION IN MOLECULAR PHOTOIONIZATION*

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We report striking non-Franck-Condon vibrational intensity distributions associated with the shape resonance in the 5σ photoionization channel of CO. This example confirms the recent theoretical prediction[1] that shape resonances are very sensitive to internuclear separation, leading to different resonance energies and profiles, and non-Franck-Condon intensities in alternative

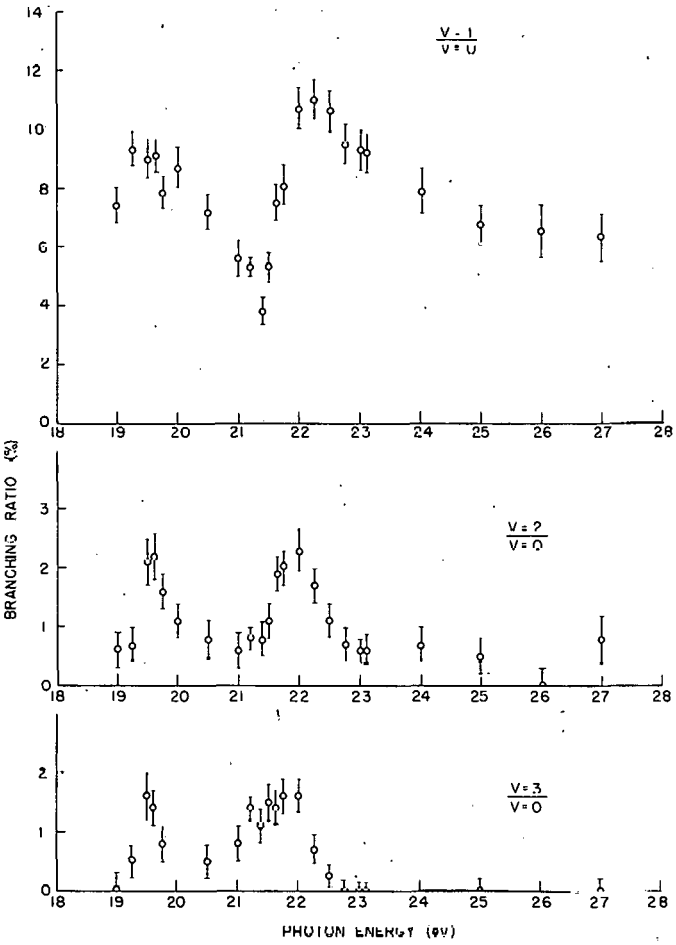

FIG. 1.--Photoionization branching ratios for the v = 0-3 levels of CO^+ $X^2\Sigma^+$.

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vibrational channels. Analogous effects are expected in connection with the widespread occurrence of shape resonances in both inner- and outer-shell molecular photoionization spectra.

The results are presented in Figure 1 as ratios of intensities of the $v = 1$, 2, and 3 levels of $CO^+ X^2\Sigma^+$ to that of the ground vibrational state of the ion, as functions of incident photon energy. Immediately apparent in Figure 1 is that, aside from the structures at $\sim$ 19.5 eV, attributable to unresolved autoionization structure, the gross pattern of spectral variation of these ratios strongly resembles that predicted[1] for the analogous states in N_2. Specifically, the $(v = 1)/(v = 0)$ curve shows an oscillation with a minimum at $\sim$ 22.3 eV and a peak-to-trough ratio of $\sim$ 3. The $(v = 2)/(v = 0)$ curves are less well defined but clearly show successively greater enhancement at $\sim$ 22 eV, relative to their weak background levels. Accordingly, we interpret the present results as the direct observation of the effects of shape resonances on vibrational intensity distributions.

Reference

1. J. L. Dehmer, D. Dill, and S. Wallace, Phys. Rev. Lett. 43, 1005 (1979).