WAVELENGTH AND VIBRATIONAL-STATE DEPENDENCE OF PHOTOELECTRON ANGULAR DISTRIBUTIONS. RESONANCE EFFECTS IN 5σ PHOTOIONIZATION OF CO*

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The dynamics of molecular photoionization have recently been shown[1] to vary rapidly with internuclear separation in the presence of a shape resonance. In a prototype calculation[1] on the $3\sigma_g$ photoionization channel of N_2, the σ_u resonance shifted by > 10 eV and exhibited large, asymmetric variations in intensity and width over a range in R spanning the ground vibrational state of N_2. This leads to a breakdown in the Franck-Condon (FC) separation and was predicted[1] to cause non-FC vibrational intensities and v-dependent photoelectron angular distributions. The effect of shape resonances on vibrational branching ratios has been confirmed experimentally in connection with the analogous f-wave-dominated σ resonances in the 5σ channel[2] of CO and the $3\sigma_g$ channel[3] of N_2. By contrast, the available data[4-9] on vibrationally-resolved photoelectron angular distributions in shape-resonant channels is too fragmentary to establish the pattern of the shape resonance effect. Here we report measurements of vibrationally-resolved photoelectron angular distributions for the 5σ channel in CO, performed in the range 16 eV ≦ hν ≦ 26 eV utilizing synchrotron radiation, in order to establish the gross pattern of variation of the asymmetry parameter β in the vicinity of the σ shape resonance at hν ∿ 24 eV.[10-15] As discussed below, unresolved autoionization structure, also capable of producing v-dependent β's is also observed and partially masks the expected shape-resonance effect. Although mainly a compilation in this particular study, detailed studies of resolved

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* Summary of a paper to be published in J. Chem. Phys.

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autoionization effects are of great importance and are being pursued separately.

The wavelength dependence of the β's for the first four vibrational levels of CO^{2} $X\,^2\Sigma^+$ is given in Figure 1. We note that the v = 0 curve is rather flat and agrees, within combined stated errors, with the vibrationally-unresolved data of Marr et al.[16] and the multiple-scattering calculations of Wallace et al.[17] and that a systematic tendency to be slightly lower than the vibrationally-unresolved data[16] reflects the small admixture of the higher vibrational levels which were resolved in this work. Also note the good agreement with the He I data of Hancock and Samson[7] for v = 0 and 1. In interpreting the gross patterns in the data, we follow the discussion of the vibrational branching ratios in Ref. 2 by tentatively defining two spectral regions with different dominant effects. Below ∿ 21 eV, we presume the main vibrational effects are caused by unresolved autoionization structure and threshold effects associated with the B $^2\Sigma^+$ state of CO^+ at 19.7 eV (although shape resonance effects are also likely to extend into this region). Above 21 eV, we assume[18] the structure is caused mainly by the shape resonance centered at ∿ 24 eV.[10-15] Focussing briefly on the "autoionization" region below ∿ 21 eV, we note that a broad dip occurs in β for each vibrational level, with a successively deeper minimum centered at ∿ 19 eV. Although this is similar to the structure in the "shape resonance" region discussed below, it is significantly different in that this gross structure comprises

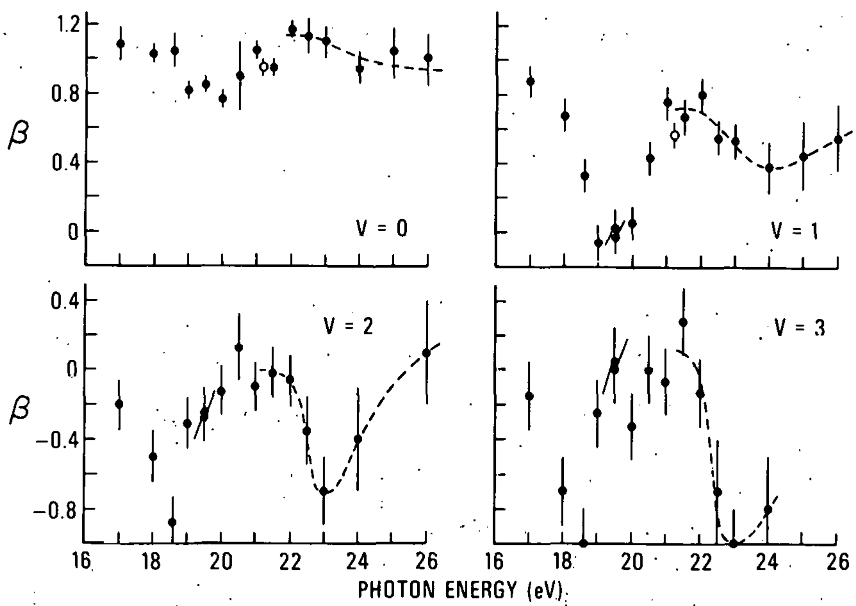

FIG. 1.--Photoelectron asymmetry parameters for the v = 0-3 vibrational levels of CO^+ $X^2\Sigma^+$ in the range 16 eV ≦ hν ≦ 26 eV. The open circles are data by Hancock and Samson[7] using He I resonance radiation. The dashed lines are hand drawn to illustrate the discussion in the text.

unresolved series of autoionizing structures. Separate studies on a much finer energy mesh are being pursued to study details of individual autoionizing structures. Above ∿ 21 eV, we believe the present eata are the first to map the pattern of variation of v-dependent β's directly reflecting the effects of a shape resonance. The following pattern emerges, as illustrated by the hand-drawn dashed lines in Figure 1: First, the v = 0 curve is relatively flat at β ∿ 1. The vibrationally unresolved data[16] (dominated by the v = 0 component) exhibit a broad, shallow dip at ∿ 28 to 30 eV, in agreement with theory.[17] Second, the v = 1 curve is substantially lower above 22 eV and exhibits a discernible minimum at ∿ 24 eV, the position of the shape resonance. Third, the v = 2 curve continues the pattern of a deeper dip (note the ordinate scale change on the lower part of Figure 1) centered at lower photon energy. Finally, the v = 3 curve, although of marginal statistical significatnce owing to the vanishingly small branching ratio, appears to indicate a deeper plunge. We emphasize that our interpretation of this pattern as a shape resonance effect is tentative, as we cannot definitely rule out influence by weak autoionization structure in this spectral range.[18] (As noted in Ref. 2, a number of autoionizing structures have been observed[18] throughout the 20 to 23 eV region; however, these are extremely weak, doubly-excited features and are assumed not to significantly interfere with the dominant one-electron character of the process discussed here.) However, the interpretation is plausible in view of related definitive work on vibrational branching ratios, particularly Refs. 1 and 3, and qualitative agreement of the present results with recent multiple-scattering model calculations[19] further supports this interpretation.

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