SPECTRAL VARIATION OF MOLECULAR PHOTOELECTRON ANGULAR DISTRIBUTIONS: VALENCE SHELLS OF N_2 AND CO *

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Angular distribution measurements probe the interference between alternative angular momentum components of the wave function of electrons ejected from a given subshell. Accurate description of these measurements requires a detailed knowledge of the relative phases of these components. These so-called phaseshifts measure the deviation of the molecular ion from a unit positive point charge. The calculation of these phaseshifts requires a realistic description of the interaction of the photoelectron with the molecular core, especially at short range where deviations from a pure Coulomb field are most pronounced. When the resulting forces affect alternative angular momenta differently, i.e., are anisotropic, then effects on the angular distribution will be most pronounced. While the main sources of anisotropic forces in atoms are many-electron interactions, anisotropic forces in molecules are considerable even at the one-electron level, because while atoms are spherical, molecules are not.

Photoelectron angular distributions have been calculated, with the multiple-scattering method[1,2] for electrons ejected from the outer shells $2\sigma_g$, $1\pi_u$, and $3\sigma_g$ of N_2, and 4σ, 1π, and 5σ of CO from threshold to 10 rydbergs electron kinetic energy. Results are given in Figure 1. Clear evidence of the σ f-wave ($\ell = 3$) shape resonance is seen in the $3\sigma_g$ spectrum of N_2 and in all three spectra of CO. Agreement with very recent wavelength-dependent measurements made at the Bonn synchrotron by Marr and Holmes[3] is generally good, but more detailed measurements and further theoretical work are needed to eliminate remaining discrepancies.

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*Summary of an article which appeared in J. Phys. B 12, L417 (1979).

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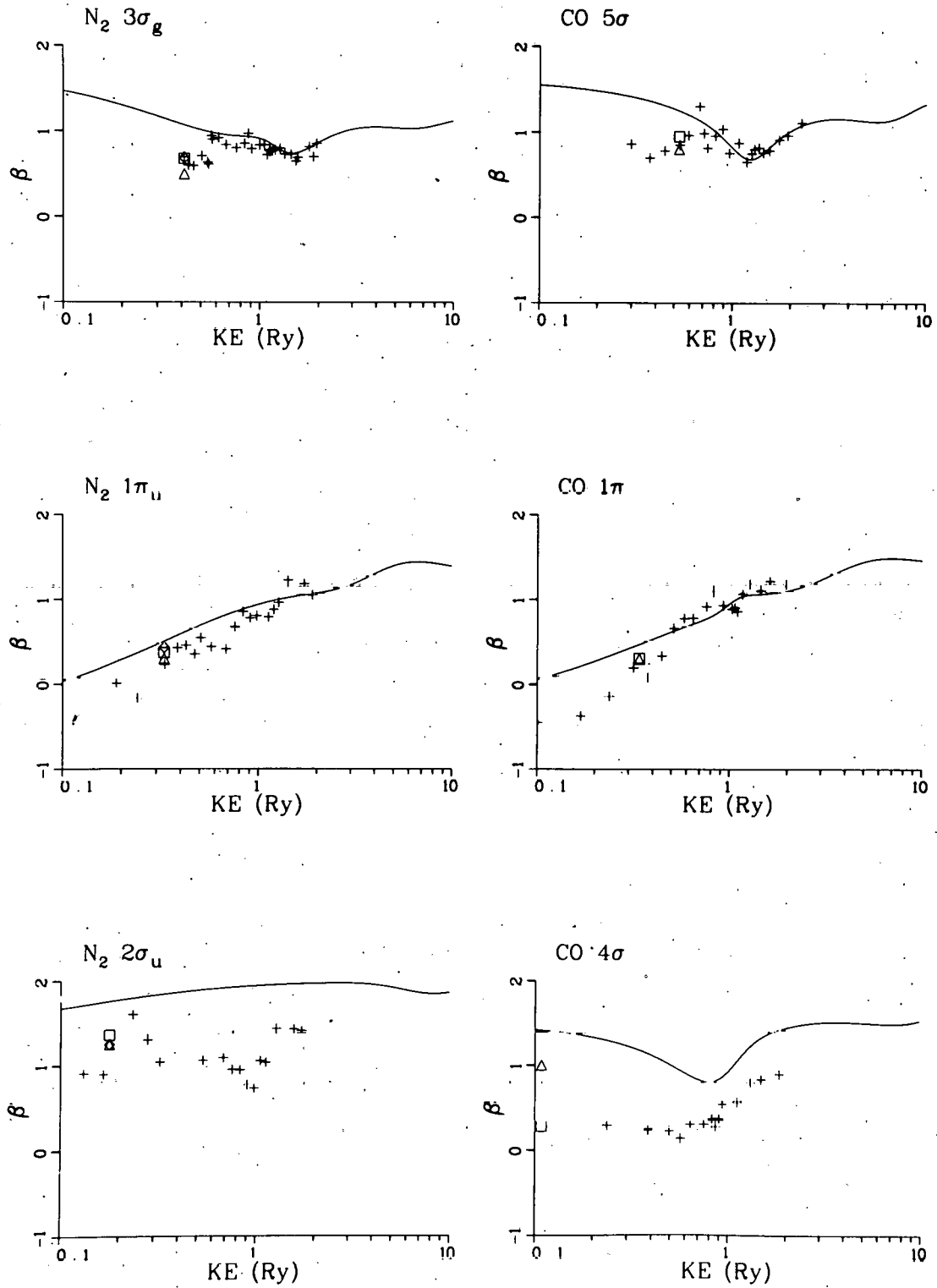

FIG. 1.--The photoelectron asymmetry parameter β as a function of electron kinetic energy for photoionization of the levels $2\sigma_g$, $1\pi_u$, and $3\sigma_g$ of N_2, and 4σ, 1π, and 5σ of CO; ——, calculation. Experimental values: +, Marr et al.;[3] □, Hancock and Sampson;[4] ◇, Morgenstern et al.[5] and Niehaus and Ruf;[6] △, Carlson and co-workers.[7]

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