

40

EFFECTS OF RESONANCES IN MOLECULAR PHOTOIONIZATION MEASURED WITH TRIPLY DIFFERENTIAL PHOTOELECTRON SPECTROSCOPY\*

A.C. Parr,<sup>1</sup> D.M.P. Holland,<sup>2</sup> D.L. Ederer,<sup>1</sup> and J.L. Dehmer<sup>3</sup>

<sup>1</sup>Synchrotron Ultraviolet Radiation Facility, NBS, Washington, DC 20234

<sup>2</sup>University of Maryland, College Park, MD 20742

<sup>3</sup>Argonne National Laboratory, Argonne, IL 60439

ABSTRACT

A variable wavelength angle resolving photoelectron spectrometer has been used to study the effects of autoionization and shape resonances upon molecular photoionization. Such resonance phenomena produce non-Franck-Condon effects in the vibrational intensity distributions and significant variations in the asymmetry parameters. Results are presented for  $C_2N_2$  and  $CO_2$ . Constant Photoelectron Energy (CPE) spectroscopy has been performed on  $C_2H_2$  and spectra are shown at four kinetic energies. The information concerning energy absorption in molecules gained from these studies is discussed.

INTRODUCTION

Triply differential photoelectron spectroscopy has been used to study the effects of autoionization and shape resonance phenomena on the photoelectron branching ratios and asymmetry parameters in small polyatomic molecules. Results are reported for  $C_2N_2$  and  $CO_2$ , and, in addition, a CPE study on  $C_2H_2$  is presented. Both autoionization and shape resonances produce non-Franck-Condon effects in the vibrational intensity distributions as well as vibrational state dependent asymmetry parameters. Autoionization is caused by the creation of an excited state of the neutral system, which lies above the ionization onset and couples to the various available ionization continua of the ion and free electron. This indirect ionization via an intermediate state leads to non-Franck-Condon variations in the overall vibrational intensities and associated photoelectron angular distributions. In shape resonance phenomena (1) the effective potential experienced by an electron becomes positive for some range of electron coordinates. This can lead to trapping of a photoexcited electron in a quasi-discrete state by the centrifugal barrier and again lead to a breakdown of the Franck-Condon principle.

\*This work was supported in part by the Office of Naval Research, the U.S. Department of Energy and NATO Grant No. 1939.

## EXPERIMENTAL

The experiments were performed using a 50 mm mean radius hemispherical electron analyzer (2) coupled to a high aperture 2m normal incidence monochromator (3) connected to the NBS-SURF II storage ring (4). With a photon bandwidth of  $0.4\text{\AA}$ , the combined resolution of the electron analyzer and monochromator was approximately 110 meV. For elliptically polarized radiation the differential cross section in the dipole approximation, assuming randomly oriented target molecules and electron analysis in a plane perpendicular to the photon propagation direction, may be written in the form (5)

$$\frac{d\sigma}{d\Omega} = \frac{\sigma_{\text{total}}}{4\pi} \left[ 1 + \frac{\beta}{4} (3P \cos 2\theta + 1) \right]$$

where  $\beta$  is the photoelectron asymmetry parameter,  $\theta$  is the photoelectron ejection angle relative to the major polarization axis, and  $P = (I_{||} - I_{\perp}) / (I_{||} + I_{\perp})$ , the polarization of the incoming light. The data analysis was carried out by decomposing the spectra into vibrational components by means of a nonlinear least squares fit to Gaussian line shapes after inclusion of the appropriate analyzer functions (6).

## RESULTS

The vibrationally resolved asymmetry parameters for the ground ionic state  $X^2\Pi_g$  of cyanogen are displayed in Figure 1. This band shows a progression in  $\nu_1$ , the  $C\equiv N$  symmetrical stretching mode. The cyanogen  $C\equiv N$  bond may be expected to possess some of the characteristics of the nitrogen  $N\equiv N$  bond and therefore, to some extent, exhibit some of the shape resonance effects which have already been predicted (7) and observed (8) in nitrogen. Below 20eV, the  $\beta$  parameters vary strongly with photon energy and show a vibrational state dependence. The total photoionization spectrum (9) is dominated by autoionizing resonance structure from close to threshold (13.36 eV) to almost 15.5 eV and, in addition, an intense broad peak is observed extending from approximately 15.5 eV to 20.5 eV, with a maximum around 16.9 eV. It is apparent that the dip observed in all three vibrationally resolved asymmetry parameters coincides with this intense peak. Hence, as a tentative conclusion, shape resonance phenomena may be responsible for the dips in the asymmetry parameters and for the intense peak in the total photoionization cross section.

The total photoionization spectrum of carbon dioxide (10) shows a variety of structure characteristic of autoionization in the first 8 eV above the ionization threshold. The wavelength region encompassing three sharp autoionizing lines at around  $752.2\text{\AA}$  (16.482eV) has been investigated (11) in order to determine the effect of autoionization on the photoelectron branching ratios and asymmetry parameters. In the wavelength region around the  $752.2\text{\AA}$  autoionizing

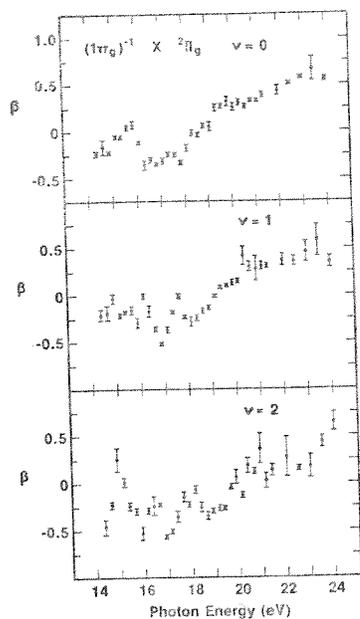


Fig. 1 The spectral variation in the vibrationally resolved asymmetry parameters for the  $v=0, 1$  and  $2$  levels of  $C_2N_2^+ X^2\Pi_g$ .

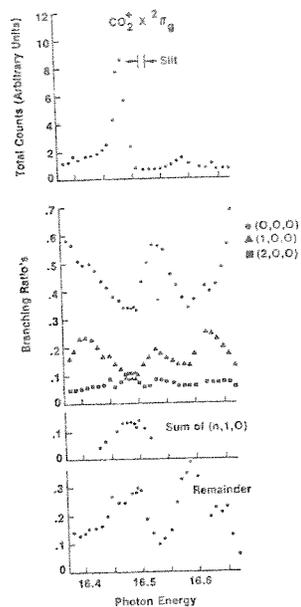
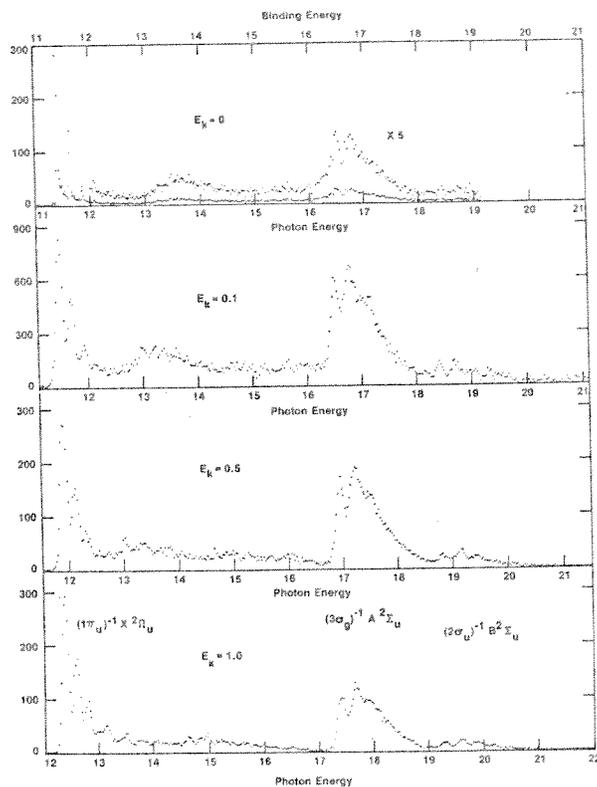


Fig. 2 The  $CO_2^+ X^2\Pi_g$  vibrational branching ratios and total electron count plotted as a function of photon energy.

resonance it was found that the simple  $(n,0,0)$  progression did not adequately describe the photoelectron spectrum. The approach that seemed to yield the best fit was allowing for single excitation of the  $\nu_2$  mode, with excitation of the  $\nu_1$  mode with  $n=1, 2$  and  $3$ . The photoelectron branching ratios in this photon energy range are shown in Figure 2. Near the resonances, the  $(0,0,0)$  and the  $(1,0,0)$  intensities drop considerably from the background Franck-Condon values. The intensity of the substructure attributed to the  $\nu_2=1$ , rises in the region around the  $752.2\text{\AA}$  resonance and makes insignificant contributions elsewhere. This suggests that this member of the Henning series contains distortions from linearity which allow for the population of bent configurations of the ionic ground state.

In CPE spectroscopy (12) the intensity of photoelectrons with a specific kinetic energy,  $E_k$ , is measured as a function of incident photon energy. Such measurements can be performed using small photon energy increments and can distinguish between direct and indirect, e.g., autoionization processes. Figure 3 shows CPE spectra of acetylene at  $E_k=0, 0.1, 0.5$  and  $1.0$  eV. Photoelectron peaks corresponding to the X, A and B ionic states appear at constant binding energies. However, two additional features can be observed, between  $13$  and  $14$  eV and between  $14.5$  and  $15.5$  eV, which remain stationary on the photon energy

Fig. 3 Constant Photoelectron Energy spectra of  $C_2H_2$  at four electron kinetic energies;  $E_k=0, 0.1, 0.5$  and  $1.0$  eV.



scale as the kinetic energy is varied. The energies at which these two features appear coincide with two broad intense autoionizing resonances in the total photoionization spectrum.

#### REFERENCES

- 1 J.L. Dehmer and D. Dill, in T. Rescigno, V. McKoy and B. Schneider (Eds.), *Electron-Molecule and Photon-Molecule Collisions*, Plenum Press, New York, 1979, pp. 225-265.
- 2 A.C. Parr, R. Stockbauer, B.E. Cole, D.L. Ederer, J.L. Dehmer and J.B. West, *Nucl. Inst. Meth.*, 172 (1980) 357-361.
- 3 D.L. Ederer, B.E. Cole and J.B. West, *Nucl. Inst. Meth.*, 172(1980) 185-190.
- 4 R.P. Madden, *Nucl. Inst. Meth.*, 172 (1980) 1-8.
- 5 J.A.R. Samson and A.F. Starace, *J. Phys.*, B8 (1975) 1806-1809.
- 6 D.M.P. Holland, A.C. Parr, D.L. Ederer, J.L. Dehmer and J.B. West, *Nucl. Inst. Meth.* 195 (1982) 331-337.
- 7 J.L. Dehmer, D. Dill and S. Wallace, *Phys. Rev. Lett.*, 43 (1979) 1005-1008.
- 8 J.B. West, A.C. Parr, B.E. Cole, D.L. Ederer, R. Stockbauer and J.L. Dehmer, *J. Phys.* B13 (1980) L105-L108.
- 9 S.K. Liston and V.H. Dibeler, *J. Chem. Phys.* 47 (1967) 4548-4555.
- 10 K.E. McCulloh, *J. Chem. Phys.* 59 (1973) 4250-4259.
- 11 A.C. Parr, D.L. Ederer, J.L. Dehmer and D.M.P. Holland, *J. Chem. Phys.* accepted.
- 12 D.M.P. Holland, J.B. West, A.C. Parr, D.L. Ederer, R. Stockbauer, R.D. Buff and J.L. Dehmer, *J. Chem. Phys.*, submitted.