PROTON ELECTRON SPECTROSCOPY OF MOLECULAR GASES

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A thesis
presented for the degree of
Doctor of Philosophy
in the
University of Adelaide
April, 1969.
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SUMMARY

The photoelectron energy spectra observed for different molecular gases at wavelengths from 584Å to the threshold energy of the electronic ground states of different molecular ions have been described in this thesis. The measurement of photoelectron spectra has been made at 5Å intervals. The branching ratios and hence the partial photoionization cross-sections for different competing processes have also been computed for these gases, viz. carbon dioxide, carbon monoxide, nitric oxide, nitrous oxide and ammonia.

The photoelectron spectrometer used for recording the energy spectra of the photoelectrons was of the retarding potential type, consisting of two concentric spherical grids and a plane grid; an earthed grid, an analysing grid to which a retarding potential of a step-function type was applied, and an anode. An incident photon beam produced by a helium capillary spark discharge lamp was dispersed by a one-metre near normal incidence monochromator with a slit width corresponding to the resolution of 0.6Å. The photoelectrons were produced in a small target area at the centre of the spherical grid system and, after being energetically analysed, were detected by a channel electron multiplier. The
best resolution obtained by the spectrometer was y.

The photoelectron spectra for these gases were obtained at different incident wavelengths and the relative areas associated with each peak in the spectra were measured. This information was combined with total photoionization cross-sections to produce partial cross-sections.

In the spectra of carbon dioxide, the four bands corresponding to $^2\Pi_u$, $^2\Pi_g$, $^2\Sigma_u^+$, $^2\Sigma_g^+$, electronic states of the ion wherever energetically possible, were clearly resolved. In carbon monoxide, nitric oxide and nitrous oxide, a low energy anomalous peak which did not vary in position with incident photon wavelength was observed in addition to peaks corresponding to direct ionization to the different excited states of the respective ions. This anomalous peak in carbon monoxide has been explained on the basis of Franck-Condon principle but in nitric oxide and nitrous oxide, the explanation of fluorescent autoionization is put forward. The photoelectron spectra of ammonia showed peaks corresponding to ground states of $\text{NH}_3^+$, $\text{NH}_2^+$ and $\text{NH}^+$ and also some other unknown peaks which may correspond to the other excited states of $\text{NH}_3^+$. In addition, a low energy anomalous peak was also observed which was explained on the basis of fluorescent
autoionization.

Photoelectron spectra have also been measured with a beam resolution of 1.6Å at wavelengths corresponding to several autoionized resonance states of O₂ in the region above 775Å, and also at neighbouring off-resonance wavelengths. The off-resonance spectra showed a single broad maximum in the strength of the O₂⁺ vibrational structure. However, the resonance spectra had additional features which are characteristic of the vibrational quantum number of the autoionized resonance. The form of these spectra were reproduced theoretically by the calculated Franck-Condon factors for the autoionizing transitions, using equilibrium internuclear distance for the autoionized state as an adjustable parameter.