PHOTOIONIZATION OF DIATOMIC MOLECULES

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SUMMARY

This thesis describes measurements of partial photoionization cross-sections for processes leading to the formation of particular ionic states. The partial cross-sections for nitric oxide and carbon monoxide as a function of the incident wavelength are presented. The effects of autoionization states of the neutral molecule on the photoelectron spectra of the gases molecular oxygen, molecular nitrogen, carbon monoxide and nitric oxide have been investigated and the results are discussed along with theoretical considerations of the mechanisms involved.

The partial photoionization cross-sections have been measured by recording the photoelectron energy spectra at 5Å intervals from 600Å to the first ionization potential with an incident beam resolution of 8Å. The photoelectron spectrometer used the retarding potential technique and was of quasi-spherical construction. It consisted of two concentric hemi-spherical grids about a "point" source of photoelectrons, a plane collecting grid and a channel-electron-multiplier as a detector. The best resolution obtainable from the spectrometer was 0.1eV (full width at half maximum) at an energy of 5eV. The light source consisted of a one-metre near normal incidence monochromator equipped with a helium capillary discharge lamp. The

relative area associated with each electronic state in a spectrum was measured and this was combined with the total photoionization cross-section data for the gas to produce the partial photoionization cross-sections for the various states at that particular wavelength.

The partial cross-sections of carbon monoxide show the thresholds for the $B^2\Sigma^+$ and $A^2\Pi$ states of CO^+, the $A^2\Pi$ continuum having a maximum just above threshold. In the wavelength region 580Å to 600Å structure was observed in the spectra which has been attributed to dissociation.

The thresholds of the $A^1\Pi$ and $a^3\Sigma^+$ states of NO^+ are evident in the partial photoionization cross-section curves for nitric oxide, and photoelectron groups corresponding to transitions to the $X^1\Sigma^+$ and $b^3\Pi$ states were resolved in spectra where they were energetically possible. Unresolved states were included in the analysis as combinations of states. The $b^3\Pi$ and $a^3\Sigma^+$ states contributed almost 50% of the cross-section between 600Å and 700Å, this value rising to a maximum of 70% at 740Å.

Photoelectron spectra have also been recorded for the gases molecular oxygen, molecular nitrogen, carbon monoxide and nitric oxide using an incident beam resolution of 1.6Å. These spectra have been recorded at wavelengths corresponding to autoionization resonances in the photoionization cross-section curve of each gas, and also at neighbouring off-resonance wavelengths. Marked differences

in the intensity distribution of the vibrational states have been observed between the on and off-resonance spectra and between different on-resonance spectra. It has been possible to determine, at certain wavelengths, the contribution by the different vibrational states to the total photoionization cross-section. In some cases it has been possible to compare the results with theoretical calculations of Franck-Condon factors and thereby determine the internuclear equilibrium distance of some of the autoionization states of the molecule.