HIGHER LYING RYDBERG STATES OF Rg·NO VAN DER WAALS COMPLEXES (Rg=Ar, Kr) STUDIED USING REMPI SPECTROSCOPY

J. D. BARR, J. M. DYKE and T. G. WRIGHT, *Chemistry Department, University of Southampton, Highfield, Southampton, U.K. SO17 1BJ*.

The results of spectroscopic studies on the Ar·NO and Kr·NO van der Waals complexes are presented. The aim of these experiments was to obtain information upon which a more quantitative understanding of the intermolecular interactions within the complexes could be based. A (2+1) REMPI scheme was employed to investigate the $\widetilde{E}^2\Sigma^+$ electronic state which correlates with the $^1\Sigma^+(4s\sigma)^1$ configuration of the NO molecule. The rotational structure observed in the REMPI spectra is analyzed using a rigid rotor Hamiltonian, where the orbital and spin angular momenta of the NO moiety are projected onto the inertial axes of the complex. For both complexes significant deviation from a T-shaped structure is found, although it was not possible to determine the absolute position of the rare gas atom within experimental uncertainty. The more pronounced deviation from T-shaped geometry of the Kr·NO complex is attributed to the greater contribution from dipole/induced-dipole intermolecular forces in the case of larger, more polarizable Kr atom. The red-shift of the T_0 value of the $\widetilde{E}^2\Sigma^+ \leftarrow \widetilde{X}^2\Pi$ from the corresponding transition in uncomplexed NO allowed the dissociation energies (D_0) of the $\widetilde{E}^2\Sigma^+$ states of Ar·NO and Kr·NO to be derived as 582 and 803 cm^{-1} respectively. These larger values in comparison to those determined for the ground and lower Rydberg states reflect the dominance of ionic interactions when the Rydberg electron resides, on average, beyond the rare gas atom.