

ROTATIONALLY RESOLVED PHOTOELECTRON SPECTROSCOPY STUDY OF THE FIRST ELECTRONIC STATES OF Ar_2^+

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The $I(1/2u)$, $I(3/2g)$, $I(1/2g)$, $I(3/2u)$ and $\Pi(1/2u)$ states of Ar_2^+ have been investigated in the region between 124650 cm^{-1} and 128150 cm^{-1} by pulsed-field-ionization zero-kinetic-energy (PFI-ZEKE) photoelectron spectroscopy following $(1 + 1')$ resonance-enhanced two-photon excitation via the 0_u^+ Rydberg state located below the $\text{Ar}^* ([3p]^5 4s' [1/2]_1) + \text{Ar} (^1\text{S}_0)$ dissociation limit of Ar_2 . By selecting single rotational levels of the intermediate state, the rotational structure of four of the six lowest ionic states of Ar_2^+ could be observed and unambiguous assignments of electronic symmetry of the ionic states could be made on the basis of photoionization selection rules. The rotational structure also provided information on the equilibrium internuclear distances R_e^+ for the $I(1/2u)$, $I(3/2g)$, $I(1/2g)$ and $\Pi(1/2u)$ states ($R_e^+(I(1/2u)) = (2.393 \pm 0.043) \text{ \AA}$, $R_e^+(I(3/2g)) = (2.993 \pm 0.005) \text{ \AA}$, $R_e^+(I(1/2g)) = (3.151 \pm 0.002) \text{ \AA}$ and $R_e^+(\Pi(1/2u)) = (3.851 \pm 0.012) \text{ \AA}$). The adiabatic ionization potentials are determined to be $\text{IP}(I(3/2g)) = (125685.3 \pm 0.7) \text{ cm}^{-1}$, $\text{IP}(I(1/2g)) = (126884.1 \pm 0.7) \text{ cm}^{-1}$, $\text{IP}(I(3/2u)) = (127044.6 \pm 1.5) \text{ cm}^{-1}$ and $\text{IP}(\Pi(1/2u)) = (128000.8 \pm 0.7) \text{ cm}^{-1}$, from which dissociation energies are obtained as $D_0^+(I(3/2g)) = (1509.3 \pm 1.2) \text{ cm}^{-1}$, $D_0^+(I(1/2g)) = (310.5 \pm 1.2) \text{ cm}^{-1}$, $D_0^+(I(3/2u)) = (150.0 \pm 1.8) \text{ cm}^{-1}$ and $D_0^+(\Pi(1/2u)) = (625.4 \pm 1.2) \text{ cm}^{-1}$. The interaction between the $I(1/2g)$ and $I(3/2g)$ states could also be observed and analyzed.