

SPECTROSCOPIC CHARACTERIZATION OF A THERMODYNAMICALLY STABLE DOUBLY CHARGED DI-ATOMIC MOLECULE: MgAr^{2+}

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Although numerous doubly positively charged diatomic molecules (diatomic dications) are known from investigations using mass spectrometry and *ab-initio* quantum chemistry, only three of them, NO^{2+} , N_2^{2+} and DCI^{2+} , have been studied using rotationally resolved optical spectroscopy^a and only about a dozen by vibrationally resolved double-ionization methods^b. So far, no thermodynamically stable diatomic dication has been characterized spectroscopically, primarily because of experimental difficulties associated with their synthesis in sufficient densities in the gas phase. Indeed, such molecules typically involve, as constituents, rare-gas, halogen, or chalcogen, and metal atoms. We report on a new approach to study molecular dications based on high-resolution PFI-ZEKE photoelectron spectroscopy of the singly charged parent molecular cation and present the first spectroscopic characterization of a thermodynamically stable diatomic dication, MgAr^{2+} . We have observed the partially resolved rotational structure of several vibrational levels of the ground electronic state of MgAr^{2+} using a resonant (1+1'+1'') three-photon excitation scheme. From the analysis of the photoelectron spectra of $^{24}\text{MgAr}^+$ and $^{26}\text{MgAr}^+$ we have determined the potential-energy function of the electronic ground state of MgAr^{2+} , its dissociation (binding) energy ($D_0 = 10690(3) \text{ cm}^{-1}$), and its harmonic ($\omega_e(^{24}\text{MgAr}^{2+}) = 327.02(11) \text{ cm}^{-1}$) and anharmonic ($\omega_e x_e(^{24}\text{MgAr}^{2+}) = 2.477(15) \text{ cm}^{-1}$) vibrational constants. The analysis enables us to explain quantitatively how the strong bond arises in this dication despite the fact that Ar and Mg^{2+} both have a full-shell rare-gas electronic configuration.

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^bJ. H. D. Eland and R. Feifel, *Double Photoionisation Spectra of Molecules* (Oxford University Press, 2018)