

High-resolution spectroscopy of the ground and low-lying excited states of MgNe^+ and MgXe^+

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Diatomic molecules RgM consisting of a rare-gas atom Rg and an alkaline-earth-metal atom M and their singly and doubly-charged cations RgM^+ and RgM^{2+} have unusual chemical properties related to the low first and second ionization energies of M and the high ionization energy of Rg . The second ionization energy of Mg is lower than the first ionization energy of Ar . Consequently, MgAr^{2+} is thermodynamically stable and Rydberg series of MgAr^+ can be observed that converge on the $X^{2+} \ ^1\Sigma^+$ ground state of MgAr^{2+} [1]. Similar behavior is expected in MgNe because of the even higher first ionization energy of Ne . In MgKr and MgXe , however, the second ionization energy of Mg is higher than the first ionization energy of the rare gas, and MgKr^{2+} and MgXe^{2+} are predicted to be metastable. In this contribution, we focus on the two extreme cases MgNe and MgXe . We present the results of spectroscopic investigations of MgNe^+ and MgXe^+ in their ground and low-lying electronically excited states that extend earlier studies of these cations [2,3].

PFI-ZEKE photoelectron spectra of the $X \ ^2\Sigma^+$ ground state were recorded from the $a \ ^3\Pi_0$ metastable state. Spectra of the lowest vibrational levels of MgNe^+ and MgXe^+ enabled the determination of the adiabatic ionization energy of metastable MgNe and MgXe . With a resonant two-photon ($1 + 1'$) excitation scheme, the PFI-ZEKE photoelectron spectrum of the $X \ ^2\Sigma^+$ state starting from the $X \ ^1\Sigma^+$ ground state of MgNe was recorded as well, giving access to the adiabatic ionization energy of the neutral ground state and the lowest singlet-triplet interval in the neutral molecule. Using isolated-core multiphoton Rydberg dissociation spectroscopy [4], transitions to electronically excited states of MgNe^+ and MgXe^+ were observed that are associated with the $\text{Rg} + \text{Mg}^+ (3p)$ dissociation limit. These states are the lowest members of Rydberg series converging on the ground state of MgNe^{2+} and MgXe^{2+} . These studies represent the first steps towards studying the doubly charged cations MgNe^{2+} and MgXe^{2+} .

[1] D. Wehrli, M. Génévriez, and F. Merkt, *Phys. Chem. Chem. Phys.*, **2021**, 23, 10978.

[2] J. E. Reddic and M. A. Duncan, *J. Chem. Phys.*, **1999**, 110, 9948.

[3] J. S. Pilgrim, C. S. Yeh, K. R. Berry, and M. A. Duncan, *J. Chem. Phys.*, **1994**, 100, 7945.

[4] M. Génévriez, D. Wehrli, and F. Merkt, *Mol. Phys.*, **2019**, 118, e1703051.