

# DOUBLE-RESONANCE SPECTROSCOPY WITH A CONTINUUM: APPLICATION TO THE $\text{Mg}(3d\delta)\text{Ar}^+ {}^2\Delta$ STATE OF $\text{MgAr}^+$

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Whereas the electronic ground states of a large number of small molecular cations have been spectroscopically characterized, much less is known concerning electronically excited states, in particular because of the low densities in which molecular ions can be formed and because of the high excitation energies required. Electronically excited states of molecular ions are commonly studied using resonance-enhanced multiphoton dissociation (REMPD) [1] or isolated-core multiphoton Rydberg dissociation (ICMRD) spectroscopy [2]. These techniques rely on the fact that the excited molecular ion either predissociates rapidly or can be efficiently excited to a dissociative state by further photoabsorption. The  $\text{Mg}(3d\delta)\text{Ar}^+ {}^2\Delta$  state of  $\text{MgAr}^+$  is an example of an electronic state that does not fulfill these conditions and cannot be studied with conventional REMPD or ICMRD. We will report on the experimental study of this state using a double-resonance spectroscopic technique we have developed. With this technique,  $\text{MgAr}^+$  molecules were prepared in their electronic ground state and then coupled, *via* an intermediate state, to *both* the  $\text{Mg}(3d\delta)\text{Ar}^+ {}^2\Delta$  state and a predissociation continuum. In contrast to double-resonance spectroscopy involving only bound states, the presence of a predissociation continuum leads to a rich variety of spectral lineshapes, which exhibit asymmetric profiles reminiscent of Fano lineshapes. We carried out detailed simulations of these lineshapes using a quantum-optics-based effective Hamiltonian and solving the time-dependent Schrödinger equation. Agreement with experimental spectra is excellent and shows that the lineshapes are the result of quantum interferences between the different photoexcitation pathways leading to dissociation. We will discuss how the lineshapes can be controlled with external parameters such as laser pulse energies and wavenumbers in order, *e.g.*, to facilitate spectroscopic analysis. The analysis of the rovibrational structure of the  $\text{Mg}(3d\delta)\text{Ar}^+ {}^2\Delta$  electronic state will be presented, with particular emphasis on the anomalous behavior of the splitting between its two spin-orbit components.

[1] P.O. Danis, T. Wyttenbach and J.P. Maier, *J. Chem. Phys.* **88**, 3451–3455 (1988)

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