

Quantum Control for Rydberg State Spectroscopy

Borrowing from techniques used for the quantum control of chemical reactions, researchers have developed a method to study the Rydberg states of molecular ions that are relevant to astrophysical plasma.

By **Stephen D. Hogan**

Rydberg atoms and molecules have one of their electrons in a state with a high principal quantum number. The “classical” orbits of these electrons extend far away from the cores of the atoms or molecules—a feature that makes these systems extremely sensitive to their environment. The Rydberg states of atoms and neutral molecules have been extensively studied, but much less is known about the Rydberg

states of molecular ions. These states are relevant, for example, to the dynamics of astrophysical plasma, because they affect reactions triggered by the collisions of ions in a plasma with other particles. Until now, only a handful of Rydberg states of molecular ions have been characterized, using spectroscopic techniques that rely on their dissociation. But many interesting Rydberg states do not dissociate. Now, Matthieu Génévriez and colleagues at the Swiss Federal Institute of Technology (ETH) in Zurich have overcome this limitation by introducing a new method for characterizing this previously inaccessible category of Rydberg states [1]. The method, derived from techniques used for the quantum control of chemical reactions, allowed the team to perform a spectroscopic characterization of the Rydberg states of the magnesium argide ion MgAr^+ (Fig. 1).

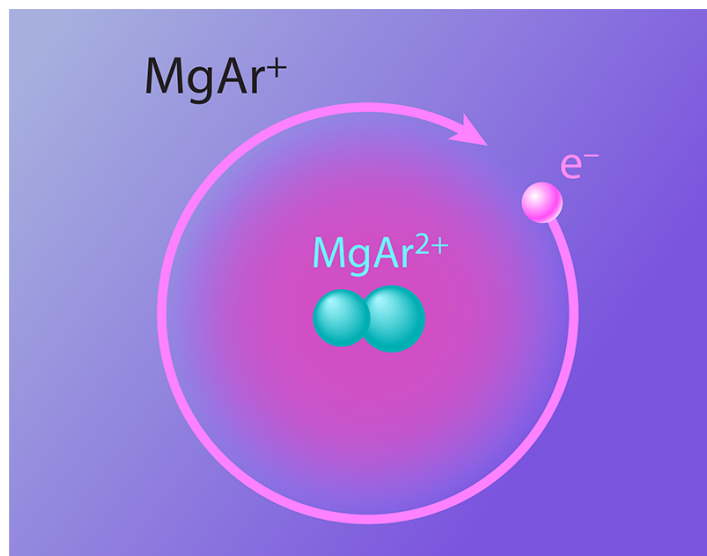


Figure 1: Génévriez and colleagues have introduced a new method for characterizing previously inaccessible Rydberg states of molecular ions, such as MgAr^+ . The molecular ion can be regarded as an ionic, doubly charged core (MgAr^{2+}) with an excited Rydberg electron occupying a distant orbit.

Credit: APS/Carin Cain

The Rydberg states of atoms and molecules bear many similarities to the states of hydrogen atoms because electrons in far-away orbits experience an effective point-like nuclear charge equal to that of a proton. Rydberg states form discrete, infinite series that converge to each quantum state of the ionic core of the atoms or molecules. Such states play important roles in many physical processes, including recombination of electrons and ions in plasmas and the production of antihydrogen in particle accelerator facilities. The large electron orbits also result in extreme sensitivity to external fields, which makes these systems interesting for sensing and quantum computing applications—Rydberg states of Ca^+ or Sr^+ ions, for instance, are promising qubit candidates [2, 3]. The Rydberg states of molecules are relevant to the precise determination, through photoelectron spectroscopy, of molecular ionization and dissociation energies, and to the study of ion-molecule reactions at low temperatures [4].

The Rydberg states of molecular ions play a particularly important role in astrophysical plasmas because they affect the outcome of interactions of ions with atoms and molecules in the plasma. When ions and other neutral particles collide, transiently populated Rydberg states influence scattering probabilities and relaxation pathways and may enhance or impede particular chemical reactions. Studying the energy-level structure and dynamics of Rydberg states in molecular ions is, however, extremely challenging and has only been achieved for a handful of states.

The first spectroscopic studies of such states were performed in 2020 on MgAr^+ [5]. In these experiments, a laser excited electrons into Rydberg states that decayed by dissociation: Once the electrons reached those states, MgAr^+ quickly broke into two fragments—a ground-state neutral Ar atom and a Mg atom in a high Rydberg state. The energy-level structure of the Rydberg states could then be determined by measuring how the Ar^+ yield changed as the laser frequency was scanned. This approach, however, can only be used to probe the ion's Rydberg states for which excitation triggers dissociation. In general, the complete characterization of Rydberg states—of MgAr^+ and of other molecular ions—requires the study of energy levels that don't rapidly dissociate.

The multiphoton excitation and dissociation scheme used by Génévriez and his co-workers allowed them to probe Rydberg states of the MgAr^+ ion for which dissociation is not the primary decay mechanism [1]. Their approach builds on recent advances in the field of quantum control of chemical reactions. Schemes for the quantum control of chemical reactions use sequences of short laser pulses to steer a molecular system toward desired quantum states of its nuclei and electrons. With such techniques, researchers have been able to control the outcome of some chemical reactions and to purify mixtures of enantiomers of chiral molecules [6].

Here, Génévriez and his co-workers used quantum-control techniques to manipulate the quantum interference between molecular photoexcitation pathways that connect bound molecular states and the dissociation continuum. They found that by using appropriate combinations of transitions, these interfering pathways, which passed through the dissociation continuum of the MgAr^+ ion, allowed the observation of nondissociative Rydberg states (Fig. 2). By monitoring the

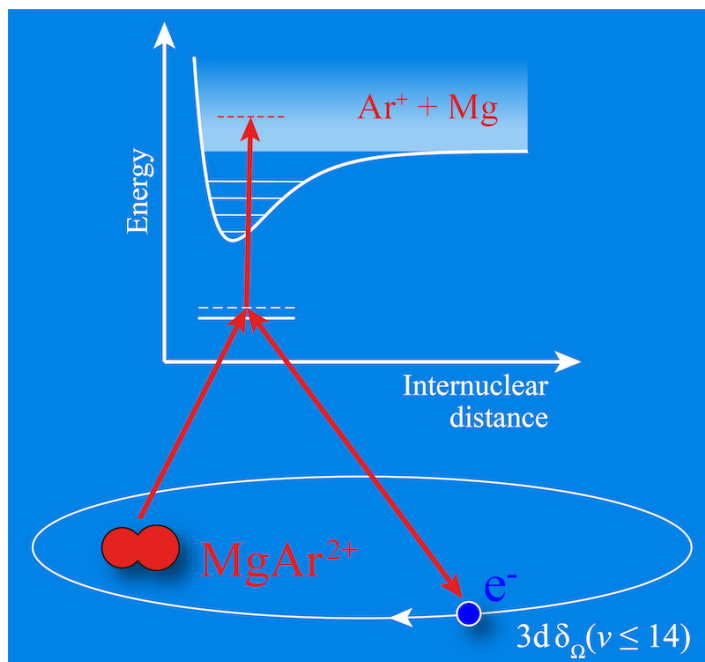


Figure 2: The quantum-control scheme used by Génévriez and colleagues involves the interference of multiple excitation pathways that connect bound molecular states of MgAr^+ , the dissociation continuum, and nondissociative Rydberg states. This interference allowed the team to relate the measured dissociation yield to the energy of otherwise unreachable Rydberg states ($3d\delta_\Omega$ with 14 or fewer quanta of vibrational excitation).

Credit: APS/Stephen Hogan

dissociation fragments, the team reconstructed the energy-level structure of the Rydberg states that other techniques cannot access.

Using this approach, the team measured, for the first time, the low vibrational levels of the $\Omega = 3/2$ and $5/2$ spin-orbit components of the $3d\delta_\Omega$ electronic state of MgAr^+ . Because of the long lifetime of these states, transitions to them have narrow linewidths, which allowed for the precise characterization of these transition frequencies. Thanks to the high precision of this characterization, the team were then able to map the structure of the molecule with higher accuracy than that achieved by previous techniques that did such a mapping using broader transitions to shorter-lived states. By virtue of their longer lifetimes, the newly characterized Rydberg states are particularly interesting because they are expected to play a

more significant role in plasma dynamics than those states that rapidly dissociate.

With this Rydberg-state characterization, Génévriez and his co-workers derived molecular potential-energy functions of MgAr^{2+} . The analysis confirms the Rydberg character of these excited states: The excited electronic states' energy structures are similar to those of the ground electronic state of the MgAr^{2+} ion, meaning that the system can be regarded as a MgAr^{2+} core with an electron in a distant orbit.

An important aspect of the quantum-control-based scheme used in this work is that it doesn't rely on continuous, narrow-band lasers that must be customized to operate at the particular wavelengths associated with the electronic transitions of each molecule of interest. Instead, the scheme uses widely tuneable, pulsed dye lasers that can be easily matched to the required electronic transitions. Thus, this approach could be used to study the electronically excited states of a wide range of molecular ions, particularly those that would require excitation at ultraviolet or vacuum ultraviolet frequencies—a region where narrow bandwidth lasers aren't readily available.

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