

# Electronic State-Dependent Conformational Changes in a Rydberg Ion Crystal

Marion Mallweger<sup>1,\*</sup> Natalia Kuk<sup>1</sup> Vinay Shankar,<sup>1</sup> Robin Thomm<sup>1</sup> Harry Parke,<sup>1</sup> Ivo Straka<sup>1</sup> Weibin Li<sup>2</sup>,  
Igor Lesanovsky<sup>2,3</sup> and Markus Hennrich<sup>1,†</sup>

<sup>1</sup>Department of Physics, *Stockholm University*, 10691 Stockholm, Sweden

<sup>2</sup>School of Physics and Astronomy and Centre for the Mathematics and Theoretical Physics of Quantum Non-Equilibrium Systems,  
*University of Nottingham*, Nottingham NG7 2RD, United Kingdom

<sup>3</sup>Institut für Theoretische Physik and Center for Integrated Quantum Science and Technology, *Universität Tübingen*,  
Auf der Morgenstelle 14, 72076 Tübingen, Germany



(Received 2 November 2025; accepted 14 May 2026; published 6 August 2026)

State-dependent conformational changes play a central role in molecular dynamics, yet they are often difficult to observe or simulate due to their complexity and ultrafast nature. One alternative approach is to emulate such phenomena using quantum simulations with cold, trapped ions. In their electronic ground state, these ions form long-lived Wigner crystals. When excited to high-lying electronic Rydberg states, the ions experience a modified trapping potential, resulting in a strong coupling between their electronic and vibrational degrees of freedom. In an ion crystal, this vibronic coupling creates electronic state-dependent potential energy surfaces that can support distinct crystal structures—closely resembling the conformational changes of molecules driven by electronic excitations. Here, we present the first experimental observation of this effect, by laser coupling a single ion at the center of a three-ion crystal to a Rydberg state. By tuning the system close to a structural phase transition, the excitation induces a state-dependent conformational change, transforming the Wigner crystal from a linear to a zigzag configuration. This structural change leads to a strong hybridization between vibrational and electronic states, producing a clear spectroscopic signature in the Rydberg excitation. Our findings mark the first experimental step toward using Rydberg ions to create and study artificial molecular systems.

DOI: [10.1103/1bqh-pmgz](https://doi.org/10.1103/1bqh-pmgz)

**Introduction**—Electronic transitions in molecules are fundamental to chemical reactions and biological processes [1–4]. A prime example of this is vision, in which a photon-induced electronic excitation of a molecule causes a conformational change, leading to stimulation of the optical nerve [5,6]. These transitions occur on timescales of femto- to picoseconds and Ångström length scales, making direct observation of the dynamics challenging. Theoretical modeling is also limited, despite the fact that the molecular constituents and their interactions are well understood. This is due to the exceedingly high-dimensional Hilbert space spanned by the electronic and nuclear degrees of freedom, which renders *ab initio* numerical simulations extremely demanding. While well-established adiabatic approximations are available [7,8], they typically break down near intersecting potential energy surfaces (PESs), with the

aforementioned process of vision being one example. These challenges create a need for a quantum simulator that can mimic the dynamics of coupled electrons and nuclei on directly accessible time and length scales. A promising platform in this regard is Wigner crystals formed by trapped ions. They combine internal electronic states with external collective vibrational modes. Recently, such a system was employed for the first direct measurement of a geometric phase near conically intersecting PESs [9,10]. The conformation of the Wigner crystal and its associated PES is commonly modified by changing trapping potential or by varying the number of ions [11]. Structural transitions in a Wigner crystal have also been reported as a result of the photoionization of an ion to a doubly charged state [12]. This is reminiscent of an electronic state-dependent conformational change, albeit irreversible, of a large molecule.

In this Letter, we study an electronic state-dependent conformational change via laser excitation of a single ion in a three-ion Wigner crystal to an electronically high-lying Rydberg state [13–15]. Because of the high polarizability of this electronic state, the excited ion experiences a local modification of its trapping potential [16]. Near a conformational change of the Wigner crystal, this results in a strongly enhanced coupling between the vibrational and electronic degrees of freedom [17–19]. This so-called

\*Contact author: [marion.mallweger@physics.ox.ac.uk](mailto:marion.mallweger@physics.ox.ac.uk)

†Contact author: [markus.hennrich@fysik.su.se](mailto:markus.hennrich@fysik.su.se)

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International](https://creativecommons.org/licenses/by/4.0/) license. Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI. Funded by [Bibsam](https://www.bibsam.org/).

vibronic coupling renders the structure of the Wigner crystal dependent on the electronic state. We present experimental evidence of this phenomenon by studying a three-ion crystal of  $^{88}\text{Sr}^+$ , which changes from a linear to a zigzag configuration when the central ion is excited to the Rydberg state. This transition leaves a clear signature in the Rydberg excitation spectrum, which further allows us to demonstrate that the structure of the Rydberg excited Wigner crystal can be shaped with the help of a microwave field. The tunability of such a setup offers the potential to directly engineer the PES for the quantum simulation of molecular processes.

*Electronic state-dependent Wigner crystals*—For ions close to their electronic ground state, the critical radial confinement  $\omega_{x,c}$  depends on the number of ions  $N$  and the axial confinement  $\omega_z$  as [11]

$$\omega_{x,c} \approx 0.629\omega_z N^{0.865}. \quad (1)$$

This approximation does not include the polarizability of the state since they are insignificantly small for ground state ions. When considering electronically excited ions, on the other hand, the polarizability  $\mathcal{P}_r \propto n^7$ , where  $n$  corresponds to the principal quantum number, can dramatically affect the shape of the PES. The state-dependent coupling to the electric fields of the Paul trap directly translates to a state-dependent radial confinement of the ion [16,20]. The sign of  $\mathcal{P}_r$  determines whether the Rydberg excitation of a single ion results in stronger ( $\mathcal{P}_r < 0$ ) or weaker ( $\mathcal{P}_r > 0$ ) radial confinement in the Rydberg state. As a result, the critical radial frequency with respect to the ground state frequency  $\omega_{x,c}$  changes as

$$\omega_{x,c}^{(r)} \approx \sqrt{\omega_{x,c}^2 + \frac{2\alpha^2 + 4\beta^2}{M}\mathcal{P}_r} \quad (2)$$

during Rydberg excitation [17]. Here,  $\alpha$  and  $\beta$  denote the trapping field gradients of the oscillating and static quadrupole fields, respectively;  $e$  is the elementary charge, and  $M$  is the ion mass.

As theoretically predicted in [17], this state-dependent change in the critical radial confinement is enough such that the Rydberg excitation of a single ion can induce a conformational change. More specifically, for radial trapping frequencies of  $\omega_{x,c}^{(r)} > \omega_x > \omega_{x,c}$ , the stable conformation of the Wigner crystal is linear, when all ions are in the ground state and zigzag (ZZ) when the central ion is excited to the Rydberg state.

This phenomenon is reminiscent of a conformational change of a molecule upon electronic excitation. For example, in the process of vision, the rhodopsin chromophore undergoes a conformational change from *cis* to *trans*, when promoted from its electronic ground state PES to a high-lying one under the absorption of a photon [5,6].

*Spectral signatures of conformational changes*—To demonstrate the state-dependent conformational change of a Wigner crystal in our experiment, we use a linear chain of three  $^{88}\text{Sr}^+$  ions confined in a linear macroscopic Paul trap. The central ion is coupled from the ground state  $|g\rangle \equiv |4^2D_{5/2}, m_J = -\frac{5}{2}\rangle$  to the highly excited state  $|r\rangle \equiv |46^2S_{1/2}, m_J = -\frac{1}{2}\rangle$  with a principal quantum number  $n = 46$  and  $\mathcal{P}_{46S} > 0$ . We probe the transition  $|g\rangle \leftrightarrow |r\rangle$  via an intermediate level  $|6^2P_{3/2}\rangle \equiv |6^2P_{3/2}, m_J = -\frac{3}{2}\rangle$ . A more detailed description of the experimental setup and level structure can be found in the End Matter.

We investigate the electronic state-dependent conformational change via its spectroscopic signatures. A direct observation with CCD camera is difficult due to the relatively short lifetimes (in the  $\mu\text{s}$  regime) of the Rydberg states. The two-photon excitation scheme allows for coherently probing this change using the Autler-Townes effect [13,21,22]. During this detection scheme, a dressed state consisting of  $|6^2P_{3/2}\rangle$  and  $|r\rangle$  is excited. The dressed state ultimately decays into another lower-lying electronic state  $|S\rangle \leftrightarrow |5^2P_{1/2}\rangle$ . This allows for state-dependent fluorescence detection using the electron shelving technique, with further details in Supplemental Material [23]. Since only the central ion is excited, Rydberg interactions between two ions do not have to be taken into account. The three-ion crystal has three motional modes in the radial direction. Under Rydberg excitation of the central ion, only the two radial modes that experience a displacement from the trap center, namely the center-of-mass (CM) and ZZ motional modes, are relevant. The Hilbert space of the two modes is spanned by the number state  $|\mathbf{n}\rangle_g = |n_{\text{cm}}, n_{\text{zz}}\rangle_g$ , where  $n_{\text{cm}}$  and  $n_{\text{zz}}$  are the phonon numbers in the CM and ZZ mode. When the central ion is coupled to the Rydberg state, the additional coupling of the induced dipole moment to the electric field changes the PES and, therefore, also the eigenmodes of the system. The Hilbert space of the Rydberg state is spanned by the phonon number states  $|\mathbf{m}\rangle_r = |m_1, m_2\rangle_r$ , with  $m_{1,2}$  denoting the phonon numbers. The new phonon number states correspond to a combination of the CM and ZZ modes of the ground state [23]. The laser coupling between the electronic states and these state-dependent modes is described by the Hamiltonian ( $\hbar \equiv 1$ ),

$$H_1 = \delta \mathbf{I}_p \otimes |r\rangle\langle r| + \frac{\Omega}{2} \left( \sum_{\mathbf{n}, \mathbf{m}} C_{\mathbf{n}}^{\mathbf{m}} |\mathbf{n}\rangle_g \langle \mathbf{m}|_r \otimes |g\rangle\langle r| + \text{H.c.} \right). \quad (3)$$

Here,  $\delta$  is the detuning between the atomic resonance frequency and the laser frequency, and  $\Omega$  is the Rabi frequency that couples states  $|g\rangle$  and  $|r\rangle$ . We have defined  $\mathbf{I}_p$  to be the identity operator of the total phonon Hilbert space.

The laser excitation from the ground to the Rydberg state depends on the Franck-Condon (FC) factors  $|C_{\mathbf{n}}^{\mathbf{m}}|^2$ , which

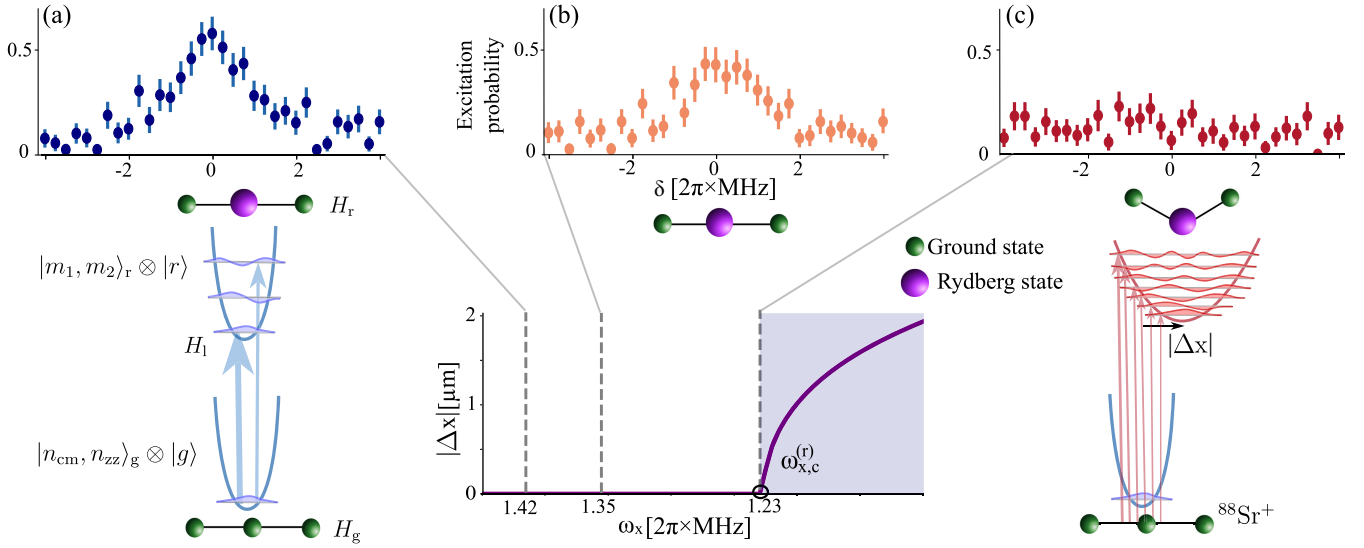


FIG. 1. Spectral signature of conformational change. Study of the Rydberg excitation probability of the central ion in a linear three-ion crystal as a function of the radial trap frequency  $\omega_x$  and detuning  $\delta$ . (a) For  $\omega_x \gg \omega_{x,c}^{(r)}$ , the PESs of the ground and Rydberg states are similar. The FC factors are large between the corresponding phonon states (thick arrow) but negligible otherwise (thin arrows). The excitation spectrum shows a clear Rydberg resonance. (b) As  $\omega_x$  approaches  $\omega_{x,c}^{(r)}$ , the Rydberg state polarizability  $\mathcal{P}_r$  modifies the PES, thereby altering the motional modes. The resulting vibronic coupling lowers the excitation probability of the Rydberg state. (c) At the conformational change to a zigzag configuration, the minima of the ground and Rydberg state PESs shift by  $|\Delta x|$ , while trap frequencies also change significantly. This broadens the distribution of the FC factors, causing the Rydberg resonance to vanish. Experimental data are shown for (a)  $\omega_x = 2\pi \times 1.42$  MHz, (b)  $\omega_x = 2\pi \times 1.35$  MHz, and (c)  $\omega_x = 2\pi \times 1.23$  MHz. The critical frequency is  $\omega_{x,c}^{(r)} = 2\pi \times 1.23$  MHz, and the axial frequency is  $\omega_z = 2\pi \times 0.778$  MHz.

are determined by the overlap of the motional wave functions,  $C_{\mathbf{n}}^{\mathbf{m}} = C_{n_{\text{cm}}, n_{\text{zz}}}^{m_1, m_2} = {}_g \langle n_{\text{cm}}, n_{\text{zz}} | m_1, m_2 \rangle_r$  [24]. In the regime far away from the conformational change, the linear Wigner crystal of ground state ions will stay in a linear configuration upon Rydberg excitation. Hence, the motional wave functions within the two PESs are similar, and, therefore, the FC factors are large when  $\mathbf{n} = \mathbf{m}$ , and close to zero otherwise. This is illustrated in Fig. 1(a), where the transition strength between the electronic and vibrational states is indicated by the thickness of the arrow. As a result, vibrational state changes under laser excitation are suppressed, and a clear spectral line is visible, centered at the expected resonance frequency, i.e.,  $\delta = 0$ . When  $\omega_x$  is lowered toward the critical frequency  $\omega_{x,c}^{(r)}$ , the PESs of the ground and the Rydberg states start to differ significantly. The vibrational eigenstates of the ground state PES have overlap with multiple vibrational eigenstates of the Rydberg state PES. There are many nonzero FC factors; hence, the transition strength gets distributed over many frequencies (as indicated by the arrows). This leads to a less pronounced spectral line, as shown in Fig. 1(b). Finally, when  $\omega_{x,c} < \omega_x < \omega_{x,c}^{(r)}$ , the linear Wigner crystal will undergo a conformational change to a ZZ configuration as the central ion is excited to the Rydberg state. The coupling to the Rydberg state drastically modifies the landscapes of the PESs such that their potential minima

are displaced, i.e.,  $|\Delta x| \neq 0$ ; see Fig. 1(c). As a result, many FC factors are nonzero and small. The FC factors corresponding to the cases shown in Fig. 1 can be found in the End Matter. Once the conformational change has taken place, the phonon state energies experience an additional mismatch due to the displacement  $|\Delta x| > 0$ , shifting the Rydberg excitation out of resonance. The combination of these effects becomes visible as a suppression of the Rydberg resonance shown in Fig. 1(c). The reduction in excitation probability close to the point of conformational change is approached. This feature will be used in the next section to investigate the critical confinement in the Rydberg state.

There are two other effects that can also lead to a reduction in the excitation amplitude [16]. First, imperfect cooling of the ion crystal will lead to a significant non-symmetric broadening and reduction of the excitation probability. We can exclude this effect because the data show no such asymmetric broadening of the resonance but only a decrease in the excitation probability. Second, another similar effect that also exhibits a decrease in excitation probability is an AC stark shift caused by an off-axis oscillating field experienced by the ions [25,26]. However, this phenomenon also causes a shift of the resonance frequency. Since the resonance amplitude in Fig. 1 only decreases and is not shifted as the point of conformational change is approached, we are certain that

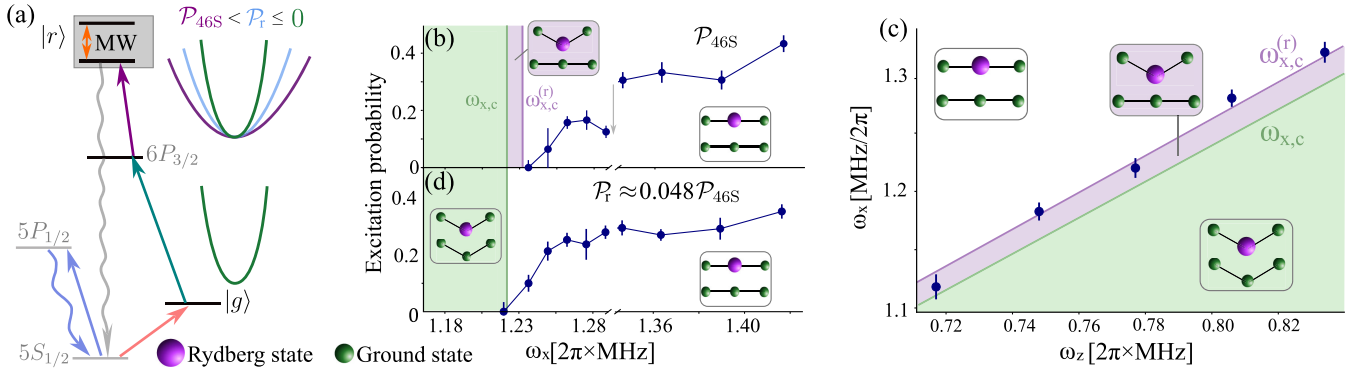


FIG. 2. Potential energy surface control. (a) Dressed Rydberg states  $|r\rangle$ , created via microwave (MW) coupling, exhibit tunable polarizability. This enables precise control over the shape of the state-dependent PESs. (b) The central ion is coupled to the Rydberg state  $|46S\rangle$  with a negative polarizability  $\mathcal{P}_{46S}$ . Because of different PESs in ground and Rydberg states, the excitation probability decreases as the conformational change is approached, leading to a drop, indicated by the arrow, between the datasets for different radial trapping frequencies. (c) Phase diagram of the conformational change of a Wigner crystal induced by excitation of the Rydberg state  $|46S\rangle$  for different trapping frequency ratios. (d) The central ion is excited to a dressed Rydberg state with reduced polarizability value. This suppresses the change in PES between the ground and excited states, leading to a recovery of the Rydberg resonance. The state-dependent conformational change of the Wigner crystal can be strongly suppressed. For all scans shown here,  $\omega_z = 2\pi \times 0.778$  MHz.

imperfect micromotion was not the cause of the spectroscopic changes. A more detailed discussion of both competing effects is found in the Supplemental Material [23].

In a ZZ configuration, the ions are far displaced from the electric field null, as shown in Fig. 1(c). The strong off-axis oscillating field is too large to allow any excitation in this configuration, limiting us currently to the indirect probing of the effect. A potential solution will be discussed in the outlook section. The simplified theoretical model developed here captures the qualitative behavior of the excitation probability close to the conformational change. Quantitative statements would require the consideration of all vibrational modes, demanding for sophisticated numerical approaches that are beyond the scope of the present work.

**Control of potential energy surfaces**—Next, we demonstrate a method for controlling the PES by engineering Rydberg states with tunable polarizabilities. By varying the polarizability  $\mathcal{P}_r$ , we can shape the PES in the Rydberg state to more closely match that of the ground state, as shown in Fig. 2(a). This control is characterized spectroscopically by its impact on the excitation probability, which depends sensitively on the conformation of the Wigner crystal. In this way, we use the conformation-dependent excitation signal to probe the influence of  $\mathcal{P}_r$ .

Before tuning  $\mathcal{P}_r$ , we first characterized the conformational change of the Wigner crystal through the laser excitation of a single Rydberg state  $|46S\rangle$  with a fixed polarizability  $\mathcal{P}_{46S}$ . Figure 2(b) shows the excitation probability at fixed axial confinement, as the radial trapping frequency is varied toward the critical radial trapping frequency  $\omega_{x,c}^{(r)}$ . With decreasing radial trapping frequencies, the overlap between the state-dependent PESs is reduced, as described in the previous section, leading to

a decrease in the excitation probability. This drop becomes particularly pronounced near the critical frequency and is indicated by the arrow in Fig. 2(b). Once the conformational change occurs at the critical frequency  $\omega_{x,c}^{(r)}$ , the Rydberg resonance in Fig. 2(b) disappears, reflecting the negligible overlap between the vibrational number states of the two PESs and the displacement of the PES of the Rydberg state. Repeating the scan for different axial trap frequencies allows us to map out the boundary of the conformational transition, shown as blue data points in Fig. 2(c). For each data point, a set of spectroscopy scans for different radial confinements close to  $\omega_{x,c}^{(r)}$  was performed. The linear decrease in the excitation probability was fitted. The crossing point of the excitation probability with the noise background of the resonance scan is defined as the conformational change. In Fig. 2(c), the green line shows the critical radial confinement predicted by Eq. (1). The purple border displays the critical radial confinement under Rydberg excitation and was calculated using Eq. (2). The disappearance of the resonance aligns well with the predicted critical value  $\omega_{x,c}^{(r)}$  for a given axial trapping frequency  $\omega_z$ .

Next, we tune the PES of the Rydberg state. The difference in PESs between the ground and Rydberg states depends on the polarizability. By significantly reducing  $\mathcal{P}_r$ , the PESs become almost state independent. We realize this by coupling the two Rydberg states  $|46S\rangle$  and  $|46P\rangle \equiv |46^2P_{1/2}, m_J = +\frac{1}{2}\rangle$  using a microwave (MW) field, as shown in Fig. 2(d). The resulting dressed state  $|r\rangle = \cos(\theta)|46S\rangle - \sin(\theta)|46P\rangle$  is a superposition between the two Rydberg states with a mixing ratio given by  $\theta$  [27]. The total polarizability of the dressed state reads  $\mathcal{P}_r = \mathcal{P}_{46S}\sin^2\theta + \mathcal{P}_{46P}\cos^2\theta$ . Since  $\mathcal{P}_{46S}$  and  $\mathcal{P}_{46P}$  have

opposing signs,  $\mathcal{P}_r$  can be tuned to almost zero [27]. The effect of reducing the polarizability, and thereby minimizing the difference between the ground and Rydberg state PESs, is depicted in Fig. 2(d).

To demonstrate the control over the state-dependent PESs, we use a dressed state with significantly reduced polarizability  $\mathcal{P}_r \approx 0.048\mathcal{P}_{46S}$ . The total value of the polarizability can be obtained experimentally by first investigating the AC Stark shift in the presence of an offset electric field [23]. The excitation probability near the conformational change of the Wigner crystal is shown in Fig. 2(d). As in Fig. 2(b), the axial trap frequency was fixed while the radial trap frequency was varied. Because of the reduced polarizability, the dressed state shows a more consistent excitation probability over a wider range of trap frequencies, including a nonzero excitation probability at the critical trap frequency where the excitation previously vanished for Rydberg states  $|46S\rangle$ . Remarkably, near the conformational transition, the excitation probability for the dressed Rydberg state exceeds that of the Rydberg state  $|46S\rangle$ , despite the fact that the excitation probability of the dressed state is reduced by a factor  $\cos^2(\theta)$  compared to the state  $|46S\rangle$ . The remaining decrease of the excitation probability takes place as the conformational change of the ground state ion crystal is approached. This indicates that the reduced polarizability causes the critical radial trap frequency for the dressed Rydberg state  $\omega_{x,c}^{(r)}$  to approach that of the ground state  $\omega_{x,c}^{(r)} \approx \omega_{x,c}$ . While Figs. 2(b) and 2(d) showcase two extreme examples,  $\mathcal{P}_r$  can be freely set between  $\mathcal{P}_{46S}$  and  $\mathcal{P}_{46P}$  by varying the detuning of the microwave field [23]. This makes the critical frequency  $\omega_{x,c}^{(r)}$  tunable.

*Summary and outlook*—We have conducted the first experimental investigation of a conformational change in a Wigner crystal via Rydberg excitation. The underlying mechanism relies on electronic state-dependent PESs that govern the spatial structure of the ion crystal. Control over the PES was achieved in our experiments by varying the ion trap parameters and by tuning the polarizability of ionic Rydberg states through microwave dressing. Our Letter opens new opportunities for the quantum simulation of molecular processes in regimes that are intractable by numerical simulations. In such a quantum simulator, the fundamental molecular shape is controlled by the number of ions and the geometry of the trapping field. The structure of the excited PES can be engineered by the interplay of external confinement, microwave control, and dipolar interactions. Possible use cases of such a simulator are the investigation of nonadiabatic processes in the vicinity of crossing PES or the study of the impact of vibronic coupling on excitation transport across large molecules [9,10,28]. For the latter, one may exploit resonant dipole-dipole interactions among several ions excited to Rydberg states, as has been shown with neutral atoms [29,30].

A further future avenue of investigation is the creation of superposition states of macroscopically different ion crystals [12,31]. In our setup, this can in principle be achieved by preparing the central ion in a superposition between states, of which one component is coupled to the Rydberg state and the other one is not. Subsequent excitation can then yield a macroscopic superposition state that may serve as a resource for addressing questions concerning quantum gravity and collapse models [32]. When scaling to larger Wigner crystals, the main limitation will be given by the quality of ground state cooling. With more ions and motional modes, cooling of the crystal and all its modes becomes more challenging. As a perspective, such long ion strings may allow the investigation of the impact of state-dependent conformational changes on excitation transport.

*Acknowledgments*—We gratefully acknowledge discussions with F. Schmidt-Kaler and G. Higgins. This work was supported by the Swedish Research Council (Grant No. 2021-05811) and by the Knut & Alice Wallenberg Foundation (Wallenberg Centre for Quantum Technology [WACQT]). W. L. acknowledges support from the EPSRC through Grant No. EP/W015641/1. This project has also received funding from the European Union’s Horizon Europe research and innovation program under Grant Agreement No. 101046968 (BRISQ). This work is supported by the ERC grant OPEN-2QS (Grant No. 101164443, DOI: 10.3030/101164443). This work was supported by the QuantERA II Programme (project CoQuaDis, DFG Grant No. 532763411) that has received funding from the EU H2020 research and innovation program under GA No. 101017733.

*Data availability*—The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

- 
- [1] O. P. Dimitriev, Dynamics of excitons in conjugated molecules and organic semiconductor systems, *Chem. Rev.* **122**, 8487 (2022).
  - [2] C. S. Ponseca, P. Chábera, J. Uhlig, P. Persson, and V. Sundström, Ultrafast electron dynamics in solar energy conversion, *Chem. Rev.* **117**, 10940 (2017).
  - [3] E. Brunk and U. Rothlisberger, Mixed quantum mechanical/molecular mechanical molecular dynamics simulations of biological systems in ground and electronically excited states, *Chem. Rev.* **115**, 6217 (2015).
  - [4] S. Gozem, H. L. Luk, I. Schapiro, and M. Olivucci, Theory and simulation of the ultrafast double-bond isomerization of biological chromophores, *Chem. Rev.* **117**, 13502 (2017).
  - [5] S. Rinaldi, F. Melaccio, S. Gozem, F. Fanelli, and M. Olivucci, Comparison of the isomerization mechanisms of human melanopsin and invertebrate and vertebrate rhodopsins, *Proc. Natl. Acad. Sci. U.S.A.* **111**, 1714 (2014).

- [6] R. W. Schoenlein, L. A. Peteanu, R. A. Mathies, and C. V. Shank, The first step in vision: Femtosecond isomerization of rhodopsin, *Science* **254**, 412 (1991).
- [7] H. Köppel, W. Domcke, and L. S. Cederbaum, Theory of vibronic coupling in linear molecules, *J. Chem. Phys.* **74**, 2945 (1981).
- [8] L. González, D. Escudero, and L. Serrano-Andrés, Progress and challenges in the calculation of electronic excited states, *ChemPhysChem* **13**, 28 (2012).
- [9] J. Whitlow, Z. Jia, Y. Wang, C. Fang, J. Kim, and K. R. Brown, Quantum simulation of conical intersections using trapped ions, *Nat. Chem.* **15**, 1509 (2023).
- [10] C. H. Valahu, V. C. Olaya-Agudelo, R. J. MacDonell, T. Navickas, A. D. Rao, M. J. Millican, J. B. Pérez-Sánchez, J. Yuen-Zhou, M. J. Biercuk, C. Hempel, T. R. Tan, and I. Kassal, Direct observation of geometric-phase interference in dynamics around a conical intersection, *Nat. Chem.* **15**, 1503 (2023).
- [11] J. P. Schiffer, Phase transitions in anisotropically confined ionic crystals, *Phys. Rev. Lett.* **70**, 818 (1993).
- [12] T. Feldker, L. Pelzer, M. Stappel, P. Bachor, R. Steinborn, D. Kolbe, J. Walz, and F. Schmidt-Kaler, Mode shaping in mixed ion crystals of  $^{40}\text{Ca}^{2+}$  and  $^{40}\text{Ca}^+$ , *Appl. Phys. B* **114**, 11 (2014).
- [13] A. Makhberi, M. Hennrich, and F. Schmidt-Kaler, Chapter Four—Trapped Rydberg ions: A new platform for quantum information processing, *Volume 69 of Advances in Atomic, Molecular, and Optical Physics* (Academic Press, New York, 2020), p. 233, [10.1016/bs.aamop.2020.04.004](https://doi.org/10.1016/bs.aamop.2020.04.004).
- [14] G. Higgins, W. Li, F. Pokorny, C. Zhang, F. Kress, C. Maier, J. Haag, Q. Bodart, I. Lesanovsky, and M. Hennrich, Single strontium Rydberg ion confined in a Paul trap, *Phys. Rev. X* **7**, 021038 (2017).
- [15] T. Feldker, P. Bachor, M. Stappel, D. Kolbe, R. Gerritsma, J. Walz, and F. Schmidt Kaler, Rydberg excitation of a single trapped ion, *Phys. Rev. Lett.* **115**, 173001 (2015).
- [16] G. Higgins, F. Pokorny, C. Zhang, and M. Hennrich, Highly polarizable Rydberg ion in a Paul trap, *Phys. Rev. Lett.* **123**, 153602 (2019).
- [17] W. Li and I. Lesanovsky, Electronically excited cold ion crystals, *Phys. Rev. Lett.* **108**, 023003 (2012).
- [18] F. M. Gabbetta, C. Zhang, M. Hennrich, I. Lesanovsky, and W. Li, Exploring the many-body dynamics near a conical intersection with trapped Rydberg ions, *Phys. Rev. Lett.* **126**, 233404 (2021).
- [19] F. M. Gabbetta, C. Zhang, M. Hennrich, I. Lesanovsky, and W. Li, Long-range multibody interactions and three-body antiblockade in a trapped Rydberg ion chain, *Phys. Rev. Lett.* **125**, 133602 (2020).
- [20] M. Niederländer, J. Vogel, A. Schulze-Makuch, B. Gély, A. Makhberi, and F. Schmidt-Kaler, Rydberg ions in coherent motional states: A new method for determining the polarizability of Rydberg ions, *New J. Phys.* **25**, 033020 (2023).
- [21] G. Higgins, C. Zhang, F. Pokorny, H. Parke, E. Jansson, S. Salim, and M. Hennrich, Observation of second- and higher-order electric quadrupole interactions with an atomic ion, *Phys. Rev. Res.* **3**, L032032 (2021).
- [22] H. Bao, A. Schulze-Makuch, and F. Schmidt-Kaler, Microwave-dressing of Rydberg states in a trapped calcium ion, [arXiv:2504.21241](https://arxiv.org/abs/2504.21241).
- [23] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/1bqh-pmgz> for more detailed description of experimental procedures, parameters, and theoretical derivation.
- [24] R. Borrelli, A. Capobianco, and A. Peluso, Franck-Condon factors—Computational approaches and recent developments, *Can. J. Chem.* **91**, 495 (2013).
- [25] G. Higgins, F. Pokorny, C. Zhang, Q. Bodart, and M. Hennrich, Coherent control of a single trapped Rydberg ion, *Phys. Rev. Lett.* **119**, 220501 (2017).
- [26] W. S. Martins, Joseph W. P. Wilkinson, M. Hennrich, and I. Lesanovsky, Impact of micromotion and field-axis misalignment on the excitation of Rydberg states of ions in a Paul trap, *Phys. Rev. A* **111**, 043106 (2025).
- [27] F. Pokorny, C. Zhang, G. Higgins, and M. Hennrich, Magic trapping of a Rydberg ion with a diminished static polarizability, [arXiv:2005.12422](https://arxiv.org/abs/2005.12422).
- [28] J. Brox, P. Kiefer, M. Bujak, T. Schaetz, and H. Landa, Spectroscopy and directed transport of topological solitons in crystals of trapped ions, *Phys. Rev. Lett.* **119**, 153602 (2017).
- [29] S. Ravets, H. Labuhn, D. Barredo, L. Béguin, T. Lahaye, and A. Browaeys, Coherent dipole-dipole coupling between two single Rydberg atoms at an electrically-tuned Förster resonance, *Nat. Phys.* **10**, 914 (2014).
- [30] S. de Léséleuc, V. Lienhard, P. Scholl, D. Barredo, S. Weber, N. Lang, H. P. Büchler, T. Lahaye, and A. Browaeys, Observation of a symmetry-protected topological phase of interacting bosons with Rydberg atoms, *Science* **365**, 775 (2019).
- [31] J. D. Baltrusch, C. Cormick, G. De Chiara, T. Calarco, and G. Morigi, Quantum superpositions of crystalline structures, *Phys. Rev. A* **84**, 063821 (2011).
- [32] D. Carney, G. Krnjaic, D. C. Moore, C. A. Regal, G. Afek, S. Bhawe, B. Brubaker, T. Corbitt, J. Cripe, and N. Crisosto, Mechanical quantum sensing in the search for dark matter, *Quantum Sci. Technol.* **6**, 024002 (2021).

## End Matter

**Experimental setup**—Spectroscopy scans of Rydberg resonances require a multitude of laser beams, aligned on the ion. A laser beam at 674 nm was used to manipulate the low-lying electronic states  $|S\rangle \equiv |5^2S_{1/2}, m_J = -\frac{1}{2}\rangle$  and  $|g\rangle$ . This beam is aligned at an angle of  $45^\circ$  to the longitudinal trapping axis. From the

opposite direction, the cooling and fluorescence detection laser and the repump lasers for the state preparation are aligned on the ion. To excite Rydberg states via an intermediate state, two ultraviolet (UV) beams at 243 and 305 nm wavelength are counterpropagating to minimize momentum transfer during the excitation. Both

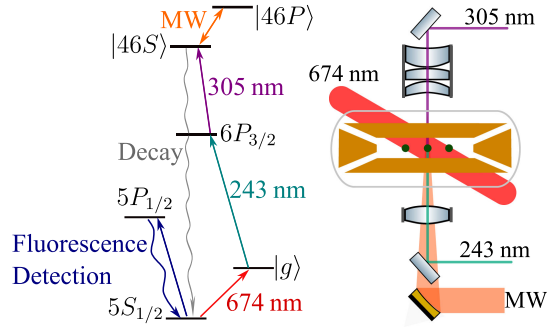


FIG. 3. Level scheme and experimental setup. Three ions are confined in a linear Paul trap (shown in orange). Coherent operations between the low-lying electronic states are driven globally by a laser at 674 nm. Individual Rydberg excitation is performed by addressing the central ion using counterpropagating laser beams at 305 and 243 nm. The MW field, aligned parallel to the 243 nm beam and perpendicular to the trap axis, is used to couple Rydberg states.

lasers are aligned in radial direction, addressing only the central ion of the chain. More specifically, the ion separation for the measurements included in this Letter is 4.6 – 5.5  $\mu\text{m}$ , and the FWHM of the beam waist of second Rydberg excitation laser beam is less than 1.5  $\mu\text{m}$ . The microwave (MW) beam at 122 GHz is created using frequency multiplication. Curved gold coated mirrors are used to align and focus the beam onto the ion from the radial direction. A level scheme and a sketch of the experimental setup can be found in Fig. 3.

At the start of each experimental sequence, the ions are first cooled using Doppler cooling, followed by sideband cooling on all motional modes except the zigzag modes. Cooling of the latter one was not possible because the frequency was too close to the carrier transition; the sideband cooling process, therefore, led to off-resonant excitations. Next, all trap frequencies are characterized for

the ground state. All ions are then excited from state  $|S\rangle$  to state  $|g\rangle$ , followed by a postselection step to ensure proper state transfer. Finally, the Rydberg resonance  $|g\rangle \leftrightarrow |r\rangle$  is probed for the central ion, using a coherent spectroscopy technique, which relies on the Autler-Townes effect emerging in a three-level system; see Refs. [13,21,22]. For the spectroscopic scans, we used Rabi frequencies of around  $2\pi \times 0.8$  MHz for the weak probe beam and  $2\pi \times 5$  MHz for the strong coupling beam. Both the intermediate state  $|6^2P_{3/2}, m_J = -\frac{3}{2}\rangle$  and the Rydberg state  $|r\rangle$  decay with about 95% probability to the lower-lying electronic state  $|S\rangle$ . This enables the following state-dependent fluorescence detection scheme to distinguish the long-lived states  $|g\rangle$  and  $|S\rangle$ ; when the ion is in state  $|g\rangle$ , the ion stays dark, and no fluorescence is detected. If the population is coupled to the Rydberg state  $|r\rangle$ , it decays to the state  $|S\rangle$ . From there, the fluorescence transition  $|S\rangle \leftrightarrow |5^2P_{1/2}\rangle$  is driven, the ion scatters photons, and a fluorescence signal is detected. Therefore, Rydberg excitation leads to photon counts, whereas no Rydberg excitation results in a dark signal. During the state-dependent fluorescence detection sequence, the ion decays from the state  $5P_{1/2}$  to the dark state  $4D_{3/2}$  with a probability of around 6%. A repump beam at 1092 nm is used to recover the decayed population from the state  $4D_{3/2}$  back to the state  $5P_{1/2}$ .

Each data point of the spectroscopy scans of the resonance in Fig. 1 consists of 50 repetitions. Error bars denote quantum projection noise (68% confidence). For the extraction of the excitation probability, the resonance spectrum was fitted using a Lorentzian function. The fit uncertainty is represented as error bars.

*Franck-Condon factors*—The FC factors, i.e., spatial overlaps  $C_{00}^{\mathbf{m}}$  of phonon modes on the lower and upper PES, strongly affect electronic coupling. Here, we use  $\mathbf{n} = \{n_{\text{cm}}, n_{\text{zz}}\}$  and  $\mathbf{m} = \{m_1, m_2\}$  to denote the Fock states of the two modes of the corresponding PES.

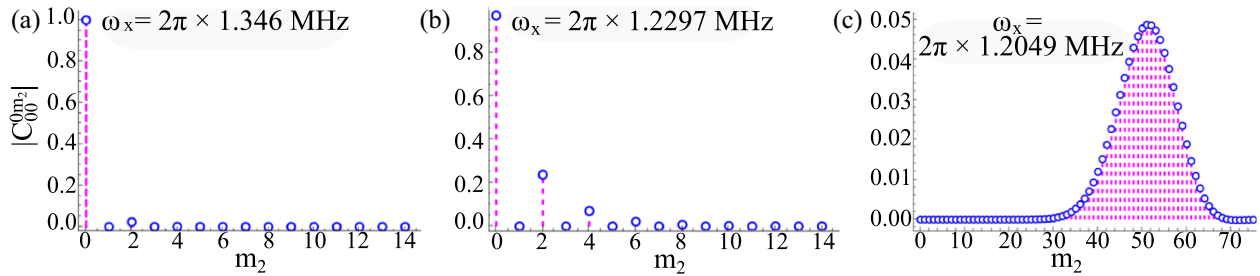


FIG. 4. Franck-Condon factors. The phonon states in the lower PES are in the vacuum state ( $n_{\text{cm}} = n_{\text{zz}} = 0$ ). We vary phonon number  $m_2$  of the modified ZZ mode. (a) Away from the critical point ( $\omega_x = 2\pi \times 1.346$  MHz), the FC factors have a narrow distribution. (b) Close to the critical point ( $\omega_x = 2\pi \times 1.2297$  MHz), the ion crystal before and after the Rydberg excitation is still in a linear configuration. However, the mode becomes soft such that the even-phonon-number states couple to the vacuum state of the CM and ZZ modes on the lower PES. When the Rydberg excitation changes the crystal from a linear to a ZZ configuration, the displacement of the equilibrium position along the  $x$  axis means that the vacuum state on the ground-state PES can only couple to very high phonon-number states on the Rydberg state PES, as shown in panel (c). In this example, for  $\omega_x = 2\pi \times 1.2049$  MHz, we find that the FC factors have a broad distribution centered around  $m_2 \approx 50$ .

The overlaps  $C_n^m$  are calculated using the Duschinsky transformation [24]. These are high-dimensional coefficients that depend on the phonon modes of the two PESs. Examples are shown in Fig. 4. For the numerical simulation, we assume that the two phonon modes on the lower PES are in the vacuum state ( $n_{\text{cm}} = 0$ ,  $n_{\text{zz}} = 0$ ). Then we vary the phonon state ( $m_2$ ) of the modified ZZ mode (with  $m_1 = 0$ ). When the trapping potential deformation is negligible, the modes of the two PESs are largely identical. The FC factor has a single peak at  $m_2 = 0$  [see Fig. 4(a)]. When the trapping potential along the  $x$  axis is weakened by the Rydberg excitation, the phonon modes on the upper PES become soft and are not orthogonal to the modes on the lower PES. This allows the vacuum state to couple to different phonon-number states [see Fig. 4(b)]. Note that

only even-numbered Fock states are coupled due to the parity symmetry of the FC coupling. In contrast, the phonon modes on the two PESs are different when a conformational change occurs. Not only do the mode frequencies differ significantly, but the centers of the phonon wave packets are also displaced. Here, we show the example with  $\omega_x = 2\pi \times 1.2049$  MHz [see Fig. 4(c)]. Without the Rydberg excitation, the crystal is in a linear configuration. After the central ion is excited to the Rydberg state, it changes to the ZZ configuration. The FC factor has a broad distribution owing to the displacement of the potential minima and modification of the trap frequencies. Rydberg excitation is significantly reduced because of the vanishing phonon coupling, even when the laser is resonant with the electronic transition.