## Quantum-State Controlled Formation of Cosmically Relevant Metallic Molecular Ions

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Metal-containing molecular ions are fundamentally important in both terrestrial and interstellar chemistry, yet their formation mechanisms have been largely unexplored experimentally. To address this lack of fundamental understanding of how these ions are created in space, we conducted an experimental study of a quantum-state-controlled reaction between  $Ca^+$  and  $C_2H_2$  to investigate a potential unifying mechanism for the formation of metallic molecules. By tuning the quantum-state populations of laser-cooled  $Ca^+$ , we demonstrate precise control over reactivity. Our results reveal a single ionic product,  $CaCCH^+$ , providing valuable insights into the mechanisms underlying the formation of metal-containing ions in space.

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Ions in space have played a pivotal role in shaping the chemical composition of the Universe. Atomic metal ions, in particular, are considered to be significant positive charge carriers in dense interstellar clouds and circumstellar envelopes [1]. For decades, it was proposed that these ions would react with the surrounding gas to form metal-bearing molecular species [2,3]. This proposal has been substantiated over the past 30 years through numerous observations of metallic molecules in the circumstellar envelope of IRC + 10216, a well-studied late-stage carbon star [4-13]. Circumstellar envelopes are characterized by low temperatures ( $T \sim 20$  K) and low densities ( $n \sim 10^5$  cm<sup>-3</sup>). This type of extreme environment allows for the formation of exotic molecules and ions. These observations have identified that there are two major classes of metallic molecules, metal polyynes (MC<sub>x</sub>H) and metal cyanopolyynes (MC<sub>x</sub>CN), where M refers to any metal and x = 2-8. However, the formation mechanisms for these species remain unclear.

Several ion-molecule reaction mechanisms have been proposed for the formation of both metal polyynes and metal cyanopolyynes [1,12,14]. As both cationic and neutral versions of these metallic molecules have been observed in space, a general unifying mechanism that includes both has eluded astrochemical modelers. One proposed ion-molecule reaction mechanism for metal polyynes is shown in Fig. 1. After formation of the ionic reaction complex,  $MC_xH_2^+$ , the reaction can proceed following two possible reaction pathways. Either a bimolecular dissociation pathway (blue arrow), or a radiative association pathway (red arrows). The key intermediate that connects the two mechanisms is the ionic complex  $MC_xH_2^{+*}$ , which has not been observed astronomically.

Very little laboratory work has been carried out to probe this potential unifying mechanism terrestrially, despite its prevalence in space. Although technically not a polyyne, the simplest organic molecule following the polyyne molecular formula is acetylene ( $C_2H_2$ ). In addition to its importance astronomically, acetylene can also be thought of as a model system for larger polyynes, where x = 2 following the reaction scheme in Fig. 1.

To further our understanding of the role of metallic molecules in the chemistry of extreme environments and evaluate long-standing theories, we need laboratory studies to determine the precise reaction mechanisms for both metal polyynes and metal carbides. With current laboratory



FIG. 1. Proposed ion-molecule reaction scheme for the formation of metal polyynes and the formation of metal carbides in circumstellar envelopes. The reactions begin with the association between a metal cation and neutral polyyne, resulting in a reaction complex denoted as  $[MC_xH_2^+]^*$ . The reaction complex can quench the excess internal energy through two main pathways that results in the formation of two distinct products. The first pathway (blue arrows) is a bimolecular reaction, where the dissociation of a H atom results in  $MC_xH^+$  and H as the final products. Alternatively the complex can follow a radiative association reaction (red arrows), which due to the low density conditions of space, radiatively decays with the emission of a photon. This is followed by a dissociative electron recombination step that results in the final neutral products,  $MC_2 + H_2$ . techniques we are able to measure the ionic products from these reactions, as well as determine the reaction rates. This gives us a precise determination of the likelihood of these reactions occurring in space, allowing us to directly probe the feasibility of the proposed reaction mechanism to form both metal carbides and metal polyyne cations. Building on these insights into the chemistry of metallic molecules, emerging advancements in experimental techniques offer new opportunities to probe reaction mechanisms with unprecedented precision.

Recent experiments have demonstrated the potential of leveraging atomic physics techniques, originally developed for ultracold matter and quantum information science, to study chemical reactions in highly controlled environments. These studies utilize laser-cooled atomic ions in a Coulomb crystal [15-21], which is an ordered structure formed by the cold, trapped ions. A key advantage of this approach is the combination of ultracold temperatures and the simultaneous preparation of multiple quantum states of the trapped ions, enabling detailed investigations into quantum-state-controlled reactivity, as shown in prior work [22–35]. Notably, many of these experiments use Group IIA metallic elements to form Coulomb crystals, making this a powerful platform for exploring ion-molecule reactions, as well as for determining precise mechanisms for the formation of metallic molecular ions.

In this Letter, we investigate the reaction mechanisms for the formation of metallic molecules through the ionmolecule reactions of  $Ca^+$  ions and  $C_2H_2$  molecules using both experimental measurements and quantum chemical calculations. Specifically, we examine the reactions that could lead to the formation of metal polyyne cations and metal carbides within a trapped Coulomb crystal. Coulomb crystal. By laser cooling Ca<sup>+</sup> to generate the Coulomb crystal, we can explore how quantum-state populations influence the reaction dynamics and branching into the two proposed in Fig. 1. We are able to directly probe the bimolecular pathway by observing a CaCCH<sup>+</sup> product. However, the radiative association reaction that produces neutral CaC<sub>2</sub> cannot be investigated in our laboratory, as it involves electron recombination, which remains inaccessible to our experimental setup. Instead, we assess the radiative association pathway (Fig. 1 red dashed lines) by detecting the  $CaC_2H_2^+$  ionic product, which can be used as a proxy for this pathway because collision probability of electrons with ions in this circumstellar envelope is so low that  $CaC_2H_2^+$  must be a long-lived species for the recombination reaction to occur. Surprisingly, we observe only the bimolecular dissociation pathway leading to the CaCCH<sup>+</sup> product. Furthermore, we find that the quantum state of Ca<sup>+</sup> is the critical factor determining whether the reaction proceeds. These results have significant implications for the reactivity of atomic ions in space and challenges our current views on the formation mechanisms for metal polyynes and metal carbides.

To mimic the conditions of circumstellar space, reactions are carried out under single-collision conditions using our custom-built ion-trapping apparatus, which has been described previously [36]. Briefly, Ca<sup>+</sup> ions are loaded into a linear quadrupolar Paul trap through nonresonant photoionization (~7 (mJ/pulse), 355 nm, 10 Hz) of an effusive beam of Ca from an oven source. The trapped Ca<sup>+</sup> ions are laser cooled to sub-Kelvin temperatures (~100 mK) using the doubled output of a Ti-sapphire laser (MSquared SolsTiS, ~397 nm, 2 mW) and a diode laser (Toptica DL Pro, ~866 nm, 2 mW). As the Ca<sup>+</sup> ions are laser-cooled inside the trap, the ions for a pseudocrystalline structure known as a Coulomb crystal. Once the Coulomb crystal is formed, reactions are initiated by introducing neutral acetylene molecules into the vacuum system through a pulsed leak valve. The acetylene results in a reaction energy with the cold ions of around 180 K (0.02 eV). As a reaction proceeds, all ionic products are retained in the trap and analyzed at various reaction time points using a time-of-flight mass spectrometer. By determining the number of ions as a function of reaction time (0-180 s), we are able to construct kinetic reaction curves and determine the reaction rate constants using the following rate equations:

$$\frac{lN_{\rm CaCCH^+}}{dt} = k_{\rm eff} N_{\rm Ca^+} \tag{1}$$

$$\frac{dN_{\rm Ca^+}}{dt} = -k_{\rm eff}N_{\rm Ca^+},\tag{2}$$

where  $N_{\text{CaCCH}^+}$  is the number of observed number of CaCCH<sup>+</sup> produced as a function of time,  $N_{\text{Ca}^+}$  is the number of trapped Ca<sup>+</sup> ions in all quantum states, and the effective rate constant,  $k_{\text{eff}}$ , is given by

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$$k_{\rm eff} = k' [C_2 H_2], \tag{3}$$

where  $[C_2H_2]$  is the concentration of neutral  $C_2H_2$  in the chamber and k' is defined as

$$k' = (k_S f_S + k_D f_D + k_P f_P), (4)$$

where  $k_S$ ,  $k_D$ , and  $k_P$  are the rate constants for reaction with Ca<sup>+</sup> in the  ${}^2S_{1/2}$ ,  ${}^2D_{3/2}$ , and  ${}^2P_{1/2}$  states, and  $f_S$ ,  $f_D$ , and  $f_P$  are the fraction of Ca<sup>+</sup> in each respective state.

Bimolecular dissociation pathway—To obtain the quantum-state-dependent reaction rate constants,  $k_{eff}$  is determined at various state populations outlined in Fig. 5 and Figs. S1 and S2 of [37]. An example of a typical measurement taken at a fixed pressure of  $2.62 \pm 0.08 \times 10^{-9}$  Torr is shown in Fig. 6, where the number of product ions (CaCCH<sup>+</sup>) grows nearly linearly, and the initial reactant ions (Ca<sup>+</sup>) deplete by roughly the same amount over the reaction time. The effective rate constant,  $k_{eff}$ , is determined by performing a global fit to all data using



FIG. 2. Quantum-state-dependent rate measurements for the  $Ca^+ + C_2H_2$  reaction. All data (blue points) were obtained at the eight points listed in Figs. 5, S1, and S2. The vertical error bars represent the 68% confidence interval from the k' fit [Eqs. (1) and (2)] and the horizontal error bars represent the 68% confidence interval from 8-level OBE fit for the  ${}^2P_{1/2}$  state population. The fit (red solid line) was obtained using Eq. (4). The dashed red lines represent the 68% confidence interval of this fit. Each set of measurements was taken with  $[C_2H_2]$  held constant at  $2.62 \pm 0.08 \times 10^{-9}$  Torr, where the uncertainty reported is purely statistical.

Eqs. (1) and (2). The resulting fit is shown as the solid lines in Fig. 6. This process was repeated to obtain reaction curves for eight unique Ca<sup>+</sup> quantum-state populations and k' was determined for each dataset using Eq. (3). The excited state rate constants  $(k_P \text{ and } k_D)$  were then obtained using the predicted populations of the excited states of Ca<sup>+</sup> by solving the 8-level optical Bloch equations (OBE). We find that the bimolecular reaction is significantly influenced by the population in the  ${}^2P_{1/2}$  state, while no dependence was observed for either the  ${}^{2}S_{1/2}$  or  ${}^{2}D_{3/2}$  states of Ca<sup>+</sup>. The rate constant, k', as a function of the  ${}^{2}P_{1/2}$  state population is presented in Fig. 2, where the  ${}^{2}P_{1/2}$ -dependent rate constant,  $k_P$ , is determined to be  $8 \pm 3 \times 10^{-11}$  cm<sup>3</sup>/s. The concentration of  $C_2H_2$  was held constant at  $2.62 \pm 0.08 \times$  $10^{-9}$  Torr for all measurements, as measured by a Bayard-Alpert ionization gauge where the uncertainty reported is purely statistical. The same procedure was done for the  ${}^{2}S_{1/2}$  and  ${}^{2}D_{3/2}$  states, shown in Figs. S3 and S4 [37], respectively. The various rate constants obtained for the bimolecular reactions are summarized in Table 1 in the Supplemental Material [37].

To increase our confidence in the claim that  $Ca^+$  ions react only in the  ${}^2P_{1/2}$  state, we also determined the concentration dependence of the effective rate constant by varying the concentration of  $C_2H_2$  at fixed laser detunings. These measurements were obtained using the



FIG. 3. Pressure dependent rate measurements with quantumstate populations that correspond to point III in Fig. 5. Each data point represents the mean and standard error of 6 measurements. The vertical error bars correspond to the 68% confidence interval from the fit, and the horizontal error bars correspond to the 68% confidence interval from the measurement of the ion gauge at each point.

cooling laser parameters that correspond to point III in Fig. 5. For each fixed concentration of  $C_2H_2$ , we determined  $k_{\text{eff}}$  using Eqs. (1) and (2). After determining  $k_{\text{eff}}$  for each C<sub>2</sub>H<sub>2</sub> concentration, a concentration-independent rate constant, k', was obtained by fitting the  $k_{\text{eff}}$ 's as a function of C<sub>2</sub>H<sub>2</sub> concentration. The reaction data and fit for these concentration-dependent measurements are shown in Fig. 3. This rate constant, k', was then adjusted based on the estimated  ${}^{2}P_{1/2}$ -state population shown in Fig. 5 to extract the state-dependent rate constant,  $k_P$ , and was determined to be  $k_P = 9.5 \pm 0.4 \times 10^{-11} \text{ cm}^3/\text{s}$  and is in good agreement with the value obtained from the statedependent measurements. Despite the statistical uncertainty in the ion gauge measurement, we are able to extract a relatively precise  $k_P$  from the concentration dependent measurements as compared to the  ${}^{2}P_{1/2}$ -state measurements. This is a result of a larger uncertainty in the estimated population fractions, arising from the error propagation of several parameters used in the 8-level OBE. On the other hand, the pressure is held constant throughout the process of taking a single reaction curve, which leads to a smaller uncertainty in  $k_P$ .

This reaction's strong dependence on the  ${}^{2}P_{1/2}$ , as well as the lack of dependence for the other two states, was also investigated using quantum chemical calculations. A potential energy surface (PES) was calculated for this reaction at the MP2/cc-pVTZ level of theory using Gaussian 16 [38] and is shown in Fig. 4. The reaction proceeds in four consecutive steps. First, a loosely bound transition state (TS 1) is formed as Ca<sup>+</sup> and C<sub>2</sub>H<sub>2</sub> approach each other.



FIG. 4. Calculated potential energy surface for the  $Ca^+ + C_2H_2$  reaction at MP2/cc-pVTZ level of theory. Dashed horizontal lines correspond to the excited state energies of  $Ca^+$  in each electronic state, which show that the reaction is barrierless only when  $Ca^+$  is in the  ${}^2P_{1/2}$  excited state. The purple spheres represent  $Ca^+$  atoms, the gray spheres represent C atoms, and the white spheres represent H atoms. Energies were zero-point energy corrected and plotted relative to ground state reactants at infinite separation.

As the reaction proceeds, a triangular reaction complex (INT 1) is formed slightly lower in energy than the entrance channel. To form the final products, the reaction complex must undergo dissociation of a single hydrogen atom, passing through a higher-energy transition state (TS 2). Following this step, the reaction yields the final products, CaCCH<sup>+</sup> and H. The quantum state of the Ca<sup>+</sup> ion plays a pivotal role in this process, as the dissociation step is barrierless only when Ca<sup>+</sup> is in the  ${}^{2}P_{1/2}$  state. This simple PES is able to explain the observed  ${}^{2}P_{1/2}$  state dependence by considering energetics alone. Although MP2 is not considered a high-level method, we are still able to capture the observed reactivity, providing further confidence in our observations.

Radiative association pathway-Despite extensive efforts, we did not detect the radiative association product,  $(CaC_2H_2^+)$ . To improve the sensitivity of our detection, we conducted additional measurements beyond those summarized in Table 1 in the Supplemental Material [37], focusing on quantum-state populations denoted by point II in Fig. 5, with a reaction time of 20 min. The results of that experiment are shown in Fig. S4 [37]. Our calculations (Fig. 4) suggest that  $CaC_2H_2^+$  should form efficiently, regardless of the Ca<sup>+</sup> quantum-state distribution. In particular, one might expect that a high population of the  ${}^{2}S_{1/2}$  state would favor the formation of  $CaC_2H_2^+$ , as it would suppress the competing pathway leading to the CaCCH<sup>+</sup> product. However, even under conditions with a high  ${}^{2}S_{1/2}$  population (point II), the formation of CaCCH<sup>+</sup> was clear and a statistically significant amount of  $CaC_2H_2^+$  was not observed.

These findings suggest that the formation of  $CaC_2H_2^+$  is not controlled by the quantum state of  $Ca^+$ , but is instead inhibited by another factor. Based on the computed potential energy surface, it is reasonable to assume that the ionic reaction complex,  $CaC_2H_2^{+*}$ , forms upon collision of the reactants. However, the excited complex's inherent instability possibly stems from an inability to dissipate excess internal energy via radiative relaxation, due to poor vibrational mode coupling between the C-C bond in  $C_2H_2$  and the Ca-C bonds in the complex. Consequently, the complex may dissociate back into the reactants. Molecular dynamics simulations would be necessary to explore the details of this potential energy surface and validate this hypothesis.

Although the absence of a detectable  $CaC_2H_2^+$  product is unexpected, there is some additional evidence that supports other pathways to creating  $MC_2$  species within circumstellar envelopes. Nearly half of all metallic molecules observed in space contain magnesium (Mg), a prevalence attributed to its high cosmic abundance. In stark contrast, only two calciumcontaining metallic molecules have been identified despite extensive searches and robust theoretical predictions. [1,39– 41]. The first calcium-bearing molecule identified in space was CaNC, which was found to be 65 times less abundant than its Mg counterpart, MgNC, in the same region [6]. This disparity is attributed to the significantly higher concentration of Mg<sup>+</sup> compared to Ca<sup>+</sup> in the region, driving the preferential formation of MgNC. However, this trend does not extend to metal dicarbide species, where a similar abundance ratio is not observed. Specifically, recent observations of both  $MgC_2$  [10] and  $CaC_2$  [13] have measured an abundance ratio of approximately 2:1 for MgC<sub>2</sub> and CaC<sub>2</sub>. This ratio directly challenges the idea that the abundance differences are solely due to the large disparity between Mg<sup>+</sup> and Ca<sup>+</sup>. Instead, the observed ratio suggests the existence of alternative chemical pathways that promote the efficient formation of CaC<sub>2</sub> relative to MgC<sub>2</sub>. Due to laser cooling limitations, we are only able to probe  $Ca^+$  at this time. However, our results indicate the possibility of an alternative mechanism because the current mechanism does not result in a radiative association product that could lead to  $CaC_2$ .

We have investigated the proposed ion-molecule reaction mechanism to form metal polyynes, through the  $Ca^+$  + C<sub>2</sub>H<sub>2</sub> reaction. We found no evidence for the radiative association pathway. However, we did find that the bimolecular dissociation pathway results in the CaCCH<sup>+</sup> product. Importantly, we also found that this reaction is quantum-state dependent and measured rate constants with various quantum-state populations and molecule concentrations. The fact that this reaction is possible only with an electronically excited state means this reaction is unlikely to occur in space, due to short exited-state lifetimes and the low collision rates in interstellar space. Although excited states of Ca<sup>+</sup> are not expected to be relevant to the chemistry of circumstellar envelopes, excited states of  $C_2H_2$ , particularly vibrational excited states, could play a role in the formation of both metal acetylides and metal carbides in space. These results highlight the importance of probing multiple quantum states for metallic reactions, especially when considering the formation of metallic molecules in space.

There is a clear need for further studies of quantum statespecific reactions to identify processes that are feasible under extreme interstellar conditions. Moreover, quantumstate-controlled reactions provide the most direct method for producing these molecular ions in a laboratory setting, facilitating high-resolution spectroscopy critical for astronomical searches. A thorough understanding of how to optimize traditional high-resolution spectroscopy experiments will allow for more targeted and efficient laboratory searches for new metallic molecules, ultimately paving the way for their detection in astronomical observations.

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*Data availability*—The data supporting this study's findings are available within the article.

- R. C. Dunbar and S. Petrie, Interstellar and circumstellar reaction kinetics of Na<sup>+</sup>, Mg<sup>+</sup>, and Al<sup>+</sup> with cyanopolyynes and polyynes, Astrophys. J. 564, 792 (2002).
- [2] T. Tsuji, Molecular abundances in stellar atmospheres. II., Astron. Astrophys. 23, 411 (1973), https://ui.adsabs.harvard .edu/abs/1973A%26A....23..411T/abstract.
- [3] T. J. Millar, Chemistry in the circumstellar medium: Unveiling the dust formation zone, Astrophys. Space Sci. 313, 223 (2008).
- [4] B. E. Turner, Observations and chemistry of interstellar refractory elements, Astrophys. J. 376, 573 (1991).
- [5] B. E. Turner, Gaseous refractory-element molecules in IRC10216, Astrophys. Space Sci. 224, 297 (1995).
- [6] J. Cernicharo, L. Velilla-Prieto, M. Agúndez, J. R. Pardo, J. P. Fonfría, G. Quintana-Lacaci, C. Cabezas, C. Bermúdez, and M. Guélin, Discovery of the first Ca-bearing molecule in space: CaNC, Astron. Astrophys. 627, L4 (2019).
- [7] J. Cernicharo, C. Cabezas, J. R. Pardo, M. Agúndez, C. Bermúdez, L. Velilla-Prieto, F. Tercero, J. A. López-Pérez, J. D. Gallego, J. P. Fonfría *et al.*, Discovery of two new magnesium-bearing species in IRC + 10216: MgC<sub>3</sub>N and MgC<sub>4</sub>H, Astron. Astrophys. **630**, L2 (2019).
- [8] J. R. Pardo, C. Cabezas, J. P. Fonfría, M. Agúndez, B. Tercero, P. de Vicente, M. Guélin, and J. Cernicharo, Magnesium radicals MgC<sub>5</sub>N and MgC<sub>6</sub>H in IRC + 10216, Astron. Astrophys. 652, L13 (2021).
- [9] M. Agúndez, Molecules from evolved stars and their role in the cycle of the ISM, EPJ Web Conf. 265, 00029 (2022).
- [10] P. B. Changala, H. Gupta, J. Cernicharo, J. R. Pardo, M. Agúndez, C. Cabezas, B. Tercero, M. Guélin, and M. C. McCarthy, Laboratory and astronomical discovery of magnesium dicarbide, MgC<sub>2</sub>, Astrophys. J. Lett. **940**, L42 (2022).
- [11] C. Cabezas, J. R. Pardo, M. Agúndez, B. Tercero, N. Marcelino, Y. Endo, P. de Vicente, M. Guélin, and J. Cernicharo, Discovery of two metallic cyanoacetylides in IRC + 10216: HMgCCCN and NaCCCN, Astron. Astrophys. 672, L12 (2023).
- [12] J. Cernicharo, C. Cabezas, J. R. Pardo, M. Agúndez, O. Roncero, B. Tercero, N. Marcelino, M. Guélin, Y. Endo, and

P. de Vicente, The magnesium paradigm in IRC + 10216: Discovery of  $MgC_4H^+$ ,  $MgC_3N^+$ ,  $MgC_6H^+$ , and  $MgC_5N^+$ , Astron. Astrophys. **672**, L13 (2023).

- [13] H. Gupta, P. B. Changala, J. Cernicharo, J. R. Pardo, M. Agúndez, C. Cabezas, B. Tercero, M. Guélin, and M. C. McCarthy, Calcium chemistry in carbon-rich circumstellar environments: The laboratory and astronomical discovery of calcium dicarbide, CaC<sub>2</sub>, Astrophys. J. Lett. **966**, L28 (2024).
- [14] D. E. Woon, *Ab initio* characterization of MgCCH, MgCCH<sup>+</sup>, and MgC<sub>2</sub>, and pathways to their formation in the interstellar medium, Astrophys. J. **456** (1996).
- [15] M. Drewsen, I. Jensen, J. Lindballe, N. Nissen, R. Martinussen, A. Mortensen, P. Staanum, and D. Voigt, Ion Coulomb crystals: A tool for studying ion processes, Int. J. Mass Spectrom. 229, 83 (2003).
- [16] S. Willitsch, Coulomb-crystallised molecular ions in traps: Methods, applications, prospects, Int. Rev. Phys. Chem. 31, 175 (2012).
- [17] R. C. Thompson, Ion Coulomb crystals, Contemp. Phys. 56, 63 (2015).
- [18] B. R. Heazlewood and T. P. Softley, Low-temperature kinetics and dynamics with Coulomb crystals, Annu. Rev. Phys. Chem. 66, 475 (2015).
- [19] E. R. Hudson, Sympathetic cooling of molecular ions with ultracold atoms, EPJ Tech. Instrum. **3**, 1 (2016).
- [20] B. R. Heazlewood and H. J. Lewandowski, Chemistry using Coulomb crystals, in *Emerging Trends in Chemical Applications of Lasers* (2021), pp. 389–410, 10.1021/bk-2021-1398.ch017.
- [21] T. P. Softley, Cold and ultracold molecules in the twenties, Proc. R. Soc. A 479, 20220806 (2023).
- [22] M. Drewsen, L. Hornekær, N. Kjærgaard, K. Mølhave, A.-M. Thommesen, Z. Videsen, A. Mortensen, and F. Jensen, Ion coulomb crystals and some applications, AIP Conf. Proc. 606, 135 (2002).
- [23] K. Okada, M. Wada, L. Boesten, T. Nakamura, I. Katayama, and S. Ohtani, Acceleration of the chemical reaction of trapped Ca<sup>+</sup> ions with H<sub>2</sub>O molecules by laser excitation, J. Phys. B **36**, 33 (2002).
- [24] B. Roth, D. Offenberg, C. B. Zhang, and S. Schiller, Chemical reactions between cold trapped Ba<sup>+</sup> ions and neutral molecules in the gas phase, Phys. Rev. A 78, 042709 (2008).
- [25] A. D. Gingell, M. T. Bell, J. M. Oldham, T. P. Softley, and J. N. Harvey, Cold chemistry with electronically excited Ca<sup>+</sup> Coulomb crystals, J. Chem. Phys. **133** (2010).
- [26] F. H. J. Hall, M. Aymar, N. Bouloufa-Maafa, O. Dulieu, and S. Willitsch, Light-assisted ion-neutral reactive processes in the cold regime: Radiative molecule formation versus charge exchange, Phys. Rev. Lett. **107**, 243202 (2011).
- [27] N. Kimura, K. Okada, T. Takayanagi, M. Wada, S. Ohtani, and H. A. Schuessler, Sympathetic crystallization of CaH<sup>+</sup> produced by a laser-induced reaction, Phys. Rev. A 83, 033422 (2011).
- [28] L. Ratschbacher, C. Zipkes, C. Sias, and M. Köhl, Controlling chemical reactions of a single particle, Nat. Phys. 8, 649 (2012).
- [29] F. H. J. Hall, M. Aymar, M. Raoult, O. Dulieu, and S. Willitsch, Light-assisted cold chemical reactions of barium ions with rubidium atoms, Mol. Phys. 111, 1683 (2013).

- [30] R. Saito, S. Haze, M. Sasakawa, R. Nakai, M. Raoult, H. Da Silva Jr, O. Dulieu, and T. Mukaiyama, Characterization of charge-exchange collisions between ultracold <sup>6</sup>Li atoms and <sup>40</sup>Ca<sup>+</sup> ions, Phys. Rev. A **95**, 032709 (2017).
- [31] J. Joger, H. Fürst, N. Ewald, T. Feldker, M. Tomza, and R. Gerritsma, Observation of collisions between cold Li atoms and Yb<sup>+</sup> ions, Phys. Rev. A 96, 030703(R) (2017).
- [32] T. Yang, A. Li, G. K. Chen, C. Xie, A. G. Suits, W. C. Campbell, H. Guo, and E. R. Hudson, Optical control of reactions between water and laser-cooled Be<sup>+</sup> ions, J. Phys. Chem. Lett. 9, 3555 (2018).
- [33] J. Greenberg, P. C. Schmid, M. Miller, J. F. Stanton, and H. J. Lewandowski, Quantum-state-controlled reactions between molecular radicals and ions, Phys. Rev. A 98, 032702 (2018).
- [34] P. C. Schmid, M. I. Miller, J. Greenberg, T. L. Nguyen, J. F. Stanton, and H. J. Lewandowski, Quantum-state-specific reaction rate measurements for the photo-induced reaction  $Ca^+ + O_2 \rightarrow CaO^+ + O$ , Mol. Phys. **117**, 3036 (2019).
- [35] A. Kilaj, S. Käser, J. Wang, P. Straňák, M. Schwilk, L. Xu, O. A. von Lilienfeld, J. Küpper, M. Meuwly, and S. Willitsch, Conformational and state-specific effects in reactions of 2, 3-dibromobutadiene with Coulomb-crystallized calcium ions, Phys. Chem. Chem. Phys. 25, 13933 (2023).
- [36] P.C. Schmid, J. Greenberg, M.I. Miller, K. Loeffler, and H.J. Lewandowski, An ion trap time-of-flight

mass spectrometer with high mass resolution for cold trapped ion experiments, Rev. Sci. Instrum. **88**, 123107 (2017).

- [37] See Supplemental Material at http://link.aps.org/ supplemental/10.1103/PhysRevLett.134.203401 for Ca<sup>+</sup> state population simulations at -50 and 30 MHz, and a table summarizing the Ca<sup>+</sup> state population fractions and the observed rate constant (k') for each of the 8 points measured in this study, additional plots of the rate constant, k', versus  ${}^{2}S_{1/2}$  and  ${}^{2}D_{3/2}$ , and a reaction curve obtained for a 20 min reaction time.
- [38] M. J. Frisch *et al.*, Gaussian 16 Revision C.01 (2016), Gaussian Inc. Wallingford CT.
- [39] S. Petrie and R. C. Dunbar, Radiative association reactions of Na<sup>+</sup>, Mg<sup>+</sup>, and Al<sup>+</sup> with abundant interstellar molecules. Variational transition state theory calculations, J. Phys. Chem. A **104**, 4480 (2000).
- [40] S. Petrie, Circumstellar calcium chemistry, Aust. J. Chem. 57, 67 (2004).
- [41] R. C. Dunbar and S. Petrie, Main group metal ion chemistry in cold interstellar and circumstellar environments, AIP Conf. Proc. 855, 281 (2006).
- [42] J. H. Singleton, Practical guide to the use of bayardalpert ionization gauges, J. Vac. Sci. Technol. A 19, 1712 (2001).

## **End Matter**

Determining population fractions of Ca<sup>+</sup>—We probe the reactivity of Ca<sup>+</sup> ions in both their ground  $({}^{2}S_{1/2})$ and excited quantum-states  $({}^{2}P_{1/2}$  and  ${}^{2}D_{3/2})$ simultaneously by utilizing laser cooling techniques. The relative populations of Ca<sup>+</sup> in these three states can be controlled by adjusting the detuning of both cooling lasers. The population of Ca<sup>+</sup> in each of the three states is estimated by solving the 8-level optical Bloch equations (OBE) using the intensity of the fluorescence from the Coulomb crystal measured on an electronmultiplied charged-coupled device camera to constrain the model. This method, described in detail by Gingell et al. [25], allows us to predict the population distribution of Ca<sup>+</sup> in the three quantum states based on the cooling lasers detunings. The resulting quantum-state populations for the states studied here are shown in Fig. 5.

*Reaction measurements of*  $Ca^+ + C_2H_2$ —For a typical measurement for the  $Ca^+ + C_2H_2$  reaction, as shown in Fig. 6, growth of the CaCCH<sup>+</sup> is observed to be nearly linear, with a corresponding decrease of the ionic reactant,  $Ca^+$ , over the reaction time. Global fits to all data are carried out to determine the effective rate constant  $k_{eff}$  using Eqs. (1) and (2), the results of which are shown as the solid lines. To ensure uniformity between measurements when determining both  $k_{eff}$ 



FIG. 5. Estimated quantum-state populations for Ca<sup>+</sup> from the 8-level OBE at various 397 nm pump laser detunings, where the 866 nm repump laser is on resonance with the transition. The blue, green, and maroon curves represent the state populations of the  ${}^{2}S_{1/2}$ ,  ${}^{2}D_{3/2}$ , and  ${}^{2}P_{1/2}$  states, respectively. The vertical lines, labeled I–V, indicate the specific laser detuning parameters used for the separate measurements from which the state-dependent rate constants were derived. See Figs. S1 and S2 [37] for the detunings of the additional data points.



FIG. 6. A typical reaction measurement for the  $Ca^+ + C_2H_2$  reaction, showing the growth of CaCCH<sup>+</sup> (blue circles, left axis) and depletion of Ca<sup>+</sup> ions (orange circles, right axis). Each data point represents the mean and standard error of 6 measurements. The solid lines correspond to a fit using Eqs. (1) and (2) to the data to determine  $k_{eff}$ , where  $[C_2H_2]$  is held constant at  $2.62 \pm 0.08 \times 10^{-9}$  Torr.

and  $k_P$ , the concentration of  $C_2H_2$  is held constant throughout each reaction's measurements. This concentration is measured using a Bayard-Alpert ionization gauge, which has reduced accuracy at pressures below  $10^{-8}$  Torr [42]. As a result, the uncertainties provided represent statistical uncertainties in the measurements and do not reflect the accuracy of the ionization gauge.

For CaCCH<sup>+</sup>, the reaction is predicted to be most exothermic when Ca<sup>+</sup> is in the  ${}^{2}P_{1/2}$  state, at a value of ~1.68 eV. Similarly, for  $CaC_2H_2^+$ , the most exothermic channel is expected to be  $\sim 3.23$  eV. The trapping potential used in this experiment was 10.1 eV in the radial direction and 1.1 eV in the axial direction. The radial trapping potential exceeds the most exothermic channels of the reaction, so ions should not be lost in this direction. The trapping potential in the axial direction is less than the most exothermic channels, however, due to the trapping dynamics in this system it is still unlikely that ions would be lost in the axial direction. This is because as the ions travel along the axial axis, they will collide with the laser-cooled Ca<sup>+</sup>, which will remove energy with each collision. By the time the product ions reach the end cap, they will have undergone enough collisions such that the end cap potential acts as a repulsive barrier and prevents product ions from escaping. Importantly, we ensure no product ions are lost from the trap by measuring the total number of reactant ions and product ions at each time step and verifying charge conservation.