

## Reversing hydride-ion formation in quantum-information experiments with $\text{Be}^+$

Brian C. Sawyer,\* Justin G. Bohnet, Joseph W. Britton, and John J. Bollinger

*Time and Frequency Division, National Institute of Standards and Technology, Boulder, Colorado 80305, USA*

(Received 26 November 2014; published 12 January 2015)

We demonstrate photodissociation of  $\text{BeH}^+$  ions within a Coulomb crystal of thousands of  ${}^9\text{Be}^+$  ions confined in a Penning trap. Because  $\text{BeH}^+$  ions are created via exothermic reactions between trapped, laser-cooled  $\text{Be}^+(^2P_{3/2})$  and background  $\text{H}_2$  within the vacuum chamber, they represent a major contaminant species responsible for infidelities in large-scale trapped-ion quantum-information experiments. The rotational-state-insensitive dissociation scheme described here makes use of 157-nm photons to produce  $\text{Be}^+$  and  $\text{H}$  as products, thereby restoring  $\text{Be}^+$  ions without the need for reloading. This technique facilitates longer experiment runtimes at a given background  $\text{H}_2$  pressure and may be adapted for removal of  $\text{MgH}^+$  and  $\text{AlH}^+$  impurities.

DOI: 10.1103/PhysRevA.91.011401

PACS number(s): 33.80.Gj, 37.10.-x, 03.67.-a, 52.27.Jt

Crystals of laser-cooled atomic ions form the basis of many experimental realizations of quantum logic gates [1–3] and simulations of quantum many-body physics [4–6]. In room-temperature vacuum systems, collisions with neutral background gas molecules limit quantum coherences and quantum logic operations [7]. Here we focus on inelastic (i.e., reactive) collisions where exothermic chemical reactions with background gas molecules can generate, in both Penning and radiofrequency (rf) traps, cotrapped molecular ions over a wide range of trapping conditions and crystal geometries [6–9]. These contaminants alter ion-crystal eigenfrequencies and can complicate quantum logic interactions [10]. Impurities may be resonantly ejected from both rf and Penning traps, but this technique is least efficient when the impurities are similar in mass to the qubit ion [11]. The rate of impurity ion formation increases linearly with the number of ion qubits in the register and the time required for loading new ions and recalibrating the register increases with the size of the system. Therefore, experimental techniques to prevent or reverse qubit-ion chemistry will be a key tool for many-ion quantum-information platforms. In this Rapid Communication we experimentally demonstrate a rotationally insensitive photodissociation (PD) technique for  $\text{BeH}^+$  accumulated within a  ${}^9\text{Be}^+$  Coulomb crystal. Beryllium ions have found frequent use in quantum-information experiments because their light mass results in tight trap confinement.

Photodissociation of molecular ions is a topic of significant interest in the atomic and chemical physics communities. Recent experimental demonstrations with trapped heteronuclear diatomic molecular ions include  $\text{MgH}^+$  [9,12],  $\text{CaH}^+/\text{CaD}^+$  [13],  $\text{HD}^+$  [14],  $\text{AlH}^+$  [15],  $\text{Hff}^+$  [16],  $\text{SrCl}^+$  [17], and  $\text{BaCl}^+$  [18]. Given the difficulty of detecting scattered photons from dilute molecular-ion samples, rotational-state-selective PD has emerged as a critical tool for molecular ion spectroscopy [15,19] and precision measurements [16,20], while rotationally insensitive dissociation schemes provide valuable tests of molecular theory [13,17,18].

Figure 1(a) shows an illustration of the Penning trap used for this work. The trap assembly is installed in the room-temperature bore of a superconducting magnet that produces a uniform, vertical magnetic field  $B$  of  $\sim 4.46$  T. The

experiment trap region consists of 12 Au-coated Ti electrodes; eight are visible in the cross section view of Fig. 1(a). Ions are confined in the vertical  $z$  direction by a quadrupole electric field  $E$  generated through application of static voltages to the trap electrodes. Radial  $r$  confinement results from  $(\vec{E} \times \vec{B})$ -induced rotation through the magnetic field. In a frame of reference rotating with the ions, confinement is described by

$$q\Phi_{\text{rot}}(r,z) = \frac{1}{2}M\omega_z^2(z^2 + \beta_r r^2), \quad (1)$$

$$\beta_r \equiv \frac{\omega_r(\Omega_c - \omega_r)}{\omega_z^2} - \frac{1}{2}, \quad (2)$$

where  $\omega_z$  is the axial confinement frequency,  $q$  ( $M$ ) is the ion charge (mass),  $\Omega_c$  is the cyclotron frequency, and  $\omega_r$  is the ion rotation frequency. For this work, we obtain an axial frequency of  $\omega_z \sim 2\pi \times 900$  kHz by applying a combination

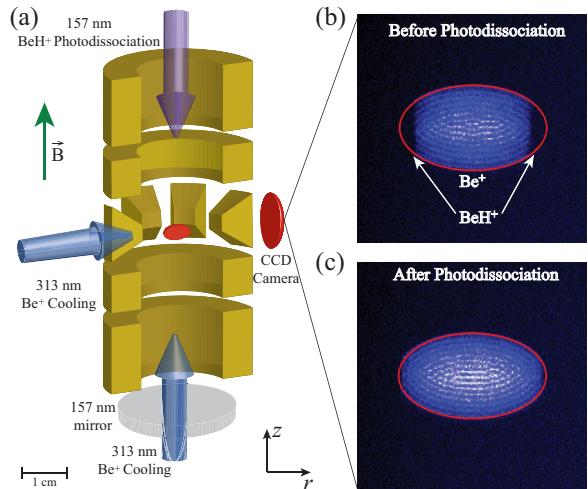


FIG. 1. (Color online) (a) Illustration of the experiment trap electrode assembly in cross section with routing of laser beams for Doppler cooling of  $\text{Be}^+$  and photodissociation of  $\text{BeH}^+$ . A spheroidal ion cloud is depicted at the center of the trap. The vertical axis of the electrode stack is aligned to the external, uniform magnetic field of 4.46 T. Also shown are side view images of the trapped Coulomb crystal of  $\sim 1.2 \times 10^4$  ions (b) before and (c) after 9000 pulses of 157-nm photodissociation light at 1.6 mJ/pulse. We measure an increase in the  $\text{Be}^+$  fraction from 81% to 97% of the constant total ion number in the crystal. Each image is  $1.2 \times 1.2$  mm $^2$ .

\*brian.sawyer@boulder.nist.gov

of 0 V to the top and bottom rings of Fig. 1(a), −400 V to all central segmented electrodes, and −200 V to the two interior ring electrodes. The ion-electrode distance is 1 cm. We apply a radial dipole rotating wall potential to the azimuthally segmented central electrodes to control the rotation frequency of the ion cloud, thereby controlling the aspect ratio of the trap potential according to Eqs. (1) and (2) [21]. With  $\omega_z = 2\pi \times 900$  kHz and  $\Omega_c = 2\pi \times 7.6$  MHz,  ${}^9\text{Be}^+$  ions experience radial confinement for  $53.7$  kHz  $< \omega_r/2\pi < 7.55$  MHz. For all experimental data presented here, we operate with  $\omega_r = 2\pi \times 110$  kHz.

Our Doppler-laser-cooling scheme for  ${}^9\text{Be}^+$  is as described in [6,22,23]. Briefly, we apply  $\sim 313$ –nm laser beams along both the axial and radial trap dimensions to produce a Coulomb crystal. The cycling transition between the  $|J=1/2, m_J=+1/2\rangle (^2S)$  and  $|3/2, +3/2\rangle (^2P)$  states yields a Doppler-cooling limit of  $\sim 1$  mK, where  $J$  and  $m_J$  are the total electronic angular momentum and its projection along the magnetic field axis, respectively. This laser cooling leads to the formation of  $\text{BeH}^+$  impurities. Since the reaction  $\text{Be}^+({}^2S) + \text{H}_2 \rightarrow \text{BeH}^+ + \text{H}$  is endothermic by 1.57 eV, only  $\text{Be}^+$  in an excited (e.g.,  ${}^2P$ ) state can react to form  $\text{BeH}^+$  [24]. As a result, the reaction rate may be varied by adjusting the saturation parameter  $s = I_c/I_{\text{sat}}$  of the  $\text{Be}^+$  cooling laser [8]. Here  $I_c$  is the cooling laser intensity and  $I_{\text{sat}} \sim 300$  mW cm $^{-2}$  is the saturation intensity of the cycling transition assuming linear polarization perpendicular to the trap  $B$  field. Previous work has shown that the reaction rate  $k_L$  between  $\text{Be}^+({}^2P)$  and  $\text{H}_2$  is in good agreement with estimates from a Langevin capture model [8], which gives  $k_L \sim 1.6 \times 10^{-9}$  cm $^3$  s $^{-1}$ .

In Fig. 2(a) we present the six lowest-energy electronic states of the  $\text{BeH}^+$  molecule as calculated in [25,26]. The given electronic states all asymptotically approach  $\text{Be}^+ + \text{H}$  at large internuclear separation; the  $\text{BeH}^+$  asymptotes possess larger energies. The ground state of  $\text{BeH}^+$  exhibits  ${}^1\Sigma^+$  symmetry, which allows for electric dipole transitions to the spin-singlet excited states  $A {}^1\Sigma^+$  and  $B {}^1\Pi$ . The minimum of the  $B {}^1\Pi$  potential is sufficiently shifted from that of the  $X {}^1\Sigma^+$  to provide a pathway for single-photon photodissociation from the lowest vibrational level ( $v'' = 0$ ) of the ground electronic state. The  $\text{BeH}^+$  ions are sympathetically cooled by the laser-cooled  $\text{Be}^+$  ions. Previous studies indicate a strong sympathetic cooling of the axial motion of the  $\text{BeH}^+$  with a resulting temperature of  $\sim 1$  mK and the formation of a centrifugally separated  $\text{BeH}^+$  crystal outside of the  $\text{Be}^+$  ions [27]. However, the cyclotron motion of the  $\text{BeH}^+$  decouples from the axial motion and is only cooled to  $\sim 1$  K. The  $\text{BeH}^+$  internal degrees of freedom are in equilibrium with the 300 K blackbody radiation of the trap chamber. At room temperature, less than 0.01% of  $\text{BeH}^+$  populate excited vibrational states, but the lowest  $\sim 10$  rotational states are thermally populated. Resonance-enhanced multiphoton dissociation, while useful for molecular ion spectroscopy [8,9,15,16], is rotational-state selective and would require a widely tunable laser for our goal of complete  $\text{BeH}^+$  removal. In the present Rapid Communication we couple the  $X {}^1\Sigma^+$  rotational states directly to the continuum with a single photon. Vibrational wave functions corresponding to the relevant bound [ $X {}^1\Sigma^+(v'' = 0)$ ] and free-particle ( $B {}^1\Pi$ ) states [see Fig. 2(a)] are calculated by numerically solving

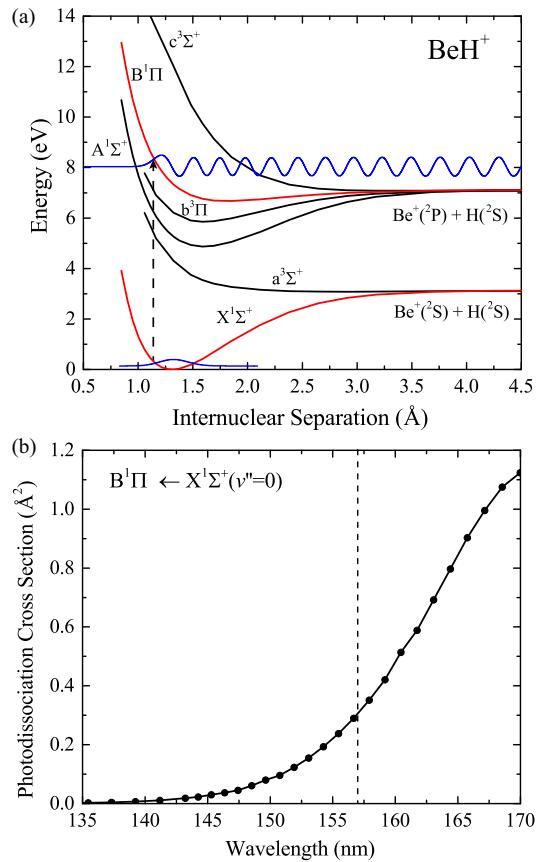


FIG. 2. (Color online) (a) Low-lying electronic states of the  $\text{BeH}^+$  molecular ion as calculated in Refs. [25,26]. We excite the  $B {}^1\Pi \leftarrow X {}^1\Sigma^+(v'' = 0)$  transition above the dissociation threshold to produce  $\text{Be}^+$  and  $\text{H}$  as given by the  $B {}^1\Pi$  asymptote. Relevant wave functions calculated as numerical solutions to the radial Schrödinger equation are depicted in blue (not drawn to scale). The vertical dashed arrow indicates the 157-nm excitation wavelength used for this work. (b) Calculated thermally averaged photodissociation cross section versus photon wavelength for the transition of interest. The vertical dashed line indicates the 157-nm excitation wavelength used for this work. The calculation is truncated at 170 nm, which is  $\sim 0.1$  eV above the dissociation threshold of the  $B {}^1\Pi$  potential.

the one-dimensional Schrödinger equation with the given electronic potentials [28].

Given the level structure of Fig. 2(a), we calculate the PD cross section for each ground rotational state  $J''$  as [29]

$$\sigma(J'') = \frac{4\pi^2}{e^2} \alpha \mu_{\text{trans}}^2 E_{\text{ph}} \left| \int_0^\infty \phi(E, R) \psi_{v''=0}(R) dR \right|^2 \times \sum_{J'm'_J m''_J} \frac{\left| \langle \Pi, J', m'_J | \hat{T}_{-1}^{(1)} + \hat{T}_{+1}^{(1)} | \Sigma, J'', m''_J \rangle \right|^2}{2(2J'' + 1)}, \quad (3)$$

where  $\alpha$  is the fine-structure constant,  $e$  ( $a_0$ ) is the electron charge (Bohr radius),  $\mu_{\text{trans}} = 1.136 ea_0$  is the  $B {}^1\Pi \leftarrow X {}^1\Sigma^+$  transition dipole moment calculated in [25,26],  $E_{\text{ph}}$  is the photon energy,  $\phi(E, R)$  is upper-state vibrational wave function with energy  $E$  above the dissociation threshold,  $\psi_{v''=0}(R)$  is the bound-state vibrational wave function, and  $R$  is the internuclear separation. A double prime indicates a lower state

and a single prime indicates an upper state throughout this Rapid Communication. The  $\hat{T}_{\pm 1}^{(1)}$  operators are dimensionless rank-1 spherical tensors signifying electric dipole coupling with linearly polarized photons propagating along  $z$  [see Fig. 1(a)].

To calculate the vibrational overlap of the bound and free states (i.e., Franck-Condon density) over a range of excitation wavelengths, we numerically solve the one-dimensional Schrödinger equation for each upper-state energy  $E$  and subsequently compute the overlap of each with the ground vibrational wave function. Finally, to produce the cross-section curve of Fig. 2(b) we perform a thermal average over rotational states  $0 \leq J'' \leq 20$  as

$$\langle \sigma(J'') \rangle_{\text{th}} \equiv Z^{-1} \sum_{J''=0}^{20} (2J'' + 1) \sigma(J'') \exp(-E_{J''}/k_b T). \quad (4)$$

In Eq. (4)  $Z$  is the partition function,  $k_b$  is Boltzmann's constant,  $T$  is room temperature, and  $E_{J''}$  is the relative energy of level  $J''$ . Note that the  $B^1\Pi$  state is predicted to support at least eight bound vibrational levels [25,26], but we neglect any off-resonance couplings to such bound states for this work as the long-wavelength limit of the cross-section calculation of Fig. 2(b) is  $\sim 0.1$  eV above the dissociation energy of the  $B^1\Pi$  potential. We additionally neglect the Penning trap magnetic field and  $\text{BeH}^+$  hyperfine structure in calculating state energies; both are small compared to the breadth of the photodissociation cross section of Fig. 2(b).

Figure 2(b) suggests a photon wavelength of  $\sim 170$  nm for the maximum PD rate. However, given the technical difficulty of making laser sources in the vacuum ultraviolet (vuv), we use a commercial excimer laser operating with  $\text{F}_2$  gas to produce 157-nm pulses with 5-ns width and a repetition rate of 500 Hz at  $\leq 2$  mJ per pulse. Molecular oxygen absorbs strongly near 160 nm, thus the entire laser beam path is purged with high-purity  $\text{N}_2$  gas so that only  $\sim 10\%$  of the beam energy is absorbed before entering the trap vacuum system through a  $\text{CaF}_2$  viewport. We measure an exponential decay length of  $\sim 8.2$  m with the  $\text{N}_2$  purge gas, while the out-of-vacuum path length from excimer laser to  $\text{CaF}_2$  viewport is 1.25 m. As depicted in Fig. 1, the excimer beam is aligned to the parallel Doppler-cooling laser beam and propagates in the opposite direction along the trap magnetic field to the ion crystal. We have installed a normal-incidence mirror with a 157-nm reflectance of  $\sim 88\%$  below the trap electrodes in order to shield a fused silica viewport at the bottom of the trap vacuum apparatus from the high-intensity vuv illumination. This dielectric-coated mirror transmits  $\sim 89\%$  of the 313-nm cooling beam intensity. Ideally, the excimer beam should be aligned such that it is reflected back along the incoming beam path, exiting the vacuum chamber through the  $\text{CaF}_2$  viewport. Geometric constraints with our current trap chamber preclude this; these constraints also cause partial blockage of the excimer beam before it enters the experimental trap zone. In the absence of blockage, we calculate a rectangular excimer beam waist at the ions of  $\sim 1.7 \times 0.85$  mm $^2$  due to our use of a  $\text{CaF}_2$  spherical lens with a focal length of 85 cm placed a distance of 1.3 m upstream from the ion crystal. This beam waist combined with the 2-mJ pulse energy gives an average intensity of  $21$  W cm $^{-2}$ .

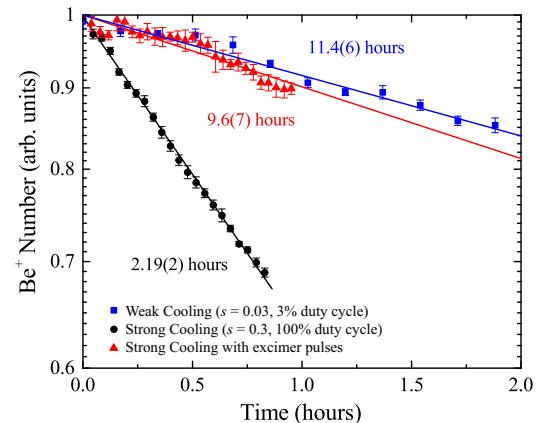


FIG. 3. (Color online) Measured (points with error bars) and fit (solid lines)  $\text{Be}^+$  exponential decay plotted on a logarithmic vertical scale. Each of the three data sets consists of one experimental run and vertical error bars represent one standard deviation. With a saturation parameter  $s$  of 0.03 and a 3% duty cycle (weak cooling), we measure a  $\text{Be}^+$  lifetime of 11.4(6) h that is limited by chemistry with background gas molecules other than  $\text{H}_2$  (■). Using a greater than 300 $\times$  larger photon flux for Doppler cooling (●), the  $\text{Be}^+$  number decays with a 2.19(2)-h time constant that is consistent with an  $\text{H}_2$  background pressure of  $7 \times 10^{-9}$  Pa ( $5 \times 10^{-11}$  Torr). To mitigate  $\text{BeH}^+$  production, we trigger 200 pulses (500-Hz repetition rate) of a 157-nm excimer laser every 2 min (▲). The resulting rate of  $\text{BeH}^+$  photodissociation is sufficient to increase the  $\text{Be}^+$  lifetime by a factor of 4.4(3) to be roughly consistent with the weak-cooling measurements.

Figure 1 shows images of  $\text{Be}^+$  ion crystals with  $\omega_r = 2\pi \times 110$  kHz before [Fig. 1(b)] and after [Fig. 1(c)] a photodissociation sequence of 9000 pulses at 1.6 mJ each. Three-dimensional ion crystals form elliptical boundaries in the Penning trap potential of Eq. (1). The outer edges of the crystal of Fig. 1(b) are dark due to heavier-mass impurity ions that centrifugally separate under the rotation of the crystal. After photodissociation, we observe that the elliptical boundary is restored with fluorescing  $\text{Be}^+$  and the total volume of the crystal is unchanged, indicating a conservation of total ion number. Fits to the  $\text{Be}^+$  fraction in the images of Figs. 1(b) and 1(c) show that we have increased from 81% to 97%  $\text{Be}^+$  and cyclotron resonance data reveal the presence of  $\text{BeO}^+$  and  $\text{BeOH}^+$  molecules in the remaining dark regions of Fig. 1(c) [30]. We note that no protons are observed within the Coulomb crystal after PD, thereby confirming the asymptote of the theoretical  $B^1\Pi$  potential of Fig. 2(a) [25,26].

To demonstrate the efficacy of this  $\text{BeH}^+$  photodissociation technique for quantum-information experiments, we measure single-exponential  $\text{Be}^+$  number decay due to conversion to impurity ions under three different conditions as shown in Fig. 3: weak Doppler laser cooling (blue squares), strong cooling (black circles), and strong cooling in the presence of photodissociation pulses (red triangles). In all cases, the relative  $\text{Be}^+$  number corresponds to the Doppler-cooling fluorescence count rate as measured on an ultraviolet-sensitive photomultiplier tube. We measure a maximum  $\text{Be}^+$  lifetime of 11.4(6) h by minimizing the parallel Doppler-cooling photon flux to a 3% duty cycle and  $s = 0.03$  saturation parameter,

thereby producing  $\text{BeH}^+$  impurities with a predicted time constant greater than 200 h. The significantly shorter 11.4(6)-h measured lifetime appears to be due to  $\text{Be}^+$  collisions with background gas molecules that produce heavier impurity ions in the absence of any Doppler-cooling light. Neutral alcohol molecules such as acetone [ $(\text{CH}_2)_3\text{CO}$ ] and/or methanol ( $\text{CH}_3\text{OH}$ ), both of which were used to clean the vacuum components, undergo exothermic reactions with ground-state  $\text{Be}^+$  and Langevin cross section estimates presented in the Appendix suggest that partial pressures of  $\sim 10^{-11}$  Pa ( $10^{-13}$  Torr) could explain both the observed conversion rate and the detected  $\text{BeO}^+$  and  $\text{BeOH}^+$  impurities [30].

After increasing the Doppler-cooling parameters to  $s = 0.3$  at 100% duty cycle, the  $\text{Be}^+$  trap lifetime drops to 2.19(2) h (black circles), consistent with a background  $\text{H}_2$  pressure of  $\sim 7 \times 10^{-9}$  Pa ( $\sim 5 \times 10^{-11}$  Torr) as  $\text{BeH}^+$  production dominates all other  $\text{Be}^+$  conversion rates. The unit duty cycle for Doppler cooling is representative of typical trapped-ion quantum-information work where the time for cooling and preparing initial qubit states is a significant fraction of the experimental sequence [6,31,32]. To demonstrate PD, we apply 200-pulse bursts of the excimer laser every 2 min with a pulse energy of 1.9 mJ and repetition rate of 500 Hz in the regime of strong cooling (red triangles). The total time for each pulse burst is 0.4 s and the Doppler cooling is switched off for this duration as well as 2 s after the photodissociation sequence, yielding a negligibly modified strong cooling duty cycle of  $\sim 98\%$ . The PD pulses yield an increased time constant for decay of 9.6(7) h, which is roughly consistent with the weak-cooling result. The small difference between the 11.4- and 9.6-h time constants is likely the result of daily fluctuations in background gas pressure. A high rate (i.e., every 2 min) of PD pulses is necessary to maintain a pure  $\text{Be}^+$  crystal since we observe that  $\text{BeH}^+$  converts to  $\text{BeO}^+$  and  $\text{BeOH}^+$  at a rate three times faster than  $\text{Be}^+(^2P) + \text{H}_2 \rightarrow \text{BeH}^+ + \text{H}$  conversion under strong-cooling conditions.

In conclusion, we have demonstrated photodissociation results exploiting the  $B^1\Pi \leftarrow X^1\Sigma^+$  electronic transition in  $\text{BeH}^+$ . This technique removes an important limitation for large-scale quantum-information experiments that rely on  $\text{Be}^+$  and does so with a commercially available turnkey laser system. We achieve a more than fourfold increase in experimental runtime with a 2% reduction of the duty cycle. Improved beam alignment would enable an experimental determination of the absolute PD cross section at 157 nm as well as optimization of the dissociation beam profile. We predict a maximum  $\text{BeH}^+$  PD rate of  $\sim 1.2 \text{ pulse}^{-1}$  from our estimated PD beam average intensity of  $21 \text{ W cm}^{-2}$  and the theory results of Fig. 2(b). The observed PD rate is lower presumably due to partial excimer beam obstruction along the 1.3-m in-vacuum path. We estimate that a 193-nm ArF excimer laser will dissociate  $\text{MgH}^+$  [33] and  $\text{AlH}^+$  [15] with dissociation cross sections of  $\sim 0.4$  and  $\sim 10^{-3} \text{ \AA}^2$ , respectively, making this technique applicable for removing a number of experimentally relevant impurity species.

This work was supported by NIST. This research was performed while J.G.B. held a National Research Council Research Associateship Award at NIST. The authors thank

E. R. Hudson, K. Chen, and J. L. Bohn for useful discussions as well as D. T. C. Allcock and Y. Wan for comments on the manuscript. This manuscript is a contribution of NIST and not subject to US copyright.

## APPENDIX: ESTIMATING $C_4$ COEFFICIENTS FOR POLAR MOLECULE-ION CHEMISTRY

As described in [7,34], we define the Langevin capture cross section between an ion and polarizable neutral particle as

$$\sigma_L = 2\pi \sqrt{\frac{C_4}{E_c}}, \quad (\text{A1})$$

where  $E_c$  is the ion-neutral collision energy and  $C_4$  is the coefficient of the attractive interaction potential between scatterers whose magnitude is proportional to  $R^{-4}$ , where  $R$  is the particle separation. Equation (A1) reveals the unique property of  $C_4$  collisions that the Langevin rate

$$k_L = \sigma_L v_{\text{rel}} = 2\pi \sqrt{\frac{2C_4}{M}} \quad (\text{A2})$$

is independent of collision energy, where  $v_{\text{rel}}(M)$  is the relative velocity (reduced mass) of the scatterers. To obtain the  $C_4$  coefficient for ion-neutral collisions, we begin with the energy shift  $W$  of a particle with polarizability  $\alpha_{\text{pol}}$  in the electric field  $E$  of an ion:

$$W = \frac{1}{2}\alpha_{\text{pol}}|E|^2 \quad (\text{A3})$$

$$= \frac{\alpha_{\text{pol}}}{2} \frac{e^2}{(4\pi\epsilon_0)^2 R^4}. \quad (\text{A4})$$

From Eq. (A4) we obtain the  $C_4$  coefficient necessary for evaluating  $k_L$ :

$$C_4 = \frac{\alpha_{\text{pol}} e^2}{2(4\pi\epsilon_0)^2}. \quad (\text{A5})$$

For colliding molecules with a permanent electric dipole moment  $\mu$  as defined in the molecule-fixed frame, one can calculate the polarizability  $\alpha_{JK}$  from the second-order Stark shift for a given rotational level  $J$  and projection  $K$  given in [35]:

$$\alpha_{JK} = \frac{1}{2J+1} \frac{\mu^2}{B} \sum_{m_J=-J}^J \left[ \frac{(J^2 - K^2)(J^2 - m_J^2)}{J^3(2J-1)(2J+1)} \right. \\ \left. - \frac{[(J+1)^2 - K^2][(J+1)^2 - m_J^2]}{(J+1)^3(2J+1)(2J+3)} \right]. \quad (\text{A6})$$

In this equation, each  $J$  level is coupled to its two nearest neighbors and  $B$  is the rotational constant. The quantum number  $K$  ( $m_J$ ) is the projection of  $J$  along the molecule symmetry (external field) axis. Both  $K$  and  $m_J$  may take the values  $\{-J, -J+1, \dots, J-1, J\}$  and Stark shifts for opposite-sign projections are identical under an external electric field. Equation (A6) represents the polarizability of the level  $(J, K)$  averaged over all possible projections  $m_J$ .

Specializing to methanol ( $\text{CH}_3\text{OH}, \mu = 0.67ea_0$ ), we begin with the rotational constants  $A = 4.222 \text{ cm}^{-1}$ ,  $B = 0.822 \text{ cm}^{-1}$ , and  $C = 0.792 \text{ cm}^{-1}$ . Since  $B \sim C$ ,

methanol is a slightly asymmetric prolate top. For this analysis, we treat methanol as a pure symmetric top whose energy levels  $U_{JK}$  are given by

$$U_{JK} = \left(\frac{B+C}{2}\right)J(J+1) + \left(A - \frac{B+C}{2}\right)K^2. \quad (\text{A7})$$

Since background molecules in the vacuum chamber are assumed to be at room temperature, we must compute a temperature-averaged polarizability if many rotational states lie below  $k_b T \sim 209 \text{ cm}^{-1}$ . With the usual Boltzmann weighting, we obtain

$$\langle\alpha_{JK}\rangle_{\text{th}} = Z^{-1} \sum_{J=0}^{50} (2J+1) \sum_{K=-J}^{+J} e^{-U_{JK}/k_b T} \alpha_{JK}, \quad (\text{A8})$$

where  $Z$  is the partition function. Including all states up to  $J = 50$ , we obtain the following average polarizability for

- methanol:
- $$\langle\alpha_{JK}\rangle_{\text{th}} \sim 2.23 \times 10^{-39} \text{ C m}^2 \text{ V}^{-1}. \quad (\text{A9})$$
- Using the above thermally averaged polarizability, we compute the Langevin reaction rate for  $\text{Be}^+$ -methanol collisions:
- $$k_L = 2\pi \sqrt{\frac{e^2 \langle\alpha_{JK}\rangle_{\text{th}}}{M(4\pi\epsilon_0)^2}} \quad (\text{A10})$$
- $$\sim 4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}. \quad (\text{A11})$$
- With a  $\text{Be}^+$  decay time constant of  $\tau = 11.4 \text{ h}$ , we extract a background methanol density estimate of
- $$\rho_{\text{methanol}} = (k_L \tau)^{-1} \quad (\text{A12})$$
- $$\sim 6.2 \times 10^3 \text{ cm}^{-3} \quad (\text{A13})$$
- $$\sim 2 \times 10^{-13} \text{ Torr}. \quad (\text{A14})$$
- 
- [1] C. Ospelkaus, U. Warring, Y. Colombe, K. R. Brown, J. M. Amini, D. Leibfried, and D. J. Wineland, *Nature (London)* **476**, 181 (2011).
  - [2] T. Monz, P. Schindler, J. T. Barreiro, M. Chwalla, D. Nigg, W. A. Coish, M. Harlander, W. Hänsel, M. Hennrich, and R. Blatt, *Phys. Rev. Lett.* **106**, 130506 (2011).
  - [3] Y. Lin, J. P. Gaebler, F. Reiter, T. R. Tan, R. Bowler, A. S. Sorensen, D. Leibfried, and D. J. Wineland, *Nature (London)* **504**, 415 (2013).
  - [4] P. Richerme, Z.-X. Gong, A. Lee, C. Senko, J. Smith, M. Foss-Feig, S. Michalakis, A. V. Gorshkov, and C. Monroe, *Nature (London)* **511**, 198 (2014).
  - [5] P. Jurcevic, B. P. Lanyon, P. Hauke, C. Hempel, P. Zoller, R. Blatt, and C. F. Roos, *Nature (London)* **511**, 202 (2014).
  - [6] J. W. Britton, B. C. Sawyer, A. C. Keith, C.-C. J. Wang, J. K. Freericks, H. Uys, M. J. Biercuk, and J. J. Bollinger, *Nature (London)* **484**, 489 (2012).
  - [7] D. J. Wineland, C. Monroe, W. M. Itano, D. Leibfried, B. King, and D. M. Meek, *J. Res. NIST* **103**, 259 (1998).
  - [8] B. Roth, P. Blythe, H. Wenz, H. Daerr, and S. Schiller, *Phys. Rev. A* **73**, 042712 (2006).
  - [9] A. Bertelsen, I. S. Vogelius, S. Jorgensen, R. Kosloff, and M. Drewsen, *Eur. Phys. J. D* **31**, 403 (2004).
  - [10] M. McAneny, B. Yoshimura, and J. K. Freericks, *Phys. Rev. A* **88**, 043434 (2013).
  - [11] P. B. Grosshans and A. G. Marshall, *Int. J. Mass. Spectrom. Ion Processes* **100**, 347 (1990).
  - [12] S. Kahra, G. Leschhorn, M. Kowalewski, A. Schiffrin, E. B. adn W. Fuß, R. de Vivie-Riedle, R. Ernstorfer, F. Krausz, R. Kienberger, and T. Schaetz, *Nat. Phys.* **8**, 238 (2012).
  - [13] A. K. Hansen, M. A. Sørensen, P. F. Staunum, and M. Drewsen, *Angew. Chem. Int. Ed.* **51**, 7960 (2014).
  - [14] J. Shen, A. Borodin, M. Hansen, and S. Schiller, *Phys. Rev. A* **85**, 032519 (2012).
  - [15] C. S. Seck, E. G. Hohenstein, C.-Y. Lien, P. R. Stollenwerk, and B. C. Odom, *J. Mol. Spectrosc.* **300**, 108 (2014).
  - [16] K.-K. Ni, H. Loh, M. Grau, K. C. Cossel, J. Ye, and E. A. Cornell, *J. Mol. Spectrosc.* **300**, 12 (2014).
  - [17] P. Puri, S. J. Schowalter, S. Kotchigova, A. Petrov, and E. R. Hudson, *J. Chem. Phys.* **141**, 014309 (2014).
  - [18] K. Chen, S. J. Schowalter, S. Kotchigova, A. Petrov, W. G. Rellergert, S. T. Sullivan, and E. R. Hudson, *Phys. Rev. A* **83**, 030501(R) (2011).
  - [19] O. O. Versolato, M. Schwarz, A. K. Hansen, A. D. Gingell, A. Windberger, Ł. Kłosowski, J. Ullrich, F. Jensen, J. R. Crespo López-Urrutia, and M. Drewsen, *Phys. Rev. Lett.* **111**, 053002 (2013).
  - [20] U. Bressel, A. Borodin, J. Shen, M. Hansen, I. Ernsting, and S. Schiller, *Phys. Rev. Lett.* **108**, 183003 (2012).
  - [21] X.-P. Huang, J. J. Bollinger, T. B. Mitchell, W. M. Itano, and D. H. E. Dubin, *Phys. Plasmas* **5**, 1656 (1998).
  - [22] B. C. Sawyer, J. W. Britton, A. C. Keith, C.-C. J. Wang, J. K. Freericks, H. Uys, M. J. Biercuk, and J. J. Bollinger, *Phys. Rev. Lett.* **108**, 213003 (2012).
  - [23] B. C. Sawyer, J. W. Britton, and J. J. Bollinger, *Phys. Rev. A* **89**, 033408 (2014).
  - [24] M. Raimondi and J. Gerratt, *J. Chem. Phys.* **79**, 4339 (1983).
  - [25] F. B. C. Machado and F. R. Ornella, *J. Chem. Phys.* **94**, 7237 (1991).
  - [26] M. Farjallah, C. Ghanmi, and H. Berriche, *Eur. Phys. J. D* **67**, 245 (2013).
  - [27] M. J. Jensen, T. Hasegawa, J. J. Bollinger, and D. H. E. Dubin, *Phys. Rev. Lett.* **94**, 025001 (2005).
  - [28] B. R. Johnson, *J. Chem. Phys.* **67**, 4086 (1977).
  - [29] S. J. Singer, K. F. Freed, and Y. B. Band, *J. Chem. Phys.* **79**, 6060 (1983).
  - [30] We use laser-cooled fluorescence mass spectroscopy on the cyclotron resonance of the impurity ions to determine their charge-to-mass ratio. As an example, see T. Baba and I. Wakil, *Jpn. J. Appl. Phys.* **35**, L1134 (1996).
  - [31] J. P. Home, D. Hanneke, J. D. Jost, J. M. Amini, D. Leibfried, and D. J. Wineland, *Science* **325**, 1227 (2009).
  - [32] K. Kim, S. Korenblit, R. Islam, E. E. Edwards, M.-S. Chang, C. Noh, H. Carmichael, G.-D. Lin, L.-M. Duane, C.-C. J. Wang *et al.*, *New J. Phys.* **13**, 105003 (2011).
  - [33] M. Aymar, R. Guérout, M. Sahlaoui, and O. Dulieu, *J. Phys. B* **42**, 154025 (2009).
  - [34] M. T. Bell and T. P. Softley, *Mol. Phys.* **107**, 99 (2009).
  - [35] C. H. Townes and A. L. Schawlow, *Microwave Spectroscopy* (Dover, New York, 1975).