



## PAPER

Determining reaction pathways at low temperatures by isotopic substitution: the case of  $\text{BeD}^+ + \text{H}_2\text{O}$ 

## OPEN ACCESS

RECEIVED  
10 August 2021REVISED  
14 September 2021ACCEPTED FOR PUBLICATION  
28 September 2021PUBLISHED  
28 October 2021

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E-mail: [yangtg@sustech.edu.cn](mailto:yangtg@sustech.edu.cn) and [bin.zhao@uni-bielefeld.de](mailto:bin.zhao@uni-bielefeld.de)**Keywords:** trapped ions, quantum information, cold reactionsSupplementary material for this article is available [online](#)**Abstract**

Trapped  $\text{Be}^+$  ions are a leading platform for quantum information science (Gaebler *et al* 2016 *Phys. Rev. Lett.* **117** 060505), but reactions with background gas species, such as  $\text{H}_2$  and  $\text{H}_2\text{O}$ , result in qubit loss. Our experiment reveals that the  $\text{BeOH}^+$  ion is the final trapped ion species when both  $\text{H}_2$  and  $\text{H}_2\text{O}$  exist in a vacuum system with cold, trapped  $\text{Be}^+$ . The  $\text{BeH}^+$  product in the  $\text{Be}^+ + \text{H}_2$  reaction further reacts with  $\text{H}_2\text{O}$  to form  $\text{BeOH}^+$ . To understand the loss mechanism, low-temperature reactions between sympathetically cooled  $\text{BeD}^+$  ions and  $\text{H}_2\text{O}$  molecules have been investigated using an integrated, laser-cooled  $\text{Be}^+$  ion trap and high-resolution time-of-flight mass spectrometer (Schneider *et al* 2014 *Phys. Rev. Appl.* **2** 034013). Among all the possible products,  $\text{BeH}_2\text{O}^+$ ,  $\text{H}_2\text{DO}^+$ ,  $\text{BeOD}^+$ , and  $\text{BeOH}^+$ , only the  $\text{BeOH}^+$  molecular ion was observed experimentally, with the assumed co-product of HD. Theoretical analyses based on explicitly correlated restricted coupled cluster singles, doubles, and perturbative triples (RCCSD(T)-F12) method with the augmented correlation-consistent polarized triple zeta (AVTZ) basis set reveal that two intuitive direct abstraction product channels,  $\text{Be} + \text{H}_2\text{DO}^+$  and  $\text{D} + \text{BeH}_2\text{O}^+$ , are not energetically accessible at the present reaction temperature ( $\sim 150$  K). Instead, a double displacement  $\text{BeOH}^+ + \text{HD}$  product channel is accessible due to a large exothermicity of 1.885 eV through a submerged barrier in the reaction pathway. While the  $\text{BeOD}^+ + \text{H}_2$  product channel has a similar exothermicity, the reaction pathway is dynamically unfavourable, as suggested by a sudden vector projection analysis. This work sheds light on the origin of the loss and contaminations of the laser-cooled  $\text{Be}^+$  ions in quantum-information experiments.

**1. Introduction**

Trapped atomic ions such as  $\text{Be}^+$ ,  $\text{Mg}^+$ ,  $\text{Ca}^+$ ,  $\text{Sr}^+$ ,  $\text{Ba}^+$ , and  $\text{Yb}^+$  are used to host qubits for quantum information processing and have been employed to construct fully programmable quantum computers [3, 4]. They have demonstrated the longest coherence times [5] and are prized for their extremely low single- and two-qubit gate error rates [1, 6, 7]. Among the various species in use,  $\text{Be}^+$  is the lightest, providing the highest motional frequency, which furnishes several advantages including reduced gate times. Though experiments are performed in ultrahigh vacuum, chemical reactions between  $\text{Be}^+$  and the

background gases (e.g. H<sub>2</sub> and H<sub>2</sub>O) are the dominant processes for qubit loss [8, 9]. For instance, Be<sup>+</sup> is known to react with H<sub>2</sub> to produce BeH<sup>+</sup> when excited to the p-state by the 313 nm cooling laser [10]. In order to reverse BeH<sup>+</sup> to Be<sup>+</sup>, photodissociation by 157 nm photons has been applied, but this did not recover all of the original Be<sup>+</sup> ions, and other impurities and the chemical reactions behind the creation of the remaining species, which may reveal similar rescue methods, are not well understood [11].

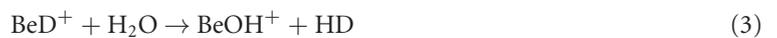
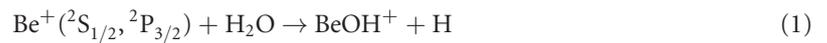
Using an ion trap-integrated high-resolution time-of-flight mass spectrometer (TOF-MS) [2, 12–14], we are able to investigate chemical reactions of laser-cooled Be<sup>+</sup> ions with different background molecules in the trap. In our previous work, we determined that Be<sup>+</sup> ions react with H<sub>2</sub>O to produce BeOH<sup>+</sup>. The reaction rate agrees with the capture theory when Be<sup>+</sup> is in the electronically-excited p-state, but a submerged barrier in the s-state reaction significantly reduces the ground-state reaction rate [15, 16]. In this work, we report that the BeH<sup>+</sup> product from the Be<sup>+</sup> + H<sub>2</sub> → BeH<sup>+</sup> + H reaction can further react with H<sub>2</sub>O to produce BeOH<sup>+</sup>. To better understand the reaction mechanism(s), isotope substitution was employed to probe details about reaction dynamics and identify reaction pathways [17–24]. To this end, gaseous D<sub>2</sub> was introduced instead of H<sub>2</sub> to initially produce BeD<sup>+</sup> in the trap, which is then allowed to react with H<sub>2</sub>O and the charged products are analyzed with the TOF-MS. Interestingly, among several possible products only a double displacement channel (BeOH<sup>+</sup> + HD) is observed experimentally. This observation is rationalized with *ab initio* electronic structure calculations of the reaction pathways, using explicitly correlated restricted coupled cluster singles, doubles, and perturbative triples (RCCSD(T)-F12) method and the augmented correlation-consistent polarized triple zeta (AVTZ) basis set.

## 2. Experiment

The apparatus employed here has been described in detail elsewhere [15, 16]. Briefly, Be<sup>+</sup> ions, produced from laser ablation of metallic Be, are trapped in a linear radio frequency Paul trap [14]. Laser cooling [25] is used to cool the translational motion of the ions, resulting in a Coulomb crystal of Be<sup>+</sup> ions, whose fluorescence is monitored by a camera in real time. A mixture of gaseous D<sub>2</sub> and H<sub>2</sub>O is made shortly before the experiment and then introduced via a room-temperature leak valve into the trapping region, where the gas reacts with the trapped ions. The exchange of H and D atom in the mixture is unlikely, which can also be inferred from the residual gas analyzer (RGA) measurement. In order to produce higher amounts of BeD<sup>+</sup> for further reaction, D<sub>2</sub> is about 100× more prevalent than H<sub>2</sub>O in the mixture. The gaseous D<sub>2</sub> is measured from the RGA, and the calibration of its fractionation has been described in our previous work [15, 16]. While the H<sub>2</sub>O density is too low for the RGA to detect accurately, its density is estimated later from the reaction rate. The ionic products remain in the trap, and are subsequently analyzed by an integrated TOF-MS [2, 12–14]. The 313 nm laser for cooling Be<sup>+</sup> ions allows manipulation of the Be<sup>+</sup> electronic quantum states; by tuning the frequency of this cooling laser, the fraction of ions in the <sup>2</sup>S<sub>1/2</sub> and <sup>2</sup>P<sub>3/2</sub> states can be precisely controlled [15].

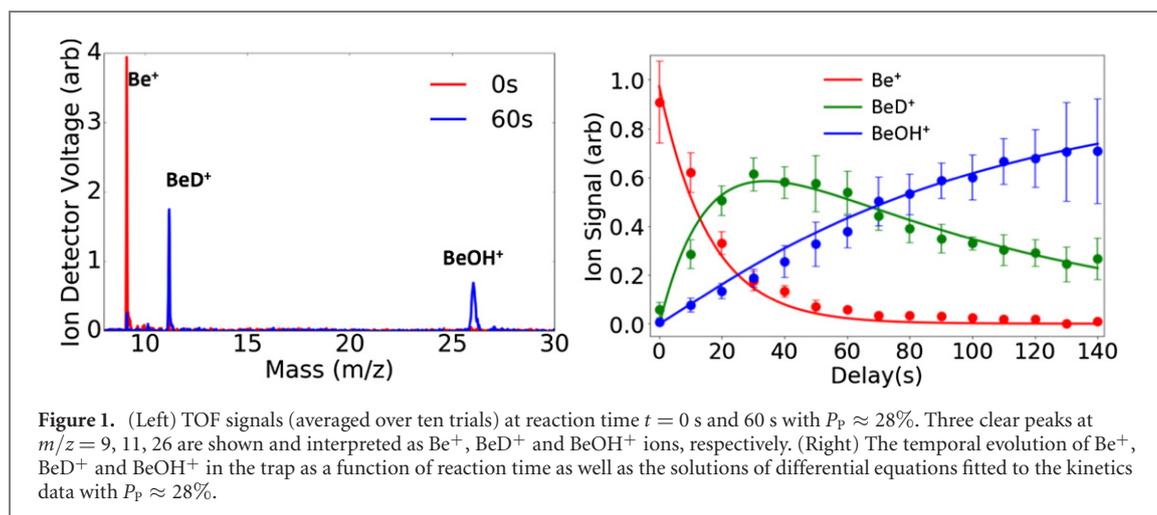
The translational energy of the laser-cooled Be<sup>+</sup> ions, including micromotion energy, is less than 1 K, while the translational and internal energy of D<sub>2</sub> and H<sub>2</sub>O is assumed to be given by a thermal distribution at 300 K. The BeD<sup>+</sup> ions from the reaction of Be<sup>+</sup> + D<sub>2</sub> are sympathetically cooled by Be<sup>+</sup> and further reacted with room-temperature H<sub>2</sub>O. The reaction temperature of BeD<sup>+</sup> + H<sub>2</sub>O is roughly 150 K. Typical TOF traces (ten sample average) at reaction time  $t = 0$  s and 60 s with 28% relative Be<sup>+</sup> <sup>2</sup>P<sub>3/2</sub> state excitation ( $P_p \approx 28\%$ ) and a full reaction curve are shown in figure 1 in the left and right panels, respectively. The reaction time zero is determined from the fluorescence signal monitored by the camera in real time, which is also used to normalize the initial ion number for the TOF. At  $t = 0$  s, only one clear peak ( $m/z = 9$ , Be<sup>+</sup>) is shown in the TOF trace (red line). After 60 s, two more peaks arise at  $m/z = 11$ , 26, which indicates that BeD<sup>+</sup> and BeOH<sup>+</sup> are the two main products for Be<sup>+</sup> + D<sub>2</sub>, H<sub>2</sub>O reactions.

The reactions of interest are:



Thus, the kinetics of the reagents and products are found from:

$$d[\text{Be}^+]/dt = -(k_1\rho_1 + k_2\rho_2) [\text{Be}^+] (t) \quad (5)$$



$$d[\text{BeD}^+]/dt = k_2\rho_2[\text{Be}^+](t) - k_3\rho_1[\text{BeD}^+](t) \quad (6)$$

$$d[\text{BeOH}^+]/dt = k_1\rho_1[\text{Be}^+](t) + k_3\rho_1[\text{BeD}^+](t), \quad (7)$$

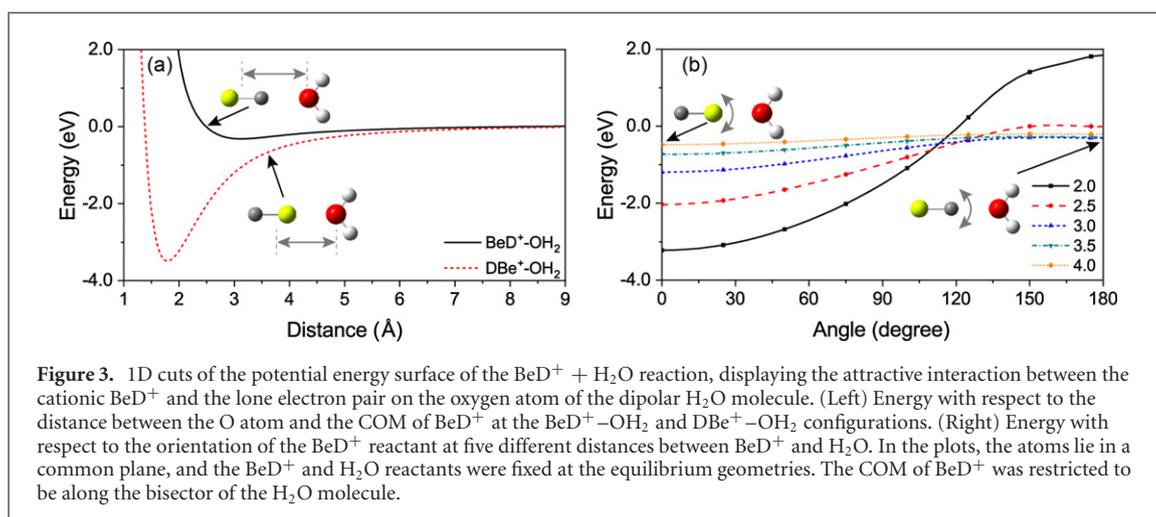
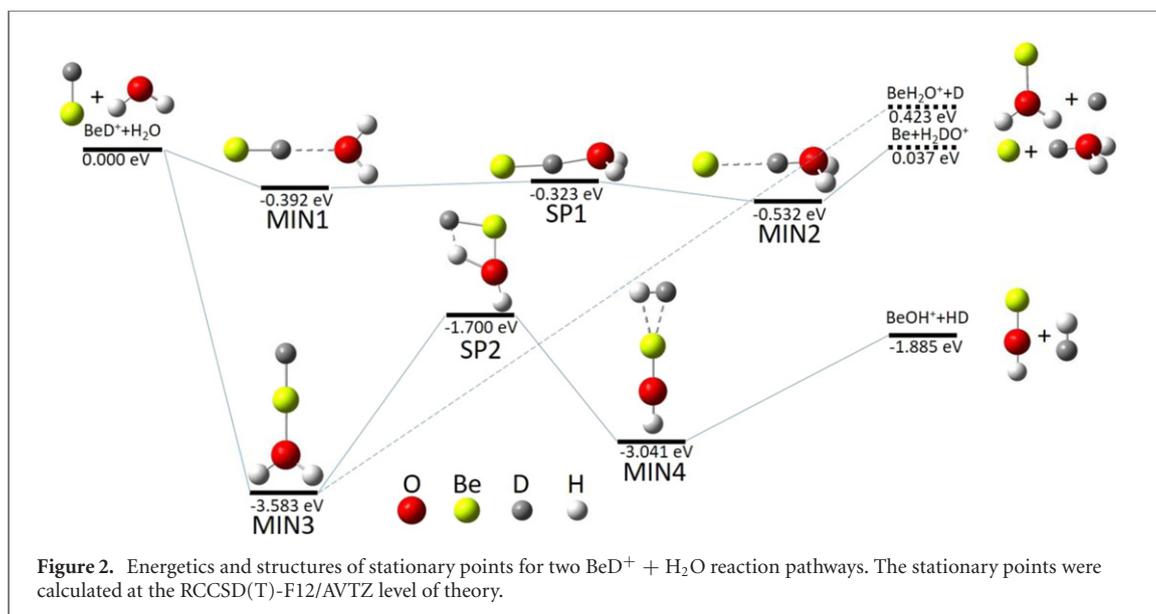
where  $k_i$  is the total reaction rate coefficient for reactions  $i = (1)–(3)$ , reaction (4) is not included in the fitting because no evidence of  $\text{BeOD}^+$  has been shown in the TOF signals (figure 1 (left)).  $k_1, k_2$  are set as known in the fitting from the previous measurements [10, 15], i.e.  $k_1 = (4.2 \times 10^{-9}) \times P_p + (2.2 \times 10^{-9}) \times (1 - P_p) \text{ cm}^3 \text{ s}^{-1}$ ,  $k_2 = (1.3 \times 10^{-9}) \times P_p \text{ cm}^3 \text{ s}^{-1}$ .  $\rho_1, \rho_2$  are the density of  $\text{H}_2\text{O}$  and  $\text{D}_2$ , respectively, where  $\rho_2$  is measured to be  $\sim 1.5 \times 10^8 \text{ molec. cm}^{-3}$  by the RGA,  $\rho_1$  and  $k_3$  are estimated from the fitting. The temporal evolution of  $\text{Be}^+$ ,  $\text{BeD}^+$  and  $\text{BeOH}^+$  in the trap as a function of reaction time are shown in figure 1 (right), as well as the solutions of differential equations fitted to the kinetics data. The reaction rate coefficient of  $k_3$  has been measured to be  $(3.5 \pm 2) \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , while  $\rho_1$  is estimated at  $\sim 3 \times 10^6 \text{ molec. cm}^{-3}$ . Therefore, the  $\text{BeD}^+$  ions are expected to react with  $\text{H}_2\text{O}$  at a rate close to reaction (1), and thus  $\text{BeOH}^+$  is the final product when both  $\text{H}_2$  and  $\text{H}_2\text{O}$  exist in a vacuum system with cold, trapped  $\text{Be}^+$ .

It is interesting to note that although reactions (3) and (4) appear to formally lead to the same products, they represent very different pathways. Reaction (3) preserves one O–H bond in the  $\text{H}_2\text{O}$  moiety, which can be achieved by breaking the Be–D and H–O bonds and forming a new H–D bond. On the other hand, the processes involved in reaction (4) are more complicated, which would require either the insertion of O into the Be–D bond or a triple displacement of the H and D atoms. Such a drastic difference cannot be distinguished if all three hydrogens are the same isotope, but the difference is revealed through isotope tagging.

### 3. Theory

To investigate the dynamics behind the experimental observation in figure 1, we theoretically explore the critical stationary points in the  $\text{BeD}^+(\text{}^1\Sigma) + \text{H}_2\text{O}$  reaction pathways using the explicitly correlated restricted coupled cluster singles, doubles, and perturbative triples (RCCSD(T)-F12) method [26] with the augmented correlation-consistent polarized triple zeta (AVTZ) basis set [27]. The results are shown in figure 2, and the structures of the corresponding stationary points are given in table S1 (<https://stacks.iop.org/NJP/23/115004/mmedia>). It should be noted that at the experimental conditions, the reactants do not have enough overall energy to overcome any significant reaction barrier. Indeed, the reaction pathways shown in figure 2 only feature submerged barriers.

Two intuitive pathways featuring the abstraction of either  $\text{D}^+$  or  $\text{Be}^+$  from  $\text{BeD}^+$  by  $\text{H}_2\text{O}$  lead to the  $\text{Be} + \text{H}_2\text{DO}^+$  and  $\text{D} + \text{BeH}_2\text{O}^+$  channels, respectively. The two pathways are initiated with barrierless attractive interaction between the cationic  $\text{BeD}^+$  and the lone electron pair on the oxygen atom of the dipolar  $\text{H}_2\text{O}$ , as shown in figure 3. Both the Be-end and the D-end of  $\text{BeD}^+$  are attracted toward the oxygen atom of the water molecule, and the former shows a much stronger attraction than the latter. In the  $\text{Be} + \text{H}_2\text{DO}^+$  channel, there exist two shallow wells (MIN1 and MIN2) corresponding to the  $\text{BeD}^+-\text{H}_2\text{O}$  and the  $\text{Be}-\text{H}_2\text{DO}^+$  complexes, which are separated by a moderate saddle point (SP1). The classical energy of the  $\text{Be} + \text{H}_2\text{DO}^+$  product channel is similar to that of the reactant. However, when zero-point energies of



the reactants and products are considered this product channel lies 0.218 eV above the reactant. As a result, it is inaccessible under the experimental conditions. The second channel,  $\text{D} + \text{BeH}_2\text{O}^+$ , involves a deep well (MIN3) formed with the Be-end pointing to the water oxygen, as the Be end has a more positive charge. The  $\text{D} + \text{BeH}_2\text{O}^+$  products are realized by breaking the Be–D bond in the  $\text{DBe}^+ - \text{OH}_2$  complex. This product asymptote is also endoergic by 0.423 eV and unlikely to occur at the present experimental reaction temperature ( $\sim 0.013$  eV), which is consistent with the absence of this products in the experiment.

The third pathway leads to the  $\text{BeOH}^+ + \text{HD}$  product channel, which lies 1.885 eV below the reactant energy. This pathway is also initiated by the barrierless formation of the ion–dipole  $\text{DBe}^+ - \text{OH}_2$  complex (MIN3), followed by a submerged saddle point (SP2) to another well (MIN4), namely the  $\text{HD} - \text{BeOH}^+$  complex. The SP2 features a double displacement process by forming a Be–O bond and transferring one H atom from  $\text{H}_2\text{O}$  to the D atom in  $\text{BeD}^+$  reactant. This double displacement reaction is difficult, evidenced by a large barrier (1.883 eV at SP2) from the  $\text{DBe}^+ - \text{OH}_2$  well (MIN3), due apparently to the breaking of two bonds (i.e. O–H and Be–D bonds). However, this difficult bond rearrangement is feasible thanks to the 1.700 eV of energy available at this submerged barrier (SP2). The reaction completes by the escape of the neutral, low-mass HD product from the trap. The production of the HD product, instead of the  $\text{H}_2$  product absent in the experiment that would only be formed from  $\text{H}_2\text{O}$ , suggests that the two hydrogens have to come from the two reactants. This observation demonstrates the power of the isotope substitution in identifying the reaction pathway.

Perhaps the most surprising result of this study is that though the isotopologue  $\text{BeOD}^+ + \text{H}_2$  product channel is also exothermic, this channel is not observed in the experiment. This product channel can be reached by either insertion of O into the  $\text{BeD}^+$  or via a triple displacement channel (shown in figure S1),

which exchanges the hydrogen moieties connected with O and Be. The first pathway, insertion of O into the  $\text{BeD}^+$ , is unlikely because the strong ion–dipole attraction between the reactants leads to either the  $\text{BeD}^+-\text{OH}_2$  (MIN1) or the  $\text{DBe}^+-\text{OH}_2$  (MIN3) wells, as shown in figure 3. Furthermore, the insertion mechanism requires the simultaneous breaking of the two O–H bonds, in addition to the Be–D bond cleavage, which are extremely difficult. The second possible mechanism, namely the triple displacement channel (shown in figure S1), would have to exchange the three hydrogen moieties connected with O and Be. From the MIN4 complex, the triple displacement channel requires two additional transition states, which have the same geometry as SP2 but different permutations of the hydrogens. In the first transition state, the D atom is transferred from Be to O, forming the  $\text{HBe}^+-\text{OHD}$  complex (MIN3'). This is followed by the second transition state, where the remaining H on O is transferred to Be, leading to the  $\text{H}_2-\text{BeOD}^+$  complex (MIN4'), which can then dissociate to form the  $\text{H}_2 + \text{BeOD}^+$  product.

The absence of this  $\text{BeOD}^+ + \text{H}_2$  product channel in the experiment can be rationalized by the sudden vector projection (SVP) model [28], which attributes the product energy disposal by the projection of a product mode onto the reaction coordinate at the transition state (SP2). The SVP model is based on the premise that the projection ( $\eta \in [0, 1]$ ) is a proxy for the coupling strength of the product mode with the reaction coordinate, thus dictating the amount of the energy flow into the corresponding product mode as the system departs from the transition state to the product channel. This model has been tested in a large number of reactions and its predictions are quite reliable [29].

SVP values (see table S2 and figure S2) for SP2 suggest that the center-of-mass (COM) separation mode between the two products has a large SVP value ( $\eta = 0.50$ ) with SP2, suggesting that a large portion of the energy release is expected to be partitioned into the translational energy between HD and  $\text{BeOH}^+$ , leading to the dissociation. This SVP prediction suggests that MIN4 is probably a short-lived species formed transiently on the way to the products. This is further supported by the fact that SP2 has a much more restricted geometry (a small volume in the phase space) than the product channel (much larger phase-space volume), as the two products can take arbitrary geometries and internal excitations. So even if the MIN4 complex were sufficiently long lived, the chances for dissociating into the product channel would be much larger than those for going back to MIN3 via SP2. The difficulties for the triple displacement pathway are further compounded by the need to pass two more SP2-like transition states, as directed by figure S1. Thus, these dynamical factors, namely the large SVP value for the dissociation coordinate and favorable entropy of the product channel, argue against the triple displacement channel, explaining the absence of the  $\text{H}_2 + \text{BeO}^+$  products.

To summarize, reactions between cold  $\text{BeD}^+$  and warm  $\text{H}_2\text{O}$  have been investigated using TOF-MS. This reaction readily produces  $\text{BeOH}^+$ . However, the  $\text{BeOD}^+$  product was never observed, despite its similar energy to  $\text{BeOH}^+$ . The reaction mechanism was analyzed using a high-level *ab initio* method and the results confirm the observation that only one reaction path, leading to  $\text{BeOH}^+ + \text{HD}$ , is realized under experimental conditions. Deuteration of the  $\text{BeH}^+$  reactant offered a unique opportunity to identify the reaction pathway in this important ion–molecule reaction, which represents a potentially important loss-channel for  $\text{Be}^+$  qubits if both  $\text{H}_2$  and  $\text{H}_2\text{O}$  residual gases exist in the vacuum chamber. While previous work has shown that  $\text{Be}^+$  qubits can be recovered from  $\text{BeH}^+$  by photodissociation at 157 nm,  $\text{Be}^+$  is unlikely to be recovered from  $\text{BeOH}^+$  at this wavelength. We estimate that photodissociation of  $\text{BeOH}^+$  requires a wavelength near 220 nm, given that the asymptotic energy of the  $\text{Be}^+(^2\text{S}) + \text{OH}(^2\text{II})$  channel lies 5.59 eV above the ground vibrational state of the  $\text{X}^1\text{S}^+$  electronic state. (See figure S3 of SI).

## Acknowledgments

The authors thank Arthur Suits for helpful discussions. The UCLA authors thank Michael Heaven and Hao Wu; BZ thanks Uwe Manthe and Wolfgang Eisfeld for helpful discussions. Funding: this work was supported by the Air Force Office of Scientific Research Grant Nos. FA9550-16-1-0018, FA9550-20-1-0323 and FA9550-18-1-0413 (HG). HG also thanks the Alexander von Humboldt Foundation for a Humboldt Research Award. TY thanks support from Guangdong Innovative & Entrepreneurial Research Team Program (Grant 2019ZT08L455) and the National Natural Science Foundation of China (Grant 22003023, NSFC Center for Chemical Dynamics).

## Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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