Rotational control of reactivity: Reaction of SiO$^+$ ions in extreme rotational states

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Abstract

Optical pumping of molecules provides unique opportunities for control of chemical reactions at a wide range of rotational energies. Chemical reactivity for hydrogen abstraction reaction SiO$^+$ + H$_2$ → SiOH$^+$ + H is investigated in an ion trap. The SiO$^+$ cation is prepared with a narrow rotational state distribution, including super-rotor states with rotational quantum number ($j$) as high as 170 using a broad-band optical pumping method. The super-rotor states of SiO$^+$ are shown to substantially enhance the reaction rate, a trend reproduced by complementary theoretical studies. The mechanism of the rotational enhancement of the reactivity is revealed to be a strong coupling of the SiO$^+$ rotational mode with the reaction coordinate at the transition state on the dominant dynamical pathway. This work reports for the first time a chemical reaction with extreme rotational excitation of a reactant and its kinetic characterization.
1 Introduction

A holy grail in chemistry is to control chemical reactions at the quantum level. One time-honored approach is by manipulating the collision energy (i.e., heating/cooling). This can be achieved with molecular beam techniques at collision energies ranging from cold (∼1 K) to hyper-thermal (>500 K) regimes [1–4]. Recent progress in cooling atoms and molecules shed valuable light on the quantum nature of reactivity at the single quantum state level under ultra-cold collision conditions (∼nK) [5–8]. An alternative approach is to deposit energy into vibrational modes of the reactants, using for example optical pumping [9]. Such quantum state selective studies have revealed strong vibrational control in some reactions [10–12].

These investigations have led to a better understanding of how various types of energy promote (or inhibit) reactivity. Half a century ago, Polanyi proposed a set of rules for understanding the relative vibrational/translational efficacy in promoting atom-diatom reactions with different types of barriers [13]. Translational energy is more effective in overcoming a barrier that resembles the reactants (reactant-like), while vibrational excitation has a higher efficacy in surmounting a product-like barrier. These Polanyi rules have been extended to polyatomic reactions. The Sudden Vector Projection (SVP) model, for example, attributes the ability of a reactant mode in promoting a reaction to its projection onto the reaction coordinate [14, 15].

Despite the tremendous progress, there have been only a few experiments probing the effect of rotational excitation on reactivity, and these existing studies have typically involved only low rotational excitations [16–19]. Since the rotational interval of a typical molecule is ∼2 orders of magnitude smaller than vibrational intervals, the impact of rotational excitation is difficult to observe. Besides, it is not entirely clear whether a fast rotating reactant would necessarily enhance the reactivity because rotation might increase the effective barrier, hence inhibiting the reaction. In this regard, super-rotor molecules which are promoted to highly excited rotational levels are particularly useful because the energy of rotation may approach or even exceed vibrational energy or even electronic energy holding the atoms together [20, 21]. Super-rotors show fascinating collisional energy exchange properties, such as strong propensity for conservation of angular momentum (both magnitude and direction) [22], collective transport properties such as generation of macroscopic vortices [23], and anisotropic diffusion [24] and quasi-resonant vibration-rotation energy transfer [25, 26].

Recently, super-rotors were detected in the interstellar medium where they can be produced by photo-dissociation of poly-atomic molecules [27] in warm proto-planetary nebulae [28] or in interstellar shock waves [29]. Due to the exotic and exceedingly diverse conditions, interstellar chemistry is very different from that on Earth. Very little is known about chemical reactions of super-rotors and their role in astro-chemical reaction mechanisms.

The main focus of experimental studies on super-rotors to date has been on probing their physical [21, 30] and collisional [31–33] properties using...
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Number Density ($x 10^6$ cm$^{-3}$)

0 10 20 30 40 50

0 0.2 0.4 0.6

Rate (min$^{-1}$)

Linear Fit

$k_0 = 1.3 (1.0) \times 10^{-10}$ cm$^{-3}$s$^{-1}$

Intensity (arb)

Super-rotor

Uncontrolled

Time (min)

Fig. 1 a: Stern-Volmer plot depicting the reaction rate as a function of H$_2$ number density; slope obtained from the linear fit gives us the bi-molecular rate constant for the reaction b: Reaction rates for SiO$^+$ pumped to super-rotor states compared to an uncontrolled rotational distribution of SiO$^+$. A higher exponential decay constant indicates that the reaction rate is faster.

an optical molecular centrifuge [20]. The molecular centrifuge method relies on a coherent population transfer by stimulated Raman processes for the preparation of super-rotors which makes it universally applicable to many small molecules. While this technique is well-suited for studying collisions, the resulting relaxation dynamics make it less ideal for studying state-dependent chemical reactions.

Some of the current authors recently demonstrated the state-preparation of trapped SiO$^+$ molecules around a target rotational state and with a narrow rotational distribution ($\Delta j = 5$) [34, 35] using optical pumping. The target states can range from the ground rotational state all the way to super-rotors with 230 rotational quanta. While optically pumping trapped molecular ions is a somewhat limited approach with regards to its applicability to a wide class of molecules, it allows for preparing super-rotors with a well-defined amount of rotational energy and sustaining them in the desired state. This makes it particularly suitable for studying reactions of super-rotors, as discussed in this work.

SiO is one of the few molecules that acts as a maser in the interstellar medium [36, 37] and was first detected in interstellar clouds [38, 39] and subsequently from supernovae explosions [40, 41]. The reaction of SiO$^+$ with H$_2$ is of significance because it could play an important role in the production of interstellar SiO [42]. This was previously studied by Fahey et al. and the bi-molecular rate constant was measured to be $3.2 (1.0) \times 10^{-10}$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$ [37]. We report here experimental and theoretical results on the reaction kinetics of the hydrogen abstraction reaction SiO$^+$ + H$_2$ → SiOH$^+$ + H in low rotational states of SiO$^+$ and compare it with the kinetics in super-rotor states. Our experimental results indicate that the rotational excitation in the SiO$^+$ reactant enhances the reactivity by a factor of 3. The trend in the rotational enhancement is reproduced by theory and attributed to a rotational
Fig. 2 a: Scatter plot showing the reaction rate outcomes from repeated measurements for uncontrolled and super-rotor SiO$^+$. The dotted lines indicate the average of each set. b: The calculated rate coefficient as a function of the SiO$^+$ rotational quantum number and the experimental results.

mode specificity related to a key transition state of the reaction. Implications of super-rotor reactions for astrochemistry are discussed.

2 Results and Discussion

2.1 Rate coefficients

SiO$^+$ ions were loaded into a linear Paul trap via ablation followed by photoinitization of SiO. At ultrahigh vacuum, H$_2$ is the background gas in the trap and is at room temperature. Due to a large excess of H$_2$, SiO$^+$ + H$_2$ $\rightarrow$ SiOH$^+$ + H is a pseudo-first order reaction. We use the technique of Laser Cooled Fluorescence Mass Spectrometry (LCFMS) [43, 44] to measure the reaction rate (see Methods). The bi-molecular rate coefficients were obtained by measuring the reaction rates as a function of H$_2$ concentration. In Fig.1a, the measured reaction rate is shown as a function of H$_2$ concentration in the trap. For these measurements, we use the nascent post-photo-ionization rotational distribution of SiO$^+$ with population in states $j = 12 - 20$ [45]; the rate of reaction for the un-pumped nascent distribution is indistinguishable from the thermal distribution at 300K and was verified experimentally to be the case. The slope of the straight-line extracted from the linear fit gives us the rate of the bimolecular reaction: 1.3 (1.0) $\times$ 10$^{-10}$ cm$^{-3}$s$^{-1}$. The previously reported rate constant measurement by Fahey et al. lies within 2$\sigma$ of our measurement [37].

We also measured the reaction rates at a number density of 7 (1) $\times$ 10$^6$ cm$^{-3}$ for the uncontrolled distribution and compared it to the reaction rates when SiO$^+$ molecules are pumped to super-rotor states $j \sim 170$ (Fig.1b). The details of the state preparation can be found in our recent publications [34, 35] and are briefly discussed in the Supplementary Information. The reaction proceeds significantly faster when the SiO$^+$ is pumped to super-rotor states (Fig. 1b). We observe a monotonic increase in the reaction rate as a function of the rotational state of SiO$^+$ (Fig. 2a). The average pseudo-first order rate of reaction when the SiO$^+$ is pumped to super-rotor states is 0.18 (0.03) min$^{-1}$
compared to 0.05 (0.02) min\(^{-1}\) for the case of the uncontrolled SiO\(^{+}\) sample. At an intermediate energy super rotor distribution centered at \(j = 60\), the rate of 0.1 (0.03) min\(^{-1}\) was observed. Also plotted are the rates when the SiO\(^{+}\) molecules are pumped to a distribution around \(j = 60\) as an intermediate.

To understand the reactivity and relative efficacies of various types of reactant excitation, a full-dimensional global adiabatic potential energy surface (PES) of the SiOH\(_2\)\(^{+}\)(\(X^2\)A\) system was constructed from high-level ab initio data. The rate coefficient was then calculated on the PES by a quasi-classical trajectory (QCT) method for various initial conditions.

In Fig. 2b, the calculated rate coefficient is compared with the experimental data as a function of the rotational excitation of SiO\(^{+}\). In agreement with the experimental trend, rotational excitation of SiO\(^{+}\), particularly above \(j=120\), greatly enhances the reactivity. Quantitatively, however, the calculated rate overestimates the experimental values at both low and high \(j\) values, but the agreement is better at \(j = 60\). The discrepancy could have several possible sources, including quantum effects such as tunneling, ro-vibrational coupling at high \(j\) values, involvement of excited electronic states, and remaining errors in the PES. This is discussed further in the Supplementary Information.

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Fig. 3 a: Energetics of the ground state reaction pathways for the SiO\(^{+}\) + H\(_2\) reaction. The yellow line represents the dominant reaction pathway, via a submerged saddle point TS1. b: Contours of the PES in reactant Jacobi coordinates along R and \(\theta_2\) with fixed \(\theta_1 = 180^\circ\) and optimized \(r_{SiO}\), \(r_{HH}\) and \(\phi\). c: Comparison of integral cross sections for rotational excitation of SiO\(^{+}\), rotational excitation of H\(_2\), and translational excitation.
### 2.2 Reaction Mechanism

As shown in Fig. 3a, the PES has a complex topography, with multiple minima and saddle points. However, there is a dominant dynamics pathway leading to the abstraction of H by SiO$^+$. This pathway, illustrated by the yellow line in Fig. 3a, featuring a loose pre-reaction well (IM1) with a depth of merely 0.31 eV, in which the H$_2$ and SiO$^+$ form a complex. This shallow well is nearly isotropically present around the SiO$^+$ moiety, suggesting an electrostatic nature. The H-abstraction saddle point (TS1) is 0.12 eV below the reactant asymptote, which features a partially broken H-H bond and an incipient H-O bond. Apparently, this reaction path is barrierless with an attractive long-range interaction, although the submerged barrier serves as a reaction bottleneck for large impact parameters. Beyond the barrier, the SiOH$^+$ product is formed exoergically.

In addition to this dominant reactive channel (the yellow pathway), there are several other channels leading to the two product asymptotes, represented in the figure by blue, red, and green lines. The formation of IM2 is blocked by a significant barrier in the entrance channel (TS0), as shown in Fig. 3a. Although access to IM3 from the reactants is barrierless (the A → D → E pathway marked in orange as shown in Fig. 3b), it is dynamically overwhelmed by a lower energy pathway A → B → C marked in yellow to the products. We have observed only a few trajectories leading to IM3 in our simulations, despite favorable energetics. Hence, these secondary reaction pathways are dynamically irrelevant. Most reactive trajectories show a striping mechanism in which the two reactants pass each other as the SiO$^+$ picks up the H from H$_2$. On the other hand, the non-reactive trajectories are usually reflected by the repulsive potential wall in close inter-monomer distances, despite existence of stable complexes such as IM2 and IM3, as discussed above.

In Fig. 3c, the integral cross sections are plotted for three scenarios - rotational excitation of SiO$^+$, rotational excitation of H$_2$, and translational excitation. It is clear that only the SiO$^+$ rotation promotes the reaction, while excitation in the relative translation and H$_2$ rotation inhibits the reaction. The inhibitory effect for translational mode is due apparently to the capture

<table>
<thead>
<tr>
<th>Mode</th>
<th>TS1</th>
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<tbody>
<tr>
<td>Rot (SiO$^+$)</td>
<td>0.42</td>
</tr>
<tr>
<td>Rot (H$_2$)</td>
<td>0.08</td>
</tr>
<tr>
<td>Vib (SiO$^+$)</td>
<td>0.05</td>
</tr>
<tr>
<td>Vib (H$_2$)</td>
<td>0.12</td>
</tr>
<tr>
<td>Translational</td>
<td>0.15</td>
</tr>
</tbody>
</table>

*Table 1* SVP values for rotational and vibrational modes of SiO$^+$ and H$_2$ projected onto the reaction coordinate at the dominant transition state (TS1).
nature of the reaction, while that for the $\text{H}_2$ rotation can be understood by the increased effective barrier with the rotational angle [15]. To explain the enhancement in reaction due to rotation of $\text{SiO}^+$, we resort to the SVP model [14]. In the sudden limit, the ability of a reactant mode to enhance the reactivity is attributed to a large projection of its normal mode onto the reaction coordinate at the relevant transition state, in this case TS1. Table 1 lists the SVP values ($0 < \zeta_i < 1$) for all the reactant modes ($i = 1-5$); evidently, the rotation of $\text{SiO}^+$ has a very large value. This implies that the $\text{SiO}^+$ rotation is strongly coupled with the reaction coordinate at TS1, as illustrated in the right panel of Fig. 3a, allowing facile energy flow into the reaction coordinate.

3 Conclusions

Optical pumping to super-rotor states provides unique opportunities for control of chemical reactions at extreme rotational energies. Preparing super-rotors with a narrow rotational distribution allows for detailed analysis of the reaction mechanism. This work reports for the first time a chemical reaction with extreme rotational excitation of a reactant and its kinetic characterization. For the reaction $\text{SiO}^+ + \text{H}_2 \rightarrow \text{SiOH}^+ + \text{H}$, we observe an increase in the reaction rate by a factor of 3 when the $\text{SiO}^+$ is pumped to super-rotor states as compared to the case when we do not optically pump the $\text{SiO}^+$. This rotational enhancement of the reactivity is supported by QCT calculations based on the newly developed PES for this reaction. Despite the complex topography of the PES, the QCT calculations suggest that a submerged barrier (TS1) has an important influence on the rotational mode specificity of the reaction. The SVP model suggests that the reactivity enhancement by exciting the $\text{SiO}^+$ rotation is due to its strong coupling with the reaction coordinate at the dominant transition state.

The observed enhancement of the reaction rate may change our understanding of chemical reactions in the interstellar media (ISM). Super-rotors are known to exist in space [27–29] where they form under the action of abundant V-UV radiation on poly-atomic molecules. At the conditions in ISM, they exist for a long time, limited by radiative decay rather than collisional relaxation processes. Therefore, they can undergo reactive collisions with other ISM species. Current astrochemical reaction models largely rely on estimated rather than measured rates, and in most cases dependence on the internal energy levels of reactants is neglected. Reactions of super rotors is an extreme example where such chemical intuition approach fails, and a deep understanding of underlying dynamics is necessary. The observed acceleration of the exoergic barrierless $\text{SiO}^+ + \text{H}_2$ reaction is counter-intuitive; similar and more significant effects may be revealed in other chemical systems with enough energy. The importance of super-rotor chemistry in the ISM is determined by the interplay between the rates of production by the V-UV photo-dissociation, radiative relaxation and reactive collisions. An interesting
possibility is the formation of super-rotors of non-polar symmetric molecules, which can have several orders of magnitude longer radiative lifetime compared to polar molecules and therefore, may survive for much longer time at lower densities in the interstellar media (ISM). While such objects have not been observed yet, photo-dissociation pathways leading to the formation of non-polar symmetric molecules, such as H\(_2\) [46] or methane [47] are known, and it is plausible that they form under the action of energetic V-UV quanta on polyatomic molecules.

Our results pave the way for the studies and control of chemical reactions at extreme rotational energies of the reactants, which are important for understanding the fundamental issues in reactivity as well as chemical processes in extreme environments.

4 Methods

4.1 Experimental Methods

SiO\(^+\) and Ba\(^+\) ions were co-loaded into the ion trap via ablation followed by photo-ionization. The Ba\(^+\) cloud comprised of around 500-1000 Ba\(^+\) ions which were continuously Doppler-cooled via transitions at 493 nm and 650 nm. Rotational control of SiO\(^+\) was achieved via broadband rotational optical pumping (Supplementary Information).

We applied a low-voltage (0.5 - 1 V) excitation chirp sweeping through frequencies from 150 kHz to 500 kHz to one of the rods in the RF trap. As the chirp hit the secular frequency of a particular species of ions in the trap, their motion was resonantly enhanced and coupled weakly to the motion of Ba\(^+\). This decreased the fluorescence of Ba\(^+\) ions in proportion to the number of that ion species. A photo-multiplier tube (PMT) was used to detect the fluorescent photons from the Ba\(^+\) cloud. A digital counter that was binned into 1 ms intervals counted the number of PMT events in each bin. As a result, each timestamp corresponded to a particular frequency over the course of one sweep. Since secular frequencies vary from one species to another as a function of their mass, this is a convenient in-situ mass spectrometry technique. Besides using LCFMS as a tool to confirm loading of SiO\(^+\) into the trap, we also used it to monitor the reaction rate of SiO\(^+\) with H\(_2\). Being small, H\(_2\) gas molecules diffuse through the vacuum chamber walls more than any other gas and therefore it is the most difficult gas to remove from the vacuum chamber. As a result, at ultra-high vacuum levels, H\(_2\) is the dominant gas in the chamber.

As SiO\(^+\) reacts away to form SiOH\(^+\), the dip in fluorescence shifts to lower frequencies, reflecting an increase in SiOH\(^+\) concentration. At any instance, the fluorescence spectrum is a combination of SiOH\(^+\) and the unreacted SiO\(^+\). The resolving power of LCFMS technique in our ion trap is \(m / \Delta m = 30\) and thus it cannot resolve the signals from SiO\(^+\) (44 amu) and SiOH\(^+\) (45 amu). Moreover, the fluorescence of Ba\(^+\) fluctuated due to drifts in frequency, on the order of a few MHz, of the lasers used to Doppler-cool Ba\(^+\). On rare occasions, this also led to a loss of SiO\(^+\) ions from the trap if the drift was larger than
5 MHz. To deal with the noise from fluorescence fluctuations, we used singular value decomposition (SVD) of the data to effectively isolate amplitude variations in fluorescence from the mass-dependent frequency shift of the fluorescence spectrum. With sufficient averaging, and by appropriately employing SVD analysis, we inferred the rate of reaction of SiO$^+$. Refer to Supplementary information for details on SVD analysis. To estimate H$_2$ concentration in the trap, we assume that \( \sim 75\% \) of the background gas is H$_2$. The ion gauge reading is corrected using appropriate gas correction factors. In fig. 1a, uncertainties for data points at low H$_2$ densities (7 \( \times \) 10$^6$ cm$^{-3}$ and 1.4 \( \times \) 10$^7$ cm$^{-3}$), are obtained from standard deviations in the sample data; for higher number densities, only one data set was available to measure the estimated reaction rate. The error bars for these have been conservatively estimated at 30\% based on the data sets taken at lower H$_2$ pressure. We repeated the measurement of the reaction rate at a given pressure several times over the course of a 5-day measurement period and during this 5-day period, the pressure reading was constant to within the error of the gauge.

4.2 Potential energy surface and quasi-classical trajectory calculations

The global adiabatic PES for SiOH$_2^+$ (X$^2$A) is obtained from 20147 ab initio points at the explicitly correlated unrestricted coupled cluster singles, doubles, and perturbative triples level of theory (UCCSD(T)-F12)[48] with the explicitly correlated correlation-consistent polarized core-valence triple-zeta basis set (pCVTZ-F12) [49], using MOLPRO [50]. These ab initio points were represented using the permutation invariant polynomial-neural network (PIP-NN) approach [51], which enforces the permutation symmetry between the two identical H nuclei. 17 PIPs [52] with the maximal order of 2 were used in the input layer of the NN, which has 2 layers with 30 and 60 and neurons in each layer. The NN training was performed using the Levenberg-Marquardt method [53] and early stop [54] was used to avoid over-fitting. The root-mean-square error (RMSE) for the best fit is 16 meV for the training set spanning the energy range of [-3.0, 7.4] eV, signaling a high-fidelity global fit of the ab initio data in the experimentally relevant energy range.

The quasi-classical trajectory (QCT) calculations were performed using the standard technique implemented in VENUS [55] The trajectories were initiated with a 16.0 Å separation between reactants (SiO$^+$ and H$_2$), and terminated when products reach a separation of 8.0 Å, or when reactants are separated by 12.0 Å for non-reactive trajectories. In the SiO$^+$ rotational state specific calculations, SiO$^+$ was treated as a rotating oscillator, with vibrational and rotational quantum numbers $v$ (0) and $j$ (0 - 140). The atomic coordinates and momenta of H$_2$ reactant were sampled randomly using a Monte Carlo approach, based on a Boltzmann distribution at 300 K. The collision energy was sampled from a Boltzmann distribution at 282 K. In the H$_2$ rotational state specific calculations, on the other hand, H$_2$ was treated as a rotating oscillator with the initial state set as vibrational ground state and excited
rotational states \( (j = 1 - 14) \), while \( \text{SiO}^+ \) was sampled randomly at 300 K. The maximal impact parameter of the collision was chosen as \( b_{\text{MAX}} = 6.0 \) Å, which was tested to be sufficient. The propagation time step was selected to be 0.05 fs, which allowed the total energy conservation better than 1 meV for all the trajectories. Batches of 10000 trajectories have been run for each rotational state to make statistical errors all within 5%.

**Supplementary information.** Supplementary information is available

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**Contributions.** S.V., I.A., P.S. developed the laboratory techniques. S.V., J.D., I.A., and P.S. took data. B.O. led the experimental effort. A.L. and H.G. performed the theoretical calculations.

**Competing Interests.** The authors declare no competing interests.

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