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Intramolecular vibrational energy relaxation in nitrous acid (HONO)

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I. INTRODUCTION

Intramolecular vibrational energy relaxation (IVR) is of paramount importance in chemical reactions owing to its influence on the outcome of such processes. The primary challenges in directly observing IVR were achieved by the advent of ultrafast lasers and the development of tunable infrared (IR) sources. One of the pioneering developments in the field was done by Laubereau and Kaiser, addressing the problem of vibrational dephasing in condensed phase systems. Two decades earlier, Whittle et al. proposed the matrix isolation technique as a mean to study chemical reaction and chemical compounds. One of their first experiments discovered the IR-driven cis-trans isomerization reaction of nitrous acid (HONO) which proved to be a prototype proton transfer system. Probably the most tantalizing aspect of this reaction is its very high cis → trans quantum yield, qualitatively approaching unity, following IR excitation of OH stretch vibration. This number is particularly surprising given the fact that the initially excited mode is not the reactive mode (the OH torsion). The trans → cis back reaction yield is significantly less, with the ratio between the two varying with temperature from 3 at 30 K to 7 at 10 K. The large ratio between the forward and backward reaction yields is suggestive since the energy reached after OH excitation of both isomers is almost identical and, after most estimates, just slightly below the barrier separating both species. Hence, the reaction must be to some extent mode specific, and the competition between IVR and the reaction rate determines its outcome. That is, if IVR was faster than the isomerization, then the reaction quantum yield would be extremely low and the outcome of the reaction would be determined by the ratio of density of states of cis- and trans-HONO. Vibrational energy relaxation of diatomic molecules in matrix environment has been studied in great detail.

The HONO system has been studied intensively both theoretically and experimentally. Neither experimental nor theoretical studies could find the reaction taking place in the gas phase with significant yields; hence, isomerization seems to be facilitated by the dissipative forces of the matrix environment. In this context we decided to investigate the isomerization of HONO in the time domain with the help of ultrafast IR pump-probe spectroscopy. We found that the cis → trans isomerization occurs on two time scales, ≈20 and ≈2 ns, and we measured a combined reaction yield of ≈30%–50% at a temperature of 30 K. Further investigations related to the temperature dependence of quantum yield, anisotropy of the two isomers, and improvements in signal to noise ratio led us to conclude that the cis → trans quantum yield at low temperatures is indeed very high (50%–70% at 15 K). Furthermore we observed that cooling of trans-HONO proceeds through the overtones of one particular mode. Based on the number of quanta we observed and the anharmonic coupling constants available in literature, we suggested that the “cooling mode” is the ONO bend vibration. This is not the lowest energy mode of the trans isomer but lies ≈60 cm⁻¹ above the OH-torsional mode (see Table I). The torsional mode is spatially very extended and, thus, strongly interacting with the surrounding matrix. The ONO bending vibration, in contrast, involves heavy atoms only and as such has smaller vibration amplitude. We suggested that this is the reason why we do not see the OH-torsional mode in the cooling process, i.e., once energy reaches the OH-torsional mode it relaxes very quickly into the matrix, while the bottleneck of relaxation is the transfer from the ONO bending vibration into the OH-torsional mode.

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TABLE I. Vibrational frequencies (in cm\(^{-1}\)) of HONO in solid Kr.

<table>
<thead>
<tr>
<th></th>
<th>trans</th>
<th>cis</th>
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<tbody>
<tr>
<td>OH stretch ((v_1))</td>
<td>3552</td>
<td>3401</td>
</tr>
<tr>
<td>N=O stretch ((v_2))</td>
<td>1681</td>
<td>1630</td>
</tr>
<tr>
<td>HON bend ((v_3))</td>
<td>1286</td>
<td>1315 (^a)</td>
</tr>
<tr>
<td>N=O stretch ((v_2))</td>
<td>799(^a)</td>
<td>849(^a)</td>
</tr>
<tr>
<td>ONO bend ((v_6))</td>
<td>608(^a)</td>
<td>616(^a)</td>
</tr>
<tr>
<td>OH torsion ((v_8))</td>
<td>550(^a)</td>
<td>637(^a)</td>
</tr>
</tbody>
</table>

\(^a\)Taken from Ref. 4.

We analyzed our pump-probe spectra in terms of a Dunham expansion for the anharmonically coupled vibrational levels,

\[ E = \sum_i \hbar \omega_i (n_i + 1/2) + \sum_{i,j} x_{ij} (n_i + 1/2)(n_j + 1/2), \]

where \( \omega_i \) is the harmonic frequency of mode \( i \), \( n_i \) its excitation level, and \( x_{ij} \) the anharmonic coupling constants. From this expression, one can derive for the transition frequency for one particular mode \( k \),

\[ \nu_{n_k-\nu_k} + 1 = \nu_k + 2n_kx_{kk} + \sum_{i \neq k} x_{ik}n_i, \]

with \( \nu_k = \omega_k + 2x_{kk} + \sum_{i \neq k} x_{ik} / 2 \). The anharmonic constants are symmetric, \( x_{ij} = x_{ji} \), and are in most cases, but not necessarily, negative since the potential energy surface softens as one climbs up the vibrational ladder. The anharmonic constants of HONO have been calculated on the CCSD(T)/cc-pVQZ level of theory \(^3\) and some of them are known experimentally \(^31,32\). Table III.

If mode \( k \) is vibrationally excited \((n_k > 0)\), then its transition frequency will be shifted due to diagonal anharmonicity \( 2n_kx_{kk} \). If, however, mode \( k \) has already relaxed to its ground state \((n_k = 0)\), but vibrational energy is in other modes of the molecule \((e.g., \text{ dark states such as overtones and combination modes that may lie in the same energy range as mode } k \text{ but do not carry any oscillator strength})\), then the transition frequency of mode \( k \) is still shifted and we observe a hot band. The frequency shift is given by the corresponding anharmonic coupling constant \( x_{kk} \) times the number of quanta of excitation. Hence, knowing the anharmonic constants, we can, in principle, follow the energy relaxation process through all modes even though we perform the spectroscopy only on one particular spectator mode \( k \). However, although the molecule is small and vibrational transitions are relatively sharp in the matrix environment, the density of states is significant in the 3000–4000 cm\(^{-1}\) region and the hot band spectra are quite congested.

The aim of the present paper is to extend our relaxation studies \(^5\) by pumping and/or probing two additional, lower-frequency modes, the N=O stretch and HON bend vibration. Thereby, the hot band spectra are thinned out due a lower density of states in the corresponding energy range. Furthermore, since the set of anharmonic constants \( x_{ik} \) is different for a different spectator mode \( k \), it might help to identify IVR through different modes \( i \). Compiling the information of the three sets of data, we obtain a very detailed picture of IVR. Furthermore, we add a few more experimental values to the list of anharmonic constants of HONO.

II. MATERIALS AND METHODS

HONO was synthesized photochemically according to a procedure reported by Hall and Pimentel.\(^3\) A gas mixture of 3:10:1000 H\(_N\)\(_3\):O\(_2\):Kr was prepared in a glass container and sprayed on a calcium fluoride window kept in a cryostat (DE-202AF/DMX-20B, Advance Research Systems, Inc.) at very low pressure (10\(^{-6}\) mbar) and a temperature of approximately 30 K, which was also the temperature of the measurements. The 3317 cm\(^{-1}\) absorption band of HN\(_3\) was used to monitor the growth of the matrix. After deposition, the matrix was irradiated with UV light from a mercury lamp, initiating photolysis of hydrazoic acid which then reacts with oxygen to form HONO. The progress of this process was monitored by the depletion of the HN\(_3\) absorption band.

Following the isomerization reaction and IVR dynamics, we use an ultrastark IR pump-probe setup. Two synchronized Ti:sapphire laser/amplifiers were used to cover time delays of up to 300 ns.\(^34\) Due to jittering of the two laser systems, our effective time resolution is \( \approx 10 \) ps. Each Ti:sapphire laser/amplifier pumped one optical parametric amplifier to generate tunable IR pulses, which are roughly 100 fs long and have a bandwidth of \( \approx 300 \) cm\(^{-1}\) full width at half maximum.\(^35\) Pump and probe beams were focused into spot sizes of 150 and 100 \( \mu m \), respectively, with a pump energy of 1.2 \( \mu J \). The repetition rate of the laser system was 1 kHz and every second pump pulse was chopped for referencing. The probe pulse was spectrally dispersed in a 190 mm spectrometer and then detected by a 63 channel HgCdTe detector array, covering a spectral range of 100–200 cm\(^{-1}\) (depending on the center wavelength and the grating used).

In some of the experiments, in order to enable selective excitation of either the cis or the trans isomer, we spectrally narrowed the pump pulses with the help of a piezocontrolled adjustable Fabry–Pérot filter (bandwidth of \( \approx 15–20 \) cm\(^{-1}\)). Furthermore, when pumping the OH-stretch vibration of cis-HONO \((\text{OH}_{\text{cis}})\), which leads to cis \( \rightarrow \) trans isomerization, the photoequilibrium was kept on the cis side by constantly exciting OH\(_{\text{trans}}\) with the help of a cw diode laser (Nanoplus GmbH, Germany, power of \( \approx 0.5 \) mW, wavelength of 3550 cm\(^{-1}\)). The detailed conditions under which the various data sets of this paper have been taken were as follows: in Fig. 1 we pumped both OH-stretch vibrations broad band (gray lines in the two panels), N=O\(_{\text{trans}}\) narrow band [black lines in panel (a)] and HON broad band [black lines in panel (b)]. In Figs. 2(a)–2(c), we used the Fabry–Pérot filter and the cw diode laser to selectively excite OH\(_{\text{cis}}\), in Figs. 2(d)–2(f) we used only the Fabry–Pérot to selectively excite the cis or trans isomer, and in Figs. 2(g)–2(i) we performed a broad band excitation since only the trans isomer carries oscillator strength.

III. EXPERIMENTAL RESULTS

In Fig. 1 we present pump-probe spectra of OH\(_{\text{trans}}\) after excitation of OH\(_{\text{trans}}\) [gray, panels (a) and (b)], N=O\(_{\text{trans}}\)
FIG. 1. Transient difference spectra of OHtrans following the excitation of OHtrans (gray lines), N=Otrans [panel (a), black lines] and HONtrans [panel (b), black lines]. Vertical dashed lines labeled 4–1 mark the spectral positions of the four hot bands observed in the trans cooling. To facilitate comparison, the delay times are chosen such that population peaks in a certain hot band. The bands labeled with * correspond to the direct anharmonic coupling between the pumped and probed vibrations (see text).

black, panel (a), and HONtrans [black, panel (b)], respectively. All spectra that we present are difference spectra with negative contributions from the bleaching ground state of the excited molecules (and, at early times and in the case of OHtrans pumping also from stimulated emission from the excited states) and positive contributions from transient, vibrationally hot species as well as the isomerized photoproduct. As discussed in our previous paper,5 the hot band starts out as a redshifted broad featureless band after OHtrans pumping (Fig. 1, gray curves) and becomes structured as the molecules cool down. Analyzing the energy spacings between the subbands, we had suggested that cooling proceeds through a cascade of overtones of one particular mode (the four dashed vertical lines in Fig. 1, labeled 4–1).

If, in contrast, we excite N=Otrans [Fig. 1(a), black line], then the early time response is initially dominated by a strong positive peak at 3545 cm−1 (labeled with a star in the 0.05 ns spectrum) due to anharmonic coupling between the pumped (ν1) and the probed mode (ν2) with x12 = −7 cm−1. This band decays with the vibrational lifetime of N=Otrans = 70 ps (Table II). After vibrational relaxation of N=Otrans, the response is strikingly similar to that after OHtrans excitation. Cooling proceeds through the same cascade; however, due to the lower excitation energy, we can identify only three quanta of that cooling mode after N=Otrans excitation (see 0.05 ns spectrum), whereas it is four after OHtrans excitation. Figure 1, panel (b) (black lines), presents the analogous experiment after exciting HONtrans. As before, the anharmonic coupling between the excited mode (ν3) and the probed mode (ν1) is observed at early delay times (labeled with a star) with an anharmonic coupling constant of x13 = −21 cm−1, and the cooling cascade starts out with only two quanta of the cooling mode.

Figure 2 gives a more complete account of IVR, where we excite and probe, in different combinations, the OH, N=O, and HON vibrations. The data are presented as a “matrix,” where rows relate to the pumped mode and columns to probed mode. The data in Figs. 2(f) and 2(i) are the same as those in Fig. 1 (black lines); the data in Fig. 2(e) differ from those in Fig. 1 (gray line) by the fact that the cis isomer is now pumped. Exciting OHcis allows us to monitor the cooling dynamics of cis molecules as well as the isomerization toward the trans side with the subsequent cooling of the latter. The transient spectra at delay times later than 100 ns [Figs. 2(a)–2(c)] perfectly match the stationary FTIR difference spectra (Fig. 2, very top), evidencing that the molecules have completely relaxed to the ground state. Excitation of the N=O and HON vibrations, on the other hand, does not result in any isomerization since the energy is too low to surmount the barrier. The absence of any reaction leads to a zero signal at later times in these cases [Figs. 2(d)–2(ii)].

The most pronounced positive bands (Fig. 2, colors green-cyan-blue-pink) are labeled with a three digit code. The first digit corresponds to the pumped mode, the second to the probed mode, and the third to the mode to which the probed mode anharmonically couples. The last two indices indicate the anharmonic constant xij, the corresponding peak determines. For example, the code 1,1,5 corresponds to a band in which we excite OHcis (ν1), probe OHtrans (ν1), and observe the anharmonic coupling of the latter to ONOcis (ν3). We will discuss the various spectra row by row.

A. OHcis pumping

In the OH region, we observe in the red part of the spectrum the bleach/stimulated emission of cis-HONO, and in the blue part the molecules that isomerized into trans-HONO [Fig. 2(c)]. The cooling of the latter proceeds through a cascade (bands 1,1,5) which is identical to that after exciting OHtrans directly.5 In analogy to cooling of trans-HONO, we assume that cis-HONO cools through the same cascade; hence, we tentatively assign peak 1,1,5 to the anharmonic coupling with ONOcis with a very small positive x15.

Evaluating the N=O spectral region [Fig. 2(b)], we observe at early delay times a cis-bleach signal paired with a positive band (1,2,1) which corresponds to the direct anharmonic coupling between OHcis and NOcis and hence determines the cis-anharmonic constant x12 = −6 cm−1. Blue-shifted from the bleach, we take note of a strong positive band (band 1,2,5) which presumably is part of the cis-cooling process (at least at later delay times) in analogy to band 1,1,5. We can also see the isomerized trans molecules and the corresponding band 1,2,5 grows in with an estimated small anharmonic shift of x25 = −0.5 cm−1. Due to the small shift, we cannot resolve the relay of cooling states.

In the spectral region of the HON bend vibration [Fig.
we can observe only the trans isomer (the HONcis cross section is very weak) and the band is strongly split due to site inhomogeneities. For each of the matrix sites, we observe a cooling cascade (bands 1,3,5, with $x_{35}=-7$ cm$^{-1}$) synchronous with band 1,1,5.

**B. N=O pumping**

In the response following the excitation of the N=O vibration [Figs. 2(d)–2(f)] we can identify at early delay times bands 2,3,2, (twice), 2,2,2, 2,2,2, 2,1,2, and 2,1,2, (see Table III for the corresponding anharmonic constants). It is interesting to note that the anharmonic constants determined from either band 1,2,1, or band 1,1,2, are indeed identical, reflecting the symmetry $x_{12}=x_{12}$. Bands 2,3,2, 2,2,2, and 2,1,2, decay with the lifetime of NOtrans ($\approx 70$ ps), whereas bands 2,2,2, and 2,1,2, follow the dynamics of NOcis (lifetime of $\approx 300$ ps, see Table II).

As discussed above, cooling of NOtrans proceeds through a cascade of up to three quanta of the cooling mode. This is evident in the OH spectral region (band 2,1,5,) and the HON spectral region (band 2,3,5,). Due to similar kinetics, we believe that band 2,2,5, follows the same cascade. In the case of NOcis, we see hot bands (bands 2,2,5, and 2,1,5,) which are probably the same as bands 1,2,5, and 1,1,5,, respectively.

**C. HON pumping**

The response after HONtrans excitation [Figs. 2(g)–2(i)] differs from that after N=Otrans excitation at early delay times due to the different excited modes (bands 3,3,3, 3,2,3, and 3,1,3, see Table III for the corresponding anharmonic constants).

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**TABLE II. Vibrational lifetimes.**

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
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<tr>
<td>OHtrans</td>
<td>8 ps</td>
<td>260 ps$^{ab}$</td>
</tr>
<tr>
<td>OHcis</td>
<td>20 ps</td>
<td></td>
</tr>
<tr>
<td>N=Otrans</td>
<td>70 ps</td>
<td></td>
</tr>
<tr>
<td>N=Ocis</td>
<td>300 ps</td>
<td></td>
</tr>
<tr>
<td>N=Otrans</td>
<td>420 ps</td>
<td>60 ps$^c$</td>
</tr>
</tbody>
</table>

$^a$Taken from Ref. 27.
$^b$Bieponential decay.
$^c$Left and right subbands.

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**FIG. 2.** (Color) Three-dimensional representation of the transient difference spectra in the spectral range of HON bend (left column), N=O stretch (middle column), OH stretch (right column), after exciting either OH$_{cis}$ (top row, the very top shows a stationary difference spectrum measured in a FTIR spectrometer as a reference), N=O$_{trans}$ and/or N=O$_{trans}$ (middle row), and HON$_{cis}$ (bottom row). Red color depicts negative stimulated emission and/or bleach signals, colors in green-cyan-blue-pink positive bands from either transient hot bands and/or the photoproduct. The positive bands are coded with a three digit label that represent pumped mode (first digit), probed mode (second digit), and the mode to which the probed mode anharmonically couples (third digit). Bands for which the assignment is speculative are labeled with an additional question mark.
TABLE III. Calculated and experimental anharmonic coupling constants \(x_{ij}\) of HONO (in \(cm^{-1}\)).

<table>
<thead>
<tr>
<th>(x_{ij})</th>
<th>(x_{ij})</th>
<th>(x_{ij})</th>
<th>(x_{ij})</th>
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<td></td>
<td>Calc.(^a)</td>
<td>Expt.(^b)</td>
<td>Expt.(^c)</td>
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<td>Expt.(^c)</td>
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<td>–6.34</td>
<td>–6.09</td>
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<tr>
<td>56</td>
<td>–8.42</td>
<td>–5.27</td>
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</tr>
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</table>

\(^a\)Theoretical values from Ref. 7.
\(^b\)Gas phase experimental values from Ref. 32.
\(^c\)Gas phase experimental values from Ref. 31.
\(^d\)This work. A typical error bar is \(\pm 1\) cm\(^{-1}\) due to the limited spectral resolution of our setup. Values in parentheses are assigned assuming that the cooling mode is indeed \(x_5\).
\(^e\)Taken from Ref. 27.

const), but they become essentially identical once the cooling cascade is entered (bands \(3,3,5, \, 2,2,5, \, 3,1,5\)). The vibrational lifetime differs for the two subbands and is \(420\) ps for the lower frequency band and \(\approx 60\) ps for the dominant higher frequency band.

Peaks \(1,2,3\), \(1,1,2\), and \(1,1,3\) in Figs. 2(b) and 2(c) deserve an extra discussion: From the perfect frequency match of peak \(1,2,3\) with peak \(2,2,2\) [Fig. 2(e)] and the fact that the size of the negative signal at the frequency of \(N=O\) (Fig. 3, squares) increases as peak \(1,2,3\) appears (Fig. 3, rhombi), one is tempted to conclude that peak \(1,2,3\) reflects direct population of \(N=O\) after relaxation of \(OH\). The additional negative signal is attributed to stimulated emission of \(N=O\) that is excited to its first vibrational state upon relaxation of \(OH\). However, if that was the whole story, then one would expect in Fig. 2(c) a signal appearing at the same time with negative frequency shift \(12=–7\) cm\(^{-1}\). This is not observed, instead, we find a peak \(1,1,2\) with a positive frequency shift, which perfectly coincides in time with peak \(1,2,3\) (see also Fig. 3, rhombi and stars). We tentatively assign the two peaks to one and the same combination mode \(v_2+n\nu_6\), which would result in different frequency shifts when observing it through the \(N=O\) vibration \((2x_{22}+n\nu_6)\) or the OH vibration \((x_{12}+n\nu_6)\). Given the long overall cooling times of tens of nanoseconds, it would appear anyway very unlikely that energy drops within 100 ps from that of \(OH\) \(3401\) cm\(^{-1}\) directly to \(N=O\) \(1630\) cm\(^{-1}\).

Hence, the \(N=O\) will be accompanied by the excitation of some other (unknown) mode. From the above discussion, this would imply \(x_{22}=0\) and \(x_{13}\), relatively large and positive. Unfortunately, this does not match with any of the theoretically calculated anharmonic constants (Table III); hence, we cannot assign the combination mode.

Band \(1,2,3\) [Fig. 2(b)], which rises as the \(OH\) stretch decays and which evolves into the cooling band \(1,1,5\), later on (we can see that bands \(1,2,3\) and \(1,1,5\) are different from their slightly different frequency shift), is probably due to excitation of those states from which the first faster isomerization step occurs. We have suggested in Ref. 23 that this first tier of states is composed of combination modes of the \(OH\) torsional and bending modes (i.e., \(4\nu_6+\nu_3\) and \(2\nu_6+2\nu_2\) that are in close resonance with the \(OH\)-stretch vibration. Interestingly, the corresponding hot band is missing in Fig. 2(c). In this experiment, the negative amplitude of the \(OH\) bleach/stimulated emission signal is not counterbalanced by corresponding positive bands, which is what would be expected as long as one assumes that the transition dipole moments of hot bands are the same as that of the corresponding transition from the ground state (i.e., in the harmonic approximation). The excited state absorption of the \(OH\) stretch vibration has been detected at \(3204\) cm\(^{-1}\) (Ref. 27) outside the spectral window observed in Fig. 2(c). The same seems to be the case for the dark states populated after the \(OH\) stretch vibration relaxes. In fact, the anharmonic constant \(x_{13}\) is predicted to be very large and negative (\(-35\) cm\(^{-1}\), see Table III), hence hot bands with excitations of \(4\nu_6+\nu_3\) or \(2\nu_6+2\nu_2\) are indeed expected to be outside this spectral window as well.

IV. DISCUSSION AND CONCLUSION

Three essential results are obtained from this two-color pump-probe study of HONO in solid Kr.
IVR in the condensed phase has been studied by IR-pump-anti-Stokes Raman probe spectroscopy, a technique that is specifically sensitive to vibrationally excited states and that potentially provides a complete spectrum of all normal modes at once. The present study shows that comparable information can also be obtained with IR pump-IR-probe spectroscopy avoiding the very weak Raman scattering process, provided that the molecule is small so that various hot bands are spectrally resolved, and provided that a reliable set of anharmonic constants is known from either theory or experiment. HONO is a small molecule sitting in a very well defined environment and may be described theoretically on the highest conceivable level. That is, high-level quantum chemistry potential energy surfaces are available and the fully coupled vibrational problem can be solved in all degrees of freedom of the molecule, full-dimensional wave-packet calculations are conceivable, and the effect of the matrix can be added on the level of mixed-quantum-classical calculations. At the same time, it is a reactive system, and the competition between IVR and the IR-driven photoisomerization determines, to a large extent, the outcome of the reaction. IVR is mode specific in HONO, e.g., the molecule cools through one particular mode, which is not the lowest frequency mode as a simple energy-gap law might suggest. The system might prove to be an ideal playground for further theoretical studies, emphasizing more the condensed phase character of the reaction than previous studies, which would give unprecedented insights into condensed phase reactions and possibly its manipulation.

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