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I. INTRODUCTION

Starting with Whittle et al.¹ in the 1950s, the matrix isolation technique has developed in a very powerful tool of investigating chemical compounds and reactions. Among many other applications, Pimentel and co-workers were also the first to observe that the formation of certain molecules, most prominently nitrous acid (HONO), may be switched by vibrational excitation with the help of IR light.²⁻⁴ Apart from being an important source of OH radicals in atmospheric chemistry,⁵⁻⁷ HONO has been studied extensively in the context of its IR driven isomerization both theoretically⁸⁻⁻²² and experimentally.²³⁻⁻³² Upon IR excitation of one quantum of the OH-stretch vibration, the molecule isomerizes in the cis→trans direction with almost unity quantum yield,⁴,²⁹ whereas the back yield is significantly smaller. The excitation reaches an energy (i.e., ≈3500 cm⁻¹) just below the barrier separating cis and trans isomers (4105 cm⁻¹ according to the best potential energy surface available⁷); hence, the reaction must be quantum with the hydrogen tunneling through that barrier. However, neither experimental³³ nor theoretical⁹⁻¹⁸ studies could find the reaction taking place in the gas phase with significant yield; hence, isomerization seems to be facilitated by the dissipative forces of the matrix environment. The high quantum yield of close to 1 is remarkable given the fact that the mode being excited (the OH-stretch vibration) is not the reaction coordinate (HON torsion).

We have recently revisited this important prototype proton transfer system using ultrafast IR spectroscopy²⁰⁻⁻³² in order to study for the first time also the course of the reaction in a time-resolved manner. We found that the cis→trans isomerization occurs in two steps, one on a fast picosecond timescale and a second one on a significantly slower nanosecond timescale. The timescales of the two isomerization steps roughly correlate with that of two energy relaxation processes: the vibrational lifetime of the initially excited OH_cis-stretch vibration (20 ps) and the overall cooling of the molecule into the matrix (≈20 ns). We have interpreted the slower reaction step by an essentially statistical picture,³¹ i.e., a feeding back of energy from a large manifold of states of the molecule into a few reactive states that act as channel for isomerization. The first step, in contrast, is related to a specific and much stronger coupling between the initially excited OH-stretch vibration and these reactive states.

At a temperature of 30 K, both isomerization steps are of roughly the same size and add up to a total quantum yield of η_cis→trans ≈30% for the cis→trans reaction. The back reaction yield is lower with η_trans→cis ≈7%.³¹ We attributed the discrepancy between the isomerization yield we observe and the close-to-unity yield reported in literature to the four times higher matrix temperature in our case [30 K versus 7 K (Refs. 4 and 29)]. In the present paper, we set out to investigate the effect of the matrix temperature on the isomerization yields.

In fact, the temperature dependence of the thermal equilibrium constant was a key ingredient in the 1950s, when the first gas phase spectra of HONO were taken, to establish that two isomers coexist. Jones et al.³⁴ as well as D’Or and Tarte³⁶ observed that the characteristic frequencies of HONO came in doublets and by varying the temperature they could change the ratio of these absorption bands. Pimentel and co-workers³³ measured the isomerization of HONO in solid N₂ and varied a wide set of parameters: relative concentration of precursors, different spectral filters to light trigger the isomerization, different isotope substitutions, deposition, and measuring temperatures. By choosing more and more selective filters, they were able to single out the 3200–3650 cm⁻¹ spectral interval as efficient to trigger the cis→trans isomerization. In order to eliminate the possibility that the reaction is triggered by bulk heating they cooled the matrix from 20 to 4 K but did not observe any change within the experiment.
to be a key observation that helps to explain the high temperature dependence of forward and backward yields proves to be a key observation that helps to explain the high temperature dependence of forward and backward yields. Nevertheless, the temperature although the cooling time stays more or less constant, in contrary to our expectation. We will see that the isomerization yield indeed increases with lowering the temperature, at the frequencies of the two isomers. Figure 1 clearly shows that the photoequilibrium ratio decreases with temperature, at lower temperatures might be significantly a problem at the lower temperature since the matrix cracks during cooling. We measure this scattering contribution at delay times larger than 100 ns, which is about the gating time of the electronic detection system, this subtraction is no longer perfect, and the quality of the data becomes worse.

We have speculated in Ref. 31 that the larger forward isomerization yield \( \eta_{\text{cis} \rightarrow \text{trans}} \) at lower temperatures might be due to a slower cooling into the matrix environment, giving the molecule more time to isomerize. Consequently, in the present paper, we study both the temperature dependence of vibrational cooling of HONO and the \( \text{cis} \rightarrow \text{trans} \) isomerization yield in a time-resolved manner. We will see that the isomerization yield indeed increases with lowering the temperature although the cooling time stays more or less constant, in contrary to our expectation. Nevertheless, the temperature dependence of forward and backward yields proves to be a key observation that helps to explain the high quantum yield of the reaction.

**II. EXPERIMENTAL METHODS**

HONO was synthesized photochemically inside the matrix according to a procedure reported by Hall and Pimentel. A gas mixture of 3:10:1000 HN₃:O₂:Kr was prepared in a glass container and sprayed on a calcium fluoride window in a cryostat (DE-202AF/DMX-20B, Advance Research Systems, Inc.) at a low pressure of 10⁻⁶ mbar and a temperature of \( \approx 30 \) K. The 3317 cm⁻¹ absorption band of HN₃ 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 HN₃ absorption band.

Two synchronized Ti:sapphire laser/amplifier systems were used for the pump-probe experiments, covering time delays up to 400 ns. Due to the time jitter of the two laser systems the effective time resolution was \( \approx 10 \) ps. Each Ti:sapphire laser/amplifier pumped one optical parametric amplifier (OPA) to generate tunable IR pulses centered at 3470 cm⁻¹, roughly 100 fs long and with a bandwidth of \( \approx 300 \) cm⁻¹ full width at half maximum. Pump and probe beams were focused to spot sizes of 150 and 100 µm, respectively, with a pump energy of 1.2 µJ. 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 (MCT) detector array, covering a spectral range from 3370 to 3580 cm⁻¹ with a resolution of 3.3 cm⁻¹. To enable selective excitation of the \( \text{cis} \) species, we used a piezo-controlled adjustable Fabry–Pérot filter with a bandwidth of \( \approx 15-20 \) cm⁻¹, resonant with \( \text{OH}_{\text{cis}} \). The pump intensities were kept low enough to be sure that we do not up-climb the vibrational ladder within the pump pulse by multiphoton excitation; hence we excite only one quantum of the OH-stretch vibration. The photoequilibrium was kept on the \( \text{cis} \) side by constantly exciting \( \text{trans} \)-HONO in excess with the help of a cw-diode laser (Nanoplus GmbH, Germany, power of \( \approx 0.5 \) mW and wavelength of 3550 cm⁻¹). The cw-laser light is not polarized. In one experiment [Fig. 2(a)] we used broad band excitation (without the Fabry–Pérot filter and without the cw-laser diode) to investigate the cooling of \( \text{trans} \)-HONO. Since the \( \text{cis} \rightarrow \text{trans} \) yield is significantly larger than the opposite direction, the photoequilibrium lies mostly on the \( \text{trans} \)-side under conditions of broad band excitation.

The matrices we prepare typically scatter significantly, thereby producing an offset of light scattered from the pump pulse into the direction of the probe pulse. This is particularly a problem at the lower temperature since the matrix cracks during cooling. We measure this scattering contribution at delay times before zero (i.e., probe pulse before the pump pulse) and subtract it from the actual data. However, for delay times larger than \( \approx 100 \) ns, which is about the gating time of the electronic detection system, this subtraction is no longer perfect, and the quality of the data becomes worse.

Due to absorption of IR light, the temperature in the measurement spot might locally exceed that of the cold finger. Nevertheless, the thermal conductivity of both the window substrate CaF₂ (Ref. 38) (and references therein) and that of the Kr matrix \( ^{39,40} \) increases with lowering the temperature so that the difference between the local and the
overall temperature is expected to be smaller at lower temperatures than at higher temperatures. The lowest temperature we can reach with our cryostat was 15 K.

III. RESULTS

Figure 2(a) compares the response of the OH\textsubscript{trans} band after excitation (i.e., pumping and probing at 3550 cm\textsuperscript{-1}) at two different temperatures (15 K, black, and 30 K, gray). This response consists of both the bleach and stimulated emission signals that appear at the same frequency and are expected to be equally strong at early delay times.\textsuperscript{30,31} The stimulated emission signal decays as the OH-stretch vibration decays into closely resonant overtones and combination modes, while the bleach signal decays as the molecule finally cools into the matrix. This leads to the characteristic biphasic decay of the overall signal with a plateau at around 1 ns in this case. The inset of Fig. 2(a) shows the excited state absorption (probing at 3387 cm\textsuperscript{-1}), which responds on the decay of the OH-stretch vibration exclusively (and not the cooling into the matrix) and hence exhibits only the faster process. A global fit of the response reveals that both relaxation times are hardly affected by temperature; if at all they are somewhat slowed down (by \(\sim 10\%\)) as the matrix is cooled down. The fit values are reported in Table I (due to the reduced time resolution of the present setup, compared to that used in Ref. 30, we were not able to resolve the faster component of the biexponential decay of the OH\textsubscript{trans} vibration, which presumably is a result of matrix inhomogeneities).

![Figure 2](image)

**FIG. 2.** Stimulated emission and bleach kinetics of OH\textsubscript{trans} [panel (A)] and OH\textsubscript{cis} [panel (B)] at 30 K (gray) and 15 K (black). The change of absorbance is given in units of optical density (OD). The inset of panel (A) represents the decay of the excited state absorption of OH\textsubscript{trans}.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>OH\textsubscript{trans} (ps)</th>
<th>trans-cooling (ns)</th>
<th>OH\textsubscript{cis} (ps)</th>
<th>cis-cooling (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 K</td>
<td>290 ± 20</td>
<td>14.4 ± 0.5</td>
<td>20\textsuperscript{2}</td>
<td>14.4 ± 1</td>
</tr>
<tr>
<td>30 K</td>
<td>270 ± 20</td>
<td>13.3 ± 0.5</td>
<td>20\textsuperscript{2}</td>
<td>13.4 ± 1</td>
</tr>
</tbody>
</table>

\textsuperscript{2}Since the time resolution of the present experiment was not sufficient to fully resolve the vibrational relaxation of the OH-stretch vibration in cis-HONO, the value (20 ps) was taken from Ref. 31 and assumed to be the same at both temperatures.

Figure 2(b) shows the corresponding response for OH\textsubscript{cis} (i.e., pumping and probing at 3400 cm\textsuperscript{-1}). A biexponential fit again reveals that both relaxation times are hardly affected by temperature (within signal-to-noise ratio, which is worse in this case because the signal is smaller, see Table I). The faster relaxation process, occurring on a 20 ps timescale\textsuperscript{30} in the case of OH\textsubscript{cis}, is not fully resolved in the present experiment due to its reduced effective time resolution of \(\sim 10\) ps.

In Fig. 3 we present IR difference spectra of OH\textsubscript{cis} [Fig. 3(b)] and OH\textsubscript{trans} [Fig. 3(a)] after pumping OH\textsubscript{cis}. In order to calculate the cis\textrightarrow trans isomerization yield, we have to compare the number of molecules that have been excited with the number of molecules that isomerized. We deduce the first number from the bleach signal at \(\sim 3400\) cm\textsuperscript{-1} at a delay time of 200 ps, i.e., the plateau between decay of stimulated emission and overall cooling (Fig. 3, left half), and the second number from the positive signal of OH\textsubscript{trans} at 3550 cm\textsuperscript{-1} at late delay times 200 ns when cooling into the matrix is completed (Fig. 3, right half). The signal at 15 K is normalized to that at 30 K in order to facilitate comparison of the isomerization yields. From the integrated intensities of the trans photoproduction bands, we estimate a 30\% rise in the cis\textrightarrow trans isomerization yield when temperature is reduced from 30 to 15 K (note that the product band is narrower at 15 K; hence the effect on the integrated intensity is smaller than that on the peak intensity). Correcting the signals in Fig. 3 with the ratio of transition dipoles of the OH-stretch vibration in cis- and trans-HONO \([1.6\text{-}2\text{ (Ref. 31)}]\), we conclude that the total quantum yield is \(\eta_{cis\textrightarrow trans} \approx 50\%\text{-}70\%\) at 15 K.

![Figure 3](image)

**FIG. 3.** Response of OH\textsubscript{cis} and OH\textsubscript{trans} after exciting OH\textsubscript{cis}. Panel (A) shows the bleach of OH\textsubscript{cis} after 200 ps and panel (B) that of OH\textsubscript{trans} at 200 ns. Gray and black lines compare the response at 30 and 15 K, respectively. The change of absorbance is given in units of OD.
However, it should be noted that this estimate of the quantum yield implicitly assumes an isotropic sample. As the sample is excited with polarized light, this is not necessarily the case; in fact, we have shown recently that at least trans-HONO does not undergo full orientational diffusion on even a minute timescale.32 Also the degree of polarization of the laser used to switch back will play a role. In the present study, we used a cw-laser diode for this purpose, which was not polarized, whereas in Ref. 31 we had used light derived from the femtosecond OPA which was polarized. This might explain the difference in absolute numbers between the present study and the results of Ref. 31. We therefore concentrate in the discussion more on the temperature induced change of quantum yield rather than the absolute values.

IV. DISCUSSION

In a first set of experiments, we measured the lifetime of the OH-stretch vibration of HONO and found little or no temperature dependence in the interval from 30 to 15 K. Also the cooling of the HONO molecules into the matrix proves to be only very weakly temperature dependent, if at all. To the best of our knowledge, there is no published work of similar experiments in which vibrational lifetimes have been studied as a function of temperature in matrix environment. The closest situation we are aware of is the vibrational relaxation of CO groups in globular proteins such as myoglobin, measured by Fayer.41 The lifetime of CO (=30 ps) changes by less than 20% in a large temperature interval from 310 to 10 K. Also the vibrational lifetimes of the OH vibration in ice42 as well as the amide I (C=O) vibrations of the backbone in peptides and proteins have been shown to be largely temperature independent.43 Our observation of essentially temperature independent relaxation rates of HONO in solid Kr is in accordance with these studies.

The cis→trans isomerization yield, on the other hand, increases by ≈30% when the temperature is lowered from 30 to 15 K, resulting in a total quantum yield of 50%–70% at 15 K. This value is still smaller than the reported quantum yield of close to 1.29 The two results are nevertheless consistent within experimental uncertainty, in particular, when considering that the temperatures are still different (15 K versus 7 K). That is, if we were to extrapolate our value to 7 K, based on what one would expect from Fig. 1, we might indeed conclude that the quantum yield could reach values close to 100%.

Due to technical limitations related to the tuning range of the cw-diode laser used in our experiment, we cannot measure the temperature dependence of the trans→cis yield directly. We can nevertheless estimate it from Fig. 1, which plots the ratio of yields, \( \eta_{cis→trans}/\eta_{trans→cis} \). This ratio increases by ≈80% when lowering the temperature form 30 to 15 K, implying that \( \eta_{trans→cis} \) actually decreases by ≈40% in the same temperature range.

We discuss the reaction mechanism in analogy to Marcus theory of nonadiabatic electron transfer. The concepts of electron transfer theory have been extended to other types of reactions, most notably proton transfer reactions, by many researchers before.44–47 We have shown in a mixed-quantum-classical simulation22 that proton transfer is driven by matrix fluctuations, i.e., transfer of population between two vibrational states takes place when they become resonant due to matrix fluctuations, and that these curve crossings are only weakly avoided due to a small tunnel coupling. These are exactly the prerequisites of Marcus theory of nonadiabatic electron transfer. Accordingly, the proton transfer rate between each pair of cis and trans vibrational states can be expressed as

\[
\frac{k_{cis→trans}}{k_{trans→cis}} = \exp \left( \frac{\Delta F}{k_B T} \right),
\]

where \( \Delta F \) is the energy gain upon isomerization, and \( F_x \) is the reorganization energy, i.e., the energy it would cost to deflect the solvation degrees of freedom to the trans situation, however, keeping the proton on the cis side. The ratio between forward and backward rates, of course, fulfills detailed balance:

\[
\frac{k_{cis→trans}}{k_{trans→cis}} = \exp \left( \frac{\Delta F}{k_B T} \right).
\]

With \( \Delta F \) positive for a downhill reaction, this ratio increases as the temperature is reduced, exactly as observed experimentally (Fig. 1). The only situation for which also the forward rate \( k_{cis→trans} \) can increase when lowering the temperature is the essentially barrierless case with \( \Delta F \approx F_x \) when the product free energy surface crosses the reactant surface close to its minimum (see black circles in Fig. 4). In this case, the \( 1/\sqrt{T} \) dependence of the pre-exponential factor of Eq. (1) exceeds that of the exponential term. In fact, the \( 1/\sqrt{T} \) term would predict a 40% increase in the forward rate when the temperature is reduced by a factor of 2, in very good agreement with our experimental value (30%). The barrierless case is also the situation that renders the rates maximal (i.e., the maximum in the so-called Marcus parabola).

Figure 4 shows a possible arrangement of the relevant vibrational states, plotted as a function of a generalized solvation coordinate.
viation coordinate. Upon IR excitation of cis-HONO, the OH-stretch vibration $\nu_{\text{stretch}}$ is reached. It has been shown in Ref. 22 that $\nu_{\text{stretch}}$ decays predominantly into $4\nu_{\text{trans}} + \nu_{\text{bend}}$, $2\nu_{\text{trans}} + 2\nu_{\text{bend}}$, and $3\nu_{\text{bend}}$ since these states are closely resonant. The two states $4\nu_{\text{trans}} + \nu_{\text{bend}}$ and $2\nu_{\text{trans}} + 2\nu_{\text{bend}}$ probably play the most important role in the isomerization reaction since they have a sufficiently large number of quanta in the torsional coordinate responsible for a significant tunneling coupling $\beta$. The temperature dependencies of both forward and backward yields suggest that the corresponding states in the trans configuration are energetically lower and furthermore cross the cis-states in essentially a barrierless manner. This special arrangement is supported by the observation that the corresponding fundamental modes are indeed lower in frequency in the trans configuration: $\nu_{\text{trans}} = 549 \text{ cm}^{-1}$ in trans-HONO versus 637 cm$^{-1}$ in cis and $\nu_{\text{bend}} = 1287 \text{ cm}^{-1}$ in trans-HONO versus 1315 cm$^{-1}$ in cis [in solid Kr (Ref. 29)]. The OH-stretch vibration, in contrast, is higher in frequency in trans-HONO (3351 cm$^{-1}$ versus 3401 cm$^{-1}$). Hence, the initially pumped OH-stretch vibration is not in resonance with the reactive modes in the trans configuration (see Fig. 4), explaining why the decay of the former is less efficient (270 ps in trans-HONO versus 20 ps in cis).

Putting these considerations together, we can now discuss the reason for the high quantum yield. The high quantum yield is merely a result of the fact that the reaction proceeds energetically downhill [Eq. (2)]. However, it is not the ground state surfaces that are relevant (for which the tunnel coupling would be negligible) but the surfaces of a few reactive states that are energetically close enough to the barrier. The second important ingredient for the high quantum yield is the cooling rate that is of the same order of magnitude as the isomerization rate. This is seen from the fact that the sum of forward and backward yields $\eta_{\text{cis} \rightarrow \text{trans}} + \eta_{\text{trans} \rightarrow \text{cis}} =$ 60%–80% is close to 1 but does not quite reach this value at 15 K. If cooling would be significantly slower, then the molecule would have time to fully thermalize on either side, in which case the ratio of forward and backward yields would be determined by the densities of states in both configurations. However, these densities of states are almost identical in the relevant energy range. On the other hand, if isomerization would be significantly slower than cooling, the molecule would not have time to isomerize and the sum of forward and backward yields $\eta_{\text{cis} \rightarrow \text{trans}} + \eta_{\text{trans} \rightarrow \text{cis}}$ would be significantly below 1. Tentatively, this is what is happening at higher temperatures.

V. CONCLUSION

In conclusion, we have studied the temperature dependence of energy relaxation processes as well as of the cis $\rightarrow$ trans isomerization yield of HONO in solid Kr. While the former are hardly temperature dependent, the cis $\rightarrow$ trans forward yield increases by $\approx$30% when lowering the temperature from 30 to 15 K. The trans $\rightarrow$ cis backward yield, in contrast, decreases by $\approx$40% in the same temperature range. This peculiar temperature dependence is the key observation that helps to explain the observed high quantum yield of this important model reaction. That is, the temperature dependen-

ACKNOWLEDGMENTS

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