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Abstract

With the help of ultrafast time-resolved infrared spectroscopy, we investigate rotational diffusion of cis- and trans-nitrous acid (HONO) in solid Kr at 30 K, as well as its reorientation upon the IR-driven cis -> trans isomerization. We find different mobilities for the two isomers: cis-HONO is pinned to the matrix with no decay of the anisotropy on the 100 ns time scale, whereas trans-HONO rotates around its long axis, reducing its anisotropy partially on that time scale. The long axis itself, defined by the terminal oxygen and hydrogen atoms of HONO, stays fixed on even a minute time scale. Accompanying molecular dynamics simulations reproduce the anisotropic rotational diffusion of trans-HONO correctly, although on a completely wrong time scale, whereas they would predict complete reorientation of cis-HONO within approximate to 10 ps, in harsh disagreement with the experiment. We attribute the mismatch of orientational time scales to either too soft interaction potentials or to the fact that HONO occupies an interstitial rather than a monosubstitutional matrix site. The experiments furthermore show that the direction of the OH bond hardly changes during the IR-driven cis -> trans isomerization, in contrast to the intuitive picture that it is mostly the light hydrogen which moves. Rather, it is the two central nitrogen and oxygen atoms that are removed during isomerization in a hula hoop fashion, whereas the terminal atoms are still pinned to the matrix cage.
Rotational dynamics of nitrous acid (HONO) in Kr matrix

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With the help of ultrafast time-resolved infrared spectroscopy, we investigate rotational diffusion of cis and trans nitrous acid (HONO) in solid Kr at 30 K, as well as its reorientation upon the IR-driven cis→trans isomerization. We find different mobility for the two isomers: cis-HONO is pinned to the matrix with no decay of the anisotropy on the 100 ns timescale, whereas trans-HONO rotates around its long-axis, reducing its anisotropy partially on that timescale. The long-axis itself, defined by the terminal oxygen and hydrogen atoms of HONO, stays fixed on even a minute timescale. Accompanying molecular dynamics (MD) simulations reproduce the anisotropic rotational diffusion of trans-HONO correctly, albeit on a completely wrong timescale, whereas they would predict complete reorientation of cis-HONO within ≈10 ps, in harsh disagreement with the experiment. We attribute the mismatch of orientational timescales to either too soft interaction potentials, or to the fact that HONO occupies an interstitial rather than a mono-substitutional matrix site. The experiments furthermore show that the direction of the OH bond hardly changes during the IR-driven cis→trans isomerization, in contrast to the intuitive picture that it is mostly the light hydrogen which moves. Rather, it is the two central nitrogen and oxygen atoms that move during isomerization in a hula hoop fashion, whereas the terminal atoms are still pinned to the matrix cage.

INTRODUCTION

The matrix isolation technique has proven to be a very powerful tool to analyze a large variety of chemical processes and compounds. Whittle and Pimentel proposed this technique in a seminal paper in the fifties [1], leading to the characterization and discovery of a large class of chemical compounds in the following decades, among which are radicals and reactive intermediates (see e.g. Ref. [2]) as well as chemical compounds with noble elements [3–5]. The molecules are isolated in a nonreactive solid, in most cases rare gases (Xe, Kr, Ar, Ne) but sometimes also N₂, CH₄. Very little is known about the orientational dynamics of molecules inside rare gas matrices and analyzing this dynamics is the purpose of the present study. Small molecules (H₂O, HCl, CN, NH₃) may rotate essentially freely in certain rare gas matrices [6, 7], as seen from rovibrational side-bands in the IR spectrum. However, somewhat larger molecules of the size of, for example, CH₄, rotate in a thermally activated, diffusive manner, a process that has been studied by electron paramagnetic resonance (EPR) [8–10] as well as by IR hole burning [11, 12]. Another technique that looks directly at diffusive rotational dynamics is polarization-resolved optical pump-probe spectroscopy. For instance, in order to study the depolarization in the process of bond breaking and bond forming, Bargheer et al. [13] used laser induced fluorescence (LIF) for two different molecules in qualitatively different surroundings: ClF in Ar and I₂ in Kr. The two systems revealed completely different results: ClF undergoes a complete depolarization on a 1.2 ps timescale, whereas the I₂ shows no depolarization whatsoever. The authors attributed this difference to the different symmetries of the immediate surroundings of the molecules. It has been suggested that ClF sits in a mono-substitutional site, i.e. an essentially isotropic surrounding, and thus it is free to rotate whereas I₂ sits in a double substitutional site, i.e. in a cylindrical cage, hence being sterically fixed [13]. Thus, polarization measurements may serve as decisive probes of the immediate surrounding of the molecules embedded in rare gas solids.

In a series of papers [14–16], we have investigated the IR-driven cis-trans isomerization of nitrous acid (HONO) as well as the accompanying intramolecular vibrational redistribution (IVR) processes. Apart from being an important source of OH radicals in atmospheric chemistry [17–19], HONO has been studied intensively both theoretically [20–32] and experimentally [33–37] because of its IR-driven isomerization reaction. Upon IR excitation of the OH stretch vibration, the molecule isomerizes in the cis→trans direction with almost unity quantum yield [34, 37], whereas the back yield is significantly smaller. Neither experimental [38] nor theoretical [21, 30] studies could find the reaction taking place in the gas phase, hence, isomerization seems to be facilitated by the dissipative forces of the matrix environment. The high quantum yield of close-to-one is remarkable given the fact that the mode being excited (the OH stretch vibration) is not the reaction coordinate (HON torsion). A recent mixed quantum-classical simu-
lution [16], treating the three degrees of freedom of the hydrogen as quantum and the remainder as classical, revealed good qualitative agreement with experimental results on a fast picosecond timescale, but also showed that energy dissipates relatively efficiently into all vibrational degrees of freedom of the molecule. Hence the reaction becomes statistical after a few 10’s of picoseconds and the quantum yield of 100% is not understood.

In the present work we investigate the rotational diffusion of the two isomers of HONO in solid Kr in order to obtain information on the interaction forces of HONO with its matrix surrounding. The work is corroborated by classical MD simulations, using the same pair potentials as the mixed quantum-classical simulation in Ref. [16]. The comparison between experiment and MD simulation suggests that these pair potentials are significantly too soft, which could either be intrinsic to the potentials, or hint to a different matrix site (i.e. an interstitial rather than a mono-substitutional site). We furthermore determine the reorientation of the ONO-body upon isomerization, suggesting that isomerization is accompanied by a hula hoop motion of the two central nitrogen and oxygen atoms, pinning the terminal atoms to the matrix cage.

MATERIALS AND METHODS

Experimental

HONO was synthesized photochemically according to a procedure reported by Hall and Pimentel [34]. A gas mixture of 3:16:1000 HN$_3$: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$^{-7}$ mbar) and a temperature of approximately 30 K. 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.

For measuring the depolarization dynamics we use a femtosecond IR pump-probe setup. For the short time scans (0-600 ps) we used one amplified Ti:S system and a conventional delay stage to achieve the retardation between pump and probe pulse, whereas two synchronized Ti:S laser/amplifier were used to cover longer time delays up to 400 ns [39]. Each Ti:S 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}$ FWHM [40]. In one experiment the wavelength of one IR-OPA was tuned in order to probe the N=O stretch region. Pump and probe beams are focused to spot sizes of 150 $\mu$m 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 (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 cis species we used a piezo-controlled adjustable Fabry-Perot filter with a bandwidth of $\approx$15-20 cm$^{-1}$. The polarization of the pump-beam was adjusted with the help of a computer-controlled $\lambda/2$-waveplate.

In our previous works [14, 15], in order not to deplete the sample, we had alternatively pumped the cis and trans OH stretch bands (OH$_{cis}$ and OH$_{trans}$) in a cyclic manner, following a scheme which took into account the different isomerization yields. This procedure was very time consuming. We now apply a cw diode laser (Nanoplus GmbH, Germany) with the wavelength slightly tunable around 3550 cm$^{-1}$ (OH$_{trans}$ in solid Kr) to constantly irradiate the sample volume, thus keeping the photo-equilibrium at an excess of the cis isomer. The linewidth of this laser is $\approx$1.5 cm$^{-1}$. We aligned its center wavelength for maximum signal, and thus excited both the dominant site bands simultaneously (see inset of Fig. 1a). In this way we can follow the cis$\rightarrow$trans isomerization using a narrow band pump pulse tuned to OH$_{cis}$, shortening the measurement time by almost one order of magnitude. The reverse trans$\rightarrow$cis reaction is studied by broad band pumping both isomers with the IR pulse directly from the IR OPA without filtering in the Fabry-Perot filter (and without the cw laser). As the cis$\rightarrow$trans quantum yield is significantly larger, the photo-equilibrium will then be mostly on the trans side, and the small cis-pumped contribution can be subtracted out using the previous experiment.

On a longer second to minute timescale, the anisotropy was measured in a Fourier transformed infrared (FTIR) spectrometer. The sample was excited with the cw diode laser mentioned above, which was coupled into the FTIR spectrometer with a flipping mirror collinear to the FTIR spectrometer beam. A rotating wire-grid polarizer was placed in front of the sample allowing collection of absorption spectra with a polarization parallel and perpendicular to the excitation beam. As in the case of the time resolved measurements, difference spectra were collected, subtracting out the non-excited molecules.

Computational

The experiments where accompanied by all-classical molecular dynamics (MD) simulations, using the classical part of an in-house code described in Ref. [16]. In brief, a MD box was set up consisting of 9 × 9 × 9 unit cells of a fcc lattice in a cubic box with periodic boundary conditions, each containing four Kr atoms with a Kr-Kr nearest neighbor distance of 3.934 Å. If not noted oth-
otherwise, HONO was placed in a mono-substitutional site, i.e. removed the central Kr atom and replaced it by either cis- or trans-HONO in its gas phase structure [32] with its position inside the cage energy-minimized. Random velocities were assigned to all atoms, resulting in a temperature equal to that in the experiment (≈30 K) after equilibration in a NVE simulation. No quantum-corrections, such as an increased effective temperature to account for zero-point energy, have been added. A cut-off of 12 Å was applied for the Lennard-Jones interactions. The equations of motion were integrated using a leapfrog scheme with time step 2 fs. HONO was modelled as a rigid body (all internal degrees of freedom frozen), using quaternions to represent its orientations [41, 42]. The interaction of HONO with the matrix cage, as well as the molecules that have isomerized to trans-HONO. The latter spectrum does not yet agree with OHtrans in Fig. 1A because the molecules are still hot 2 ns after excitation and the signal is red shifted due to intramolecular anharmonicity [14].

### EXPERIMENTAL RESULTS

**Background: Pump-Probe Spectroscopy of HONO**

To set the stage, Fig. 1A shows an absorption spectrum of HONO in solid Kr in the OH stretch region. The bands at ≈3400 cm$^{-1}$ and ≈3550 cm$^{-1}$ correspond to the cis and trans isomers, respectively. Both bands exhibit some substructure due to matrix inhomogeneities (Fig. 1A, inset). Fig. 1B shows typical transient pump-probe difference spectra at 2 ns delay time. The black line depicts the response after selective excitation of OHcis, whereas the gray line presents the response after broadband pumping. In the second case, both cis$\rightarrow$trans and trans$\rightarrow$cis reactions happen at the same time, however, since the cis$\rightarrow$trans quantum yield is significantly larger, the photo-equilibrium will mostly be on the trans side. In such transient difference spectra, negative signals originate from bleaching species (stimulated emission, also leading to negative signals, has decayed after 2 ns [15]), and positive signals from photo-products. For example, when pumping OHcis (Fig. 1B, black line), we see a bleach at the wavelength of OHcis and a broader positive band around 3525-3550 cm$^{-1}$ originating from molecules that have isomerized to trans-HONO. The latter spectrum does not yet agree with OHtrans in Fig. 1A because the molecules are still hot 2 ns after excitation and the signal is red shifted due to intramolecular anharmonicity [14].

![FIG. 1: (A) FTIR spectrum of HONO in the OH stretch region. The inset enlarges OHtrans. (B) Transient absorption spectra 2 ns after selectively pumping either OHcis (black) or broadband pumping both isomers (gray). Inset: Kinetics at 3550 cm$^{-1}$ after pumping OHcis, reporting on the formation of cold trans-HONO.](image)

**Rotational Diffusion**

In a first step, we study orientational diffusion of both cis and trans HONO. To this end, we pump the OH-stretch band of either isomer and measure the anisotropy of the negative bleach and stimulated emission signals of the pumped species, both appearing at the same frequency, i.e. the frequency of the initially pumped transition. The anisotropy of the bleach signal originates from HONO molecules that have not been pumped, hence it is not affected by absorbing any photon. The stimulated emission contribution, of course, originates from molecules that have absorbed a photon, but as long as they show stimulated emission they have not dissipated the photon energy. Hence the molecules and their sur-

<table>
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<th>$\epsilon$ [cm$^{-1}$]</th>
<th>Kr</th>
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<td>19.1</td>
<td>15.4</td>
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<td>2.003</td>
<td>1.368</td>
<td>1.561</td>
<td>1.621</td>
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**TABLE I**: Lennard Jones parameters used in the MD simulation [15, 22, 43]
as such potentially affect orientational diffusion times (we on the other hand, recovery of the excited molecules back originating from the CaF$_2$ within our instrumental response function, however, is 

t = decay time constant due to free motion governed by 

and/or the fact that the sample is not perfectly homo-

geneous and isotropic. When estimating the anisotropy 
does not start from the theoretical value $r = 0.4$, which is the value expected from orientational averaging in an isotropic sample [45]. We attribute this discrepancy to either the fact that the molecules can rotate freely in a small restricted cone on a sub-picosecond timescale and/or the fact that the sample is not perfectly homogeneous and isotropic. When estimating the anisotropy decay time constant due to free motion governed by the inertia moment $I_{\text{HONO}} = 9.6 \times 10^{-47}$ kgm$^2$ we get 

\[ t = \sqrt{\frac{I}{k_B T}} \approx 0.5 \text{ ps} \]  

This would, in principle, be entirely isotropic.

Fig. 2B shows the anisotropy decay of OH$_{cis}$, defined as:

\[ r = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}} \]  

(2)

which was calculated from the bleach/stimulated emission signals shown in Fig. 2A with parallel and perpendicular polarizations of pump- and probe pulses. The anisotropy stays essentially constant at around $r = 0.3$ during the entire time window from 1 ps to 100 ns. It does not start from the theoretical value $r = 0.4$, which is the value expected from orientational averaging in an isotropic sample [45]. We attribute this discrepancy to either the fact that the molecules can rotate freely in a small restricted cone on a sub-picosecond timescale and/or the fact that the sample is not perfectly homogeneous and isotropic. When estimating the anisotropy decay time constant due to free motion governed by the inertia moment $I_{\text{HONO}} = 9.6 \times 10^{-47}$ kgm$^2$ we get 

\[ t = \sqrt{\frac{I}{k_B T}} \approx 0.5 \text{ ps} \]  

This would, in principle, be entirely isotropic.

Fig. 3 shows the anisotropy decay of OH$_{trans}$, using broad-band excitation. In this configuration we excite both isomers at the same time but we will argue (vide infra) that this experiment is essentially a trans-pump trans-probe experiment. Inherently, the photo-equilibrium under broad band radiation strongly favors the trans isomer with ratios that vary from 3 to 7, depending on temperature [14]. Moreover, the molecules that isomerize from cis to trans-HONO are hot up to a few nanosecond timescale, and as a consequence they are red shifted from the OH$_{trans}$ bleach/stimulated emission frequency and do not interfere with this signal. To illustrate this effect, we plot in Fig. 1B, inset, the response after pumping OH$_{cis}$ and probing at the frequency of pump and probe pulses still overlap partially in time (we therefore disregard the data before 1 ps). Nevertheless, this initial drop in anisotropy is small and the molecule exhibits no further rotation up to 100 ns. The anisotropy measured in two different scans (black and gray squares) behave qualitatively identically, albeit with a small offset. We attribute this offset to the fact that the two measurements have been performed in different matrices. Rare gas matrices are usually poly-crystalline and because the focus of the probe beam is small ($\approx 100 \mu$m), the region of the matrix sampled by the probe beam might not be entirely isotropic.

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cold trans-HONO. The signal stays essentially zero up to a few nanoseconds, although isomerization has already occurred. On longer timescale, the OH\textsubscript{trans} pumped signal can be singled out by subtracting the properly scaled OH\textsubscript{cis}-pumped response (where the scaling factor is deduced from the small bleach of OH\textsubscript{cis}).

The rotational dynamics of trans-HONO (Fig. 3B) is qualitatively different from that of cis-HONO. The anisotropy again starts with a value \( r = 0.38 \) slightly below the theoretical value 0.4, but, in contrast to cis-HONO, then decays to \( r \approx 0.2 \) in a highly non-exponential manner stretching from 1 ps to 100 ns. On an even longer second to minute timescale, this value \( r \approx 0.2 \) stays constant (Fig. 3B, black circles).

### Computational Results

Fig. 4 shows the anisotropy decay deduced from a classical MD simulation, using the Lennard Jones parameters listed in Tab. I and assuming HONO occupies a mono-substitutional matrix site. The anisotropy is calculated from the common expression [45]:

\[
    r(t) = \frac{2}{5} \langle P_2(\hat{\mu}(0) \cdot \hat{\mu}(t)) \rangle
    = \frac{1}{5} \left( 3 \langle (\hat{\mu}(t) \cdot \hat{\mu}(0))^2 \rangle - 1 \right)
\]  

(3)

where \( P_2 \) denotes the second Legendre polynomial, \( \hat{\mu}(t) \) a unit vector parallel to the OH bond (in this particular case), and \( \langle (...) \rangle \) an average over a 5 ns long equilibrium trajectory. While the overall timescale is wrong by many orders of magnitude, the MD simulation does reveal a qualitative difference between cis and trans-HONO: The anisotropy of cis-HONO decays essentially mono-exponentially like a spherical top (not seen in the experiment on a 100 ns timescale), while trans-HONO decays only partially with a long-time pedestal, just like in the experiment (Fig. 3). Analyzing the trajectories reveals that the fast initial component in the anisotropy decay of trans-HONO reflects the rotation of the molecule around its long-axis, whereas the long-axis itself does not rotate on the timescale of the MD trajectory (5 ns). In order to determine the nature of the long-axis, we integrate the angle \( \langle \hat{\mu}(0) \cdot \hat{\mu}(t) \rangle \) in Eq. 3 over a cone with opening \( \theta \):

\[
    r(\infty) = \frac{1}{40} (3 \cos 2\theta + 1)^2
\]  

(4)

This is the anisotropy pedestal expected at long delay times when the molecule has equilibrated completely around the long-axis, but when we assume the long-axis itself remains fixed. We find in the MD simulation \( r(\infty) \approx 0.13 \), corresponding to an angle \( \theta = 32^\circ \), which agrees perfectly with the angle between the OH bond and a vector connecting the terminal hydrogen and oxygen atoms. Hence, the two ends of the molecule are tightly fixed by the matrix cage during this rotation, whereas the in-between N-O group rotates in a bicycle manner.

The long-time pedestal we observe experimentally, \( r(\infty) \approx 0.2 \), is somewhat larger, which is explained by the fact that the OH\textsubscript{trans} transition dipole, which is our experimental observable, is slightly tilted with respect to the OH bond (Fig. 5A). From Eq. 4, we can estimate an angle of \( \theta = 24^\circ \) for the angle between the OH\textsubscript{trans} transition dipole and rotation axis \( r(\infty) \) was up-scaled in order to account for the fact that the initial anisotropy \( r(0) \) does not start from the theoretical value 0.4, or \( 8^\circ \) for the angle between the OH\textsubscript{trans} transition dipole and the OH bond. The latter value agrees reasonably well with the result of 22\(^\circ\) obtained from a gas-phase QCISD/cc-pVDZ quantum-chemistry calculation [44]. The discrepancy between both values might be explained by a matrix effect. For instance, the absorption frequencies of OH\textsubscript{cis} and OH\textsubscript{trans} are shifted by 25 cm\(^{-1}\) and 38 cm\(^{-1}\), respectively, from the gas phase values [32], and we might just as well expect an effect on the direction of the transition dipoles.

### Rotation upon Isomerization

In a second step, we investigate the rotation of the molecule during its IR-driven cis\textrightarrow trans isomerization. To this end, we excite OH\textsubscript{cis} and measure the anisotropy of trans-HONO photo-product bands. The angle \( \alpha \) between both transitions can then be evaluated by using an expression equivalent to Eq. 3, but now interpreting \( \hat{\mu}(0) \) as the direction of the pumped transition dipole, and \( \hat{\mu}(t) \) as the direction of the probed transition dipole:

\[
    r = \frac{1}{5} (3 \cos^2 \alpha - 1)
\]  

(5)
This expression ignores the possibility that trans-HONO undergoes orientational diffusion around the long-axis after the photo-isomerization has occurred. In order to obtain redundant information and thereby making the result more robust against errors, we measured the relative angle of two transition dipoles: The angle $\alpha$ between the OH$_{cis}$ and OH$_{trans}$ transition dipoles and the angle $\beta$ between the OH$_{cis}$ and N=O$_{trans}$ transition dipoles (see Fig. 5C).

Fig. 6A presents transient spectra 300 ns after pumping OH$_{cis}$ (after isomerization and cooling is complete) and probing in the OH stretch region. From the integrated band intensities, we find for the anisotropy of the OH$_{cis}$ bleach $r \approx 0.3$, equivalent to Fig. 2. The anisotropy of OH$_{trans}$ is $r=0.18$. We have seen in Fig. 2 that cis-HONO does not rotate, but it may rotate around the long-axis once it has isomerized to trans-HONO, reducing the long-time anisotropy to $r \approx 0.2$ (Fig. 3). The fact that both anisotropies – pumping OH$_{cis}$ and probing OH$_{trans}$ (Fig. 6A) versus pumping OH$_{trans}$ and probing OH$_{trans}$ (Fig. 3) – are essentially the same leads to the conclusion that the angle $\alpha$ between OH$_{cis}$ and OH$_{trans}$ transition dipoles is small.

A second, independent angle is measured when probing in the N=O spectral region (Fig. 6B). The response around 1630 cm$^{-1}$ originates from N=O$_{cis}$ with a negative anisotropy $r=-0.12$, which is related to an angle between the OH$_{cis}$ and N=O$_{cis}$ transition dipoles of $\gamma = 69^\circ$ (Fig. 5C). This result agrees well with the corresponding value obtained from a QCISD/cc-pVDZ quantum-chemistry calculation, $\gamma = 76^\circ$ [44]. The anisotropy does not change over time, in agreement with our conclusion from Fig. 2 that cis-HONO does not rotate in equilibrium. The response around 1680 cm$^{-1}$, on the other hand, originates from the N=O$_{trans}$ of the trans photo-product with an anisotropy of $r=0.14$, related to an angle $\beta = 41^\circ$.

With these two angles, $\alpha \approx 0^\circ$ and $\beta = 41^\circ$ (or, $180^\circ - \alpha \approx 180^\circ$ and/or $180^\circ - \beta = 139^\circ$), one can try to determine the orientation of the trans photo-product relative to the reactant cis-HONO (three angles would in principle be needed to uniquely determine the orientation, if rotation occurs in all three dimensions). However it turns out that there is no solution for the particular values of the two angles. The uncertainty originating from experimental noise, the quantum-chemistry calculation, the crystal which is not perfectly isotropic, the unresolved free rotation in a small restricted cone on a sub-picosecond timescale, as well as the complication of rotation around the long-axis in the trans-state results in
an overall, mostly systematic error whose size is difficult to assess.

We can nevertheless exclude the situation which one might consider the most intuitive one: Fig. 5B depicts the transition dipoles assuming that the ONO-body is not moving during the isomerization, i.e. assuming that isomerization is essentially a motion of the lightest atom, the hydrogen. In this case, we would predict an angle between \( \text{OH}_{\text{cis}} \) and \( \text{OH}_{\text{trans}} \) transition dipoles, \( \alpha = 113^\circ \), which would result in a negative anisotropy \( r = -0.11 \), clearly outside the combined error. We know from Fig. 3b that the molecule is rotating around the long axis, once it is isomerized to the \( \text{trans} \) configurations. If we take this additional effect into account by integrating Eq. 5 over a cone whose axis is tilted by \( \alpha \), we would expect an anisotropy that is reduced to \( r = -0.08 \), still not in agreement with the experimental results. Any further random rotation, e.g. due to local heating, would reduce the anisotropy even further to \( r = 0 \), but never flip the sign. In Ref. [15], we had energy-minimized the molecule in a mono-substitutional site in both the \( \text{cis} \) and the \( \text{trans} \) configurations (Fig. 6 of Ref. [15]), revealing a small 2° rotation angle of the ONO-body, which however would go into the direction to render the anisotropy again more negative.

Fig. 5C, on the other hand, depicts a possible solution of the problem, minimizing the deviations from the measured angles \( \alpha \) and \( \beta \) and at the same time taking into account that the angle \( \beta \) is probably better determined than \( \alpha \). The former is less affected by the rotation around the long-axis in the \( \text{trans} \) state, since the N=O\(_{\text{trans}}\) transition dipole is essentially parallel to that axis. In Fig. 5C, the OH\(_{\text{cis}}\) and OH\(_{\text{trans}}\) transition dipoles are essentially parallel, responsible for the observed large positive anisotropy. As a result, the vectors connecting the terminal oxygen and hydrogen atoms are close to parallel as well. This would suggest, very surprisingly and counter-intuitively, that isomerization is happening for the central N-O atoms in a space-saving, hula hoop fashion, while HONO is pinned to the Kr cage by the terminal atoms, just like during rotational diffusion of the \( \text{trans} \)-isomer.

**DISCUSSION AND CONCLUSION**

We have studied the orientational diffusion of \( \text{cis} \) and \( \text{trans} \) HONO in solid Kr as well as its reorientation during the IR-driven \( \text{cis} \rightarrow \text{trans} \) isomerization. In the first case, we cannot identify any rotation of \( \text{cis}-\text{HONO} \) on the 100 ns timescale (apart from a small unresolved drop of the anisotropy on a sub-picosecond timescale, see Fig. 2). It is interesting to note that even local heating of the matrix cage after recovery of the ground state, occurring after \( \gtrsim 2 \) ns, does not lead to any significant drop of anisotropy, i.e. does not accelerate rotational diffusion. Furthermore, the constant anisotropy argues against energy migration as a result of resonant inter-molecular vibrational energy transfer, as it has been suggested in the past [35]. Such a process would transfer energy to molecules with random orientations, and as such reduce the anisotropy, an effect whose concentration dependence has been studied in detail for example for HOD dissolved in H\(_2\)O [47].

The response of \( \text{trans} \)-HONO, on the other hand, is considerably more complex: Its anisotropy decays partially in a highly non-exponential manner, stretching from 1 ps to 100 ns, but then stays constant on a second to minute timescale (Fig. 3). Guided by accompanying MD simulations, we attribute this partial decay to a rotation around the long-axis of the molecule, whereas the terminal oxygen and hydrogen atoms are tightly fixed to the matrix cage, hindering the rotation of the long-axis itself. The non-exponentiality of the initial decay might be related to matrix inhomogeneities. Fig. 1A, inset, enlarges the absorption spectrum of OH\(_{\text{trans}}\), revealing a substructure composed of two dominant peaks and a weaker one. It is believed that this substructure corresponds to different matrix sites and there have been assignments that range from interstitial [22] to mono- and double-substitutional [37]. The interaction forces between HONO and the matrix cage will be very different in these sites, and so will be the orientational diffusion times (due to the 3.3 cm\(^{-1}\) spectral resolution in our pump-probe setup we cannot address the sub-bands independently). One must furthermore keep in mind that a significant amount of O\(_2\) and N\(_2\) is present in the matrix as a result of the procedure we chose to synthesize HONO (see Materials and Methods). Both are spectroscopically dark but possibly responsible for additional matrix inhomogeneities [48].

Albeit the good qualitative agreement between MD simulation and experiment, what the partial decay of the anisotropy of \( \text{trans} \)-HONO is concerned, the overall timescales are completely wrong. Two possible reasons for this discrepancy come into ones mind:

- The Lennard Jones parameters (Tab. 1) may severely underestimate the interaction forces between HONO and the Kr cage. In fact, these Lennard Jones parameters, which were adapted from Ref. [43], can be traced back to a quantum-chemistry calculation from the year 1982 [49], and clearly there are more advanced methods available today. Furthermore, the Lennard Jones model *per se* might be inadequate in this case, since it ignores the possibility of anisotropic interactions as well as the polarizibility of the Kr atom interacting with the charges of HONO.

- HONO may occupy an interstitial rather than a mono-substitutional matrix site, in which case it would be fixed more tightly. Although this possibil-
ity may seem rather unlikely, since the in situ synthesis from an \( \text{HN}_3 + \text{O}_2 \) complex must have taken place in an even larger site, we discuss this scenario as well. Using the same Lennard Jones parameters as before, the MD simulation indeed reveals a significantly slower orientational diffusion time for an interstitial site. We saw only one rotational flip for cis-HONO and none for trans-HONO on a 70 ns timescale, hence, orientational diffusion is now too slow (the ‘statistics’ of one flip is, of course, insufficient to draw conclusions about the difference between cis and trans-HONO). We furthermore tried the two possible interstitial sites in a fcc-lattice, the octahedral \( \text{O}_8 \) (6 nearest neighbors) and the tetrahedral \( \text{T}_d \) (4 nearest neighbors) site, as an initial condition for the MD simulation, however HONO disturbs the local structure of the matrix cage to an extent that the difference between these two sites is no longer apparent. If the non-exponential decay of the anisotropy of trans-HONO (Fig. 3) indeed reflects a distribution of mono-substitutional and interstitial sites, then the spread of rates predicted from the MD simulation is too large.

In a second set of experiments, we studied the rotation of HONO during its IR-driven cis–trans photo-isomerization. Probing two vibrational bands of the trans photo-product, we could determine two independent angles (\( \alpha \) and \( \beta \)), which are totally inconsistent with a picture in which essentially the hydrogen is isomerizing whereas the ONO-body stays fixed in the matrix cage (Fig. 5B). On the other hand, if we assume that isomerization is accompanied by a hula hoop motion of the two center atoms, pinning the terminal oxygen and hydrogen atoms to the matrix cage (Fig. 5C), we obtain angles \( \alpha \) and \( \beta \) that are consistent with experiment within error. Any matrix site, interstitial or mono-substitutional, imposes less constraints to the center of the molecule than to the terminal atoms, explaining why these atoms are more free to move. According to the best potential energy surface available, the barrier against isomerization is higher than the energy put into the molecule by the IR photon [29]. It is very hard to imagine that the two central heavy atoms are tunneling through this barrier. However, from an intramolecular point of view, it is probably still be the proton which is tunneling, just that this process is coupled to a rotational motion of the molecule as a whole. In Ref. [16], we had modelled the isomerization reaction of HONO in a mixed-quantum-classical simulation, treating the motion of the hydrogen as quantum, whereas the ONO-body was assumed to be rigid. Fig. 5C seems to suggest that this is insufficient, and that one would have to extent the quantum part of the simulation to all degrees of freedom of the molecule i.e. all six intramolecular (internal) degrees of freedom as well as at least the three rotational (external) degrees of freedom.

Similar conclusions have been drawn for the isomerization of the retinal chromophore in rhodopsin [50, 51], responsible for the initial step during the process of vision. In this case, the chromophore is tightly fixed to the protein, and the 11–cis to all-trans isomerization occurs in a space-saving manner with only minor motion of the involved atoms, leaving the trans photo-product in a highly distorted, twisted structure. However, in contrast to the present case, nuclear motion is typically considered classical in molecular systems like rhodopsin.

In conclusion, the measurement of orientational dynamics provides a framework for a very decisive discrimination of various matrix sites as well as for the mechanism of isomerization. This, however, requires more reliable models for the matrix-solute interaction forces which are within reach of modern quantum chemistry methods.

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