State-to-state photodynamics of nitrous oxide and the effect of long-range interaction on the alignment of O(1D2)


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Abstract

The photodissociation of N2O was studied around 203–205 nm by preparation of the parent molecule in a single rovibrational quantum state using a hexapole state-selector. The resulting photofragments N(v, J) and O(1D2) were quantum-state selectively detected and their angular recoil distribution was measured using ion-imaging techniques. Information on the electronic alignment of the 1D2 state is obtained from analysis of the polarization sensitivity of the O(1D2) images using two different probe schemes. We present a theoretical analysis based on ab initio potential energy surface calculations and a semiclassical model incorporating the effects of the long-range quadrupole–quadrupole interaction between the N2 and O(1D2) fragments. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Photodissociation experiments provide information about (anisotropic) molecular forces and the dynamics on the excited state potential energy surfaces involved in the ‘half-reaction’. Selection of the quantum states of the parent molecule prior to dissociation as well as knowledge of the internal energy and angular distribution of the photofragments will contribute to a complete understanding of the dissociation dynamics. Two-dimensional ion-imaging detection has proven to be a valuable technique in the study of photofragmentation processes. It provides the three-dimensional angular and velocity distribution of state-selected fragments [1,2], which often contains information on alignment effects. The photodissociation of nitrous oxide, N2O, has received considerable attention in the past decade as it is an important stratospheric process [3,4]. Photodissociation around 200 nm forms almost exclusively [5] oxygen atoms in the excited 1D2 state and N2 in the electronic ground state,

\[ \text{N}_2\text{O} + h\nu \rightarrow \text{N}_2\left(1\Sigma_g^+, v, J\right) + \text{O}(1\text{D}_2). \] (1)
In this Letter two-dimensional ion-imaging experiments are described in which quantum state-probed 
N_2(\nu, J) and O(\textsuperscript{1}D_2) fragment angular distributions are obtained after photolysis of rovibrationally state-selected N_2O. The initial quantum state of the parent molecules prior to dissociation is selected, using the hexapole state-selection technique. Previously, this state-selection technique was successfully combined with resonance-enhanced multi-photon ionization (REMPI) and ion-imaging detection in studies on the photodissociation of oriented CD\textsubscript{3}I \cite{6}. The first results of our state-selected experiments on the photolysis of N\textsubscript{2}O were communicated before \cite{7}.

Recently, the photodissociation of nitrous oxide using non-state-selected pulsed beams was studied by the groups of Chandler \cite{8,9}, Suzuki \cite{10}, and Suits \cite{11}. In the experiments by Chandler and co-workers a strong dependence of the angular recoil parameter, $\beta$, on the rotational level $J$ of the N\textsubscript{2} fragment was observed. Furthermore, a detailed analysis was made of the correlation of the alignment of the O(\textsuperscript{1}D\textsubscript{2}) state with the rotational state of the N\textsubscript{2}(\nu, J) fragment. Very recently, Suits and co-workers \cite{11} reported on a two laser ion imaging experiment photolyzing nitrous oxide at 193 nm and probing at 203.8 nm. From analysis of their data on the O(\textsuperscript{1}D\textsubscript{2}) fragment using various geometries of pump and probe polarization, they observed coherences between the $m$-components of the \textsuperscript{1}D\textsubscript{2} state.

In the experimental section on single quantum state-selected photolysis of N\textsubscript{2}O, we report on single laser experiments using different schemes to probe the O(\textsuperscript{1}D\textsubscript{2}) alignment. Two laser pump–probe experiments have been performed in our laboratory in Amsterdam as well, using single quantum state prepared nitrous oxide parent molecules \cite{12}. A detailed analysis using the theoretical formalism recently reported by Suits and co-workers \cite{13} and Zare and co-workers \cite{14} to search for coherences among the $m$-levels of the O(\textsuperscript{1}D\textsubscript{2}) is in progress and will be reported elsewhere. From the single laser state-selected experiments analyzed here we find a dependence of the $m$-state populations of the O(\textsuperscript{1}D\textsubscript{2}) fragment on the recoil velocity. These results are correlated with the rotational state of the N\textsubscript{2}(\nu, J) fragment. To obtain a better understanding of the observed trends we present a semiclassical model in which we relate the angle between the N\textsubscript{2} axis and the recoil velocity of the O fragment at the point of dissociation (the scattering angle) to the rotational angular momentum $J$ of the N\textsubscript{2} fragment as well as the $m$-state population of the O fragment. The $m$-state population is determined by first-order degenerate perturbation theory including only the quadrupole–quadrupole interaction between the N\textsubscript{2} molecule and the O atom.

In Section 2 we present the experimental technique, in Section 3 the measured results, in Section 4 the ab initio calculations and the semiclassical model. In Section 5 we summarize our results and conclusions.

2. Experimental

The experimental apparatus is described briefly here, a more detailed description was given before \cite{6}. A rotationally cold molecular beam of N\textsubscript{2}O is generated by expanding a mixture of N\textsubscript{2}O seeded in Ar or Kr through a pulsed nozzle. Vibrationally excited N\textsubscript{2}O molecules in the $\textit{\nu}_2$ bending mode possess an angular momentum along the molecular axis by $l$-type doubling. While traveling through the inhomogeneous electric field of the hexapole, molecules with a positive Stark effect experience a force towards the hexapole axis where the field strength vanishes. In the rotationally cooled N\textsubscript{2}O beam, a single ($\nu_2, J, l, M$) state can be selected and focussed in the dissociation region by choosing a proper hexapole voltage. Here $\nu_2$ is the bending vibrational quantum number, $J$ is the total rotational quantum number, $l$ is the vibrational angular momentum component along the molecular axis, and $M$ is the projection of the total angular momentum along the (external) electric field vector. In the experiments reported here we did not use our guiding and orientation fields downstream of the hexapole to spatially orient N\textsubscript{2}O in the laboratory frame. This implies that the $M$ quantum number is scrambled in the dissociation region. All the images reported in this Letter (see Section 3) are obtained from photolyzing N\textsubscript{2}O selected in the ($\nu_2 = 1, J = 1, l = 1$) state.

The tripled output from a Nd:YAG pumped tunable dye laser (running at 10 Hz) photolyzes the
parent molecule and subsequently ionizes the photofragments using 2
\( \text{q} \)
<table>
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<th>REMPI with</th>
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<td>・ 203.7 nm probing ( \text{O}^{{(1)} D_2} ) via the ( 1F_3 \leftarrow 1D_2 ) transition;</td>
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<tr>
<td>・ 205.4 nm probing ( \text{O}^{{(1)} D_2} ) via the ( 1P_1 \leftarrow 1D_2 ) transition;</td>
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<tr>
<td>・ 203–204 nm probing ( \text{N}_2(\nu, J = 60–85) ) via the ( \alpha^2 ^1 \Sigma^+_g \leftarrow X^1 \Sigma^+_g ) transition.</td>
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In case of the \( \text{O}^{{(1)} D_2} \) detection, the two-photon levels \( (^1F_3 \) or \( ^1P_1 \)) lie above the first ionization threshold. From these states ionization can take place by autoionization, or by absorption of a third photon to a higher ionization continuum. To account for the large Doppler shift the laser was scanned slowly over the absorption line while an image was taken. The ions are accelerated by an extraction field perpendicular to the laser beams into a short time-of-flight (TOF) tube (17 cm). At the end of the TOF tube the ions hit a mass gated micro-channel-plate (MCP) detector. From the back of the MCP electrons are accelerated onto a fast phosphor screen, which converts the electron spray into light. The fluorescence light is collected with a high-quality camera lens and imaged on a charge-coupled-device (CCD) camera. When the total ion yield is measured, the CCD camera is replaced by a photomultiplier tube.

3. Results

3.1. \( \text{N}_2 \) fragments

The \( \text{N}_2 \) REMPI spectrum reveals high rotational excitation, with the peak of the distribution at \( J = 74 \). Fig. 1 shows ion images of \( \text{N}_2 \) photofragments at two different laser wavelengths, detecting rotational levels \( J = 70 \) and 82. These images (300 × 300 pixels) are obtained by subtraction of a background image from the image of state-selected \( \text{N}_2 \text{O} \). A background image is measured under exactly the same experimental conditions as the state-selected image, but with zero voltage on the hexapole rods. The intensity of the signal from the direct (non-state-selected) beam is typically less than 20% of the intensity of state-selected \( \text{N}_2 \text{O} \).

Because the laser bandwidth is too narrow to detect all the \( \text{N}_2 \) fragments independent of their velocity, images are taken by scanning the dye laser wavelength over \( \sim 1 \text{ cm}^{-1} \). The intensity of each image in Fig. 1 is scaled to the maximum intensity, which is set at 255. The polarization of the laser, used both for photolysis and ionization, is vertical in Fig. 1 and parallel to the detection plane. The images show two projected polar caps along the direction of the laser polarization, which is characteristic of a parallel transition. The images exhibit a very narrow velocity distribution because the quantum state-selected \( \text{N}_2(J) \) corresponds to a single exit channel.
of the O(D) cofragment, and therefore has a very well-defined recoil velocity. The images are Abel-inverted [15] to reconstruct the three-dimensional angular distribution from the two-dimensional projections.

Since the Q-band transition used to probe N₂ is relatively insensitive to alignment the expected angular distribution of each N₂(J) fragment was fitted to the usual angular expression with a J-dependent anisotropy parameter β_j:

\[ I_{N_2(J)} \propto [1 + \beta_j P_2(\cos \gamma)]. \]  

(2)

In this equation γ is the angle between the direction of the linear polarization of the photolysis field and the lab frame direction of the recoil velocity of the N₂ fragment. It is found that the anisotropy parameter β = 0.96 for J = 66, and that it decreases with increasing N₂ rotation. This decreasing trend in the β parameter upon going to higher N₂ rotational levels was also observed in the photodissociation experiments on non-state-selected N₂O by Chandler and co-workers [8]. The N₂O(ν₂ = 1) molecules have a substantially higher dissociation cross-section than N₂O molecules in which the bending mode is not excited [16]. Therefore, the ν₂ = 1 molecules can be expected to be relatively important also in the non-state-selected experiment, which explains the similarity between the state-selected and non-state-selected observations. The effect that the bending mode excitation substantially increases the dissociation cross-section can be easily understood since the electronic transitions involved are forbidden at the linear geometry of N₂O, see Section 4.

3.2. O(D) fragments

Fig. 2 shows ion images of the O(D) fragments, detected via (a) the ¹P₁ ← ¹D₂ transition at 205.4 nm and (b) the ¹F₁ ← ¹D₂ transition at 203.7 nm. Again a background image (no hexapole state selection) is subtracted from the image of state-selected N₂O(ν₂ = 1, J = 1, l = 1). The N₂O molecules are photolyzed and the fragments are ionized using the same laser. Both O(D) images show a broad translational energy distribution (radius of the image), caused by the variable amount of rotational energy taken up by the N₂ fragment. Compared to the ¹F₁ ← ¹D₂ image, the ¹P₁ ← ¹D₂ image is more peaked along the vertical axis, and shows a dimple at the horizontal axis. The differences in the O(D) images using different detection schemes arise from variations in the detection probabilities for the various m-levels. For analysis, the Abel-inverted images are divided into shells with different radii corresponding to a range of translational energies. Each shell corresponds to a range of rotational levels in the N₂ fragment. At first we tried to simulate the recoil distributions by fitting the data with

\[ l_{image} \propto [1 + \beta_j P_2(\cos \gamma)] \times \sum_{k=0,2,4} \rho(k\hat{P}_2(j, j') P_4(\cos \gamma)), \]  

(3)
where $\rho^{(k)}_m$ denote multipole moments of rank $(k)$ with component zero for the $\text{O}^1\text{D}$ atoms and the $\vec{p}_k(j, j_r)$ are the geometrical factors given by Mo and Suzuki [17] ($j = 2$ for $\text{O}^1\text{D}$) and $j_r = 1$ and 3 for the $^1\text{P}_1 \leftrightarrow ^1\text{D}_2$ and $^3\text{F}_3 \leftrightarrow ^3\text{D}_2$ detection schemes, respectively). The quantization axis for the multipole moments is the recoil velocity vector. For the $\beta_j$ parameter we used the value from the $\text{N}_2$ image. The multipole moments are proportional to the alignment parameters $A^{(k)}_0$ defined by Zare [18].

In particular, they are related to the populations $n_m$ of the magnetic substates of $\text{O}^1\text{D}$ via [19]

$$\rho^{(k)}_m = \sqrt{2k+1} \sum n_m (-1)^{j_r-m} \binom{j_i}{k} \binom{j_r}{m} \binom{k}{m}.$$  

(4)

Note that because of the symmetries of the $3 - j$ symbol we are not sensitive to the sign of $m$.

In this way it was not possible to simulate the images satisfactorily, especially so for the $^1\text{P}_1 \leftrightarrow ^1\text{D}_2$ images. Therefore, we decided to treat the $\text{O}^1\text{D}$ and $\text{O}^3\text{D}$ states independently, assigning a $\beta_{j,m}$ parameter to each $m$ level, similar to the data analysis used in the non-state-selected experiments [9]. When only a single $m$ state is populated, the multipole moments $\rho^{(k)}_{0,m}$ for each $m$ can be easily calculated from Eq. (4). We fitted the data to the following expression,

$$I_{\text{image}} \propto \sum_m n_{j,m} \left[ 1 + \beta_{j,m} P_2(\cos \gamma) \right] \times \sum_{k=0,2,4} \rho^{(k)}_{0,m} \vec{p}_k(j, j_r) \cos \gamma.$$  

(5)

In the simulations the sum of the populations is kept equal to one ($\sum_m n_{j,m} = 1$) and the weighted average of the $\beta_{j,m}$ parameters ($\sum_m n_{j,m} \beta_{j,m}$) is kept equal to the $\beta_j$ deduced from the corresponding $\text{N}_2$ image. The parameters $\beta_{j,m}$ and $n_{j,m}$ are varied till the angular recoil distributions are reproduced well for both the $^1\text{P}_1 \leftrightarrow ^1\text{D}_2$ and $^3\text{F}_3 \leftrightarrow ^3\text{D}_2$ images. Although for these fitted data relatively large error bars have to be taken into account, the $|m| = 1$ population shows a clear trend in going from 0.63 for $J = 66$ to 0.12 for $J = 82$. Both the $m = 0$ and the $|m| = 2$ populations increase for higher $J$. In Table 1 we show the parameters extracted from the $\text{N}_2$ and $\text{O}^1\text{D}_2$ images. A fit using the simpler, one-state expression of Eq. (3), even though it does not simulate the experiment well, gives a similar trend in the $|m|$-populations. In the non-state-selected experiments reported before [9] a qualitatively similar trend was observed, although the $|m| = 2$ populations turned out to be somewhat lower. In our experiment we have a pure single-state parent beam, whereas in the non-state-selected experiments we expect contributions from both ground state and vibrationally excited state $\text{N}_2\text{O}$ dissociation. This may be the cause of the small differences. Suits and co-workers [11], incorporating coherences between the $m$-states, averaged their results of the extracted density matrix over all scattering angles and obtained $m$-state populations of 0.34, 0.54 and 0.12 for $|m| = 0, 1$ and 2, respectively. It should be noted, however, that these coherence experiments were photolyzing $\text{N}_2\text{O}$ at 193 nm and using a non-state-selected beam. So their results can, in principle, be somewhat different from our 203–205 nm results, as the 193 nm wavelength is much closer to the peak in the room-temperature absorption spectrum.

In the following section we will discuss the trends observed in our data in relation to the dissociation dynamics and the excited state potentials involved.

### 4. Ab initio calculations and semiclassical model

$\text{N}_2\text{O}$ has 16 valence electrons, and belongs to the $C_{nv}$ symmetry group when it is in its electronic ground state $X^1\Sigma^+ \left(4s^2 5s^2 6s^2 1p^6 3p^6 2\pi^2 2\pi^2 \right)$ configuration. The lowest electronically excited singlet states are the $A^1\Sigma^+$, the $B^1\Delta$, and the $C^1\Pi$ states. Upon bending the $C_n$ symmetry group applies giving

| $J_{n_j}$ | $\beta_j$ | $|m|$-population | $\beta_{j,m}$ |
|----------|----------|-----------------|------------|
| 0        | 0.96     | 0.38, 0.63, 0   | 2.0, 0.34, 0 |
| 1        | 0.85     | 0.33, 0.63, 0.05| 2.0, 0.32, 0 |
| 2        | 0.76     | 0.31, 0.40, 0.29| 1.2, 0.97, 0 |
| 3        | 0.44     | 0.34, 0.28, 0.38| 0.5, 0.96, 0 |
| 4        | 0.58     | 0.53, 0.12, 0.35| 0.3, 0.93, 0.9 |
rise to the $1^1\Lambda(1^1\Sigma^+)$ and the $1^1\Lambda(1^1\Sigma^-)$ states. The $\Pi$ and $\Delta$ states split into $\Lambda$ and $\Lambda'$ components, see Fig. 3.

The potential surfaces shown in Fig. 3 are computed with the MOLPRO ab initio program package [20], at the internally contracted multireference configuration interaction (MRCI) level [21,22]. The molecular orbitals are obtained in a state-averaged complete active space self-consistent field (CAS-SCF) calculation [23,24], using the aug-cc-pVDZ basis set [25,26]. The first six $\alpha$ orbitals are kept over the ground state probability density. It is found that the excitation is $\sim 97\%$ to the $2^1\Lambda(1^1\Delta)$ state (this transition is parallel to the plane of the molecule) and $\sim 3\%$ to the $1^1\Lambda(1^1\Sigma^-)$ state (a perpendicular transition). Furthermore, we find that the transition dipole vector for the $2^1\Lambda \leftarrow \chi$ transition is parallel to the NO bond within a few degrees for $\theta < 45^\circ$. This is relevant since a larger deviation could contribute to a lowering of the $\beta$-parameter of the photodissociation process.

Both surfaces show a large anisotropy which is consistent with the observed high rotational excitation of the $N_2$ fragment. Our two-dimensional interpolated surfaces, communicated before [29], are consistent with very recently published ab initio calculations of the lowest three surfaces of $N_2O$ by Brown et al. [30].

We have not yet performed (quantum) dynamical calculations on these surfaces. However, the rotational excitation of the $N_2$ fragment is clearly a result of the anisotropy of the excited state potential energy surface, which causes the $N_2O$ molecule to bend upon excitation. Hence, we assume that a larger bending of the molecule correlates with a higher rotational excitation of the $N_2$ fragment. The bending also leads to a lower recoil anisotropy ($\beta_j$). At present we do not have a model to interpret the variation of the $\beta_j,m$ parameters with $|m|$ (Table 1). However, we can account for the observed trends in the $|m|$-populations (Table 1) by analyzing the electronic wavefunctions as a function of the scattering angle $\theta$. For large separation between $N_2$ and $O(1D_2)$, this analysis can be done with a model which only takes into account the long-range quadrupole–quadrupole (QQ) interaction between the fragments. This treatment follows a similar analysis used to interpret orientation effects in reactive scattering of metastable $Ca(1D_2)$ with oriented $CH_3F$, $CH_4Cl$,
Fig. 4. Dependence of the \( |m| = 1 \) state population on the lowest five long-range quadrupole–quadrupole (QQ) surfaces as a function of the \( \text{N}_2\text{O} \) bending angle \( \theta \). The population is directly obtained from the eigenvectors of the \( 5 \times 5 \) interaction matrix (Eq. (6)). The populations do not depend on the relative strength of the two quadrupole moments. The \( 1A' \) surface correlates with the ground state \( X^1\Sigma^+ \) surface, the \( 2A' \) with the \( 1\Delta \) surface and the \( 1A^1 \) with the \( 1\Sigma^- \) surface in the Franck–Condon region at linear geometry. Note how the population in \( |m| = 1 \) decreases significantly with increasing bending angle for both the \( 2A' \) and the \( 1A^1 \) surfaces which are populated from the ground state after excitation in the 205 nm region.

CH\(_3\)Br [31,32]. For large \( R \) we apply first-order degenerate perturbation theory to obtain the five adiabatic electronic surfaces that correlate with the five substates of \( \text{O}^1\text{D}_2 \). This calculation involves the diagonalization of the \( 5 \times 5 \) QQ interaction matrix over the five substates of \( \text{O}^1\text{D}_2 \)

\[
V_{\mu,m}(\theta, R) \propto R^{-5}(-1)^m \sum_{\mu} C_{2\mu}(\cos \theta, 0)
\times \left( \begin{array}{ccc} 2 & 2 & 4 \\ \mu & -\mu & 0 \end{array} \right) \left( \begin{array}{ccc} 2 & 2 & 2 \\ -m & -\mu & m \end{array} \right),
\]

(6)

where \( C_{2\mu} \) is a spherical harmonic in Racah normalization. Diagonalization of the matrix yields the adiabatic states. The \( |m| \)-populations in the adiabatic states are obtained as the squares of the components of the eigenvectors. For \( \theta = 0 \) the lowest state is of \( \Sigma \) symmetry and correlates adiabatically with the \( X^1(1A') \) ground state. The other states are of \( \Pi \) and \( \Delta \) symmetry. Upon bending \( (\theta > 0) \) we obtain three \( A' \) and two \( A'' \) surfaces. In Fig. 4 we show the \( |m| = 1 \) populations for all five surfaces as a function of \( \theta \). It is observed that for the \( 2A'(1\Delta) \) surface the population in \( |m| = 1 \) is decreasing from a maximum at linear geometry to a minimum around 50°. Also for the \( 1A''(1\Sigma^-) \) surface the \( |m| = 1 \) population decreases monotonically with increasing bending angle. In Fig. 5 we show the \( |m| = 0, 1 \) and \( 2 \) populations assuming contributions from the \( 2A' \) (97%) and \( 1A'' \) (3%) surfaces as mentioned above. It is observed that the population in both \( m = 0 \) and \( m = 2 \) is increasing up to angles of \( \approx 50° \). Included in Fig. 5 at \( \theta = 30° \) and \( \theta = 45° \) are the \( |m| \)-populations from our experiments at two different O-atom speeds, corresponding with different \( J \) states \((J = 70 \text{ and } J = 82)\) of the \( \text{N}_2 \) cofragment. The bending angles are chosen to give the best agreement between the model and the experiment. Note, however, that the smaller angle corresponds to a lower rotational excitation, as one would expect already from a simple impulsive model. Also, the minimum of the excited state potential energy for both \( 2A' \) and \( 1A'' \) surfaces is around angle \( \theta = 50° \) (see Fig. 3). The trend observed in the experimental results showing a de-

Fig. 5. Dependence of the \( |m| \)-population using the long-range QQ interaction, for excitation of 97% to the \( 2A'(1\Delta) \) surface and 3% to the \( 1A''(1\Sigma^-) \) surface. Added are the observed \( m \)-distributions at two different O-atom speeds correlating to two different \( \text{N}_2 \) rotational states around \( J = 70 \) and \( J = 82 \).
crease of the $|m| = 1$ population with increasing rotational state $J$, is represented qualitatively by this simple model. This suggests that the dissociation proceeds mainly adiabatically on the $2A'$ and $1A'$ surfaces until the separation between the fragments is large enough to allow the $m$-populations to be derived from our long-range model. To determine this critical separation and to obtain a direct relation between the rotational $J$-state and the angle $\theta$, we are performing semiclassical trajectory calculations similar to Ref. [32]. The present long-range model is also applicable to explain the results reported before in the non-state-selected experiments by Chandler and co-workers [9]. At this point it appears very encouraging that from analysis of the long-range interaction we can qualitatively understand the alignment produced in the dissociation of nitrous oxide in this wavelength region.

5. Conclusions

The two-dimensional ion-imaging detection of photodissociation fragments yields a wealth of information on the angular recoil distribution and the alignment of the fragments. In this study ion images are presented of both N$_2$ and O(1D$_2$) fragments formed in the photodissociation of rovibrationally single-state-selected N$_2$O around 205 nm. The N$_2$ REMPI spectrum reveals high rotational excitation in the N$_2$ fragment. Furthermore, the N$_2$ images show a decrease in the $\beta$-parameter with increasing $J$ of N$_2$. Dissociation occurs via the $2^1\Sigma$ and the $1^1\Sigma$ bent excited state. In going from the linear ground state to a bent excited state, the N$_2$ fragment experiences a torque causing high rotational excitation. A larger bending angle can explain both the lower anisotropy ($\beta_x$) for high N$_2$ rotational states, and the decrease in $|m| = 1$ population in the O(1D$_2$) fragments. Experiments are in preparation on state-selected nitrous oxide isotopomers, in order to study the photodynamics in the stratospheric solar window 200–210 nm. These state-to-state photodynamics measurements may provide us with a better fundamental understanding of the role of the bending vibration which may be (partially) responsible for the observed anomalies in the fractionation of nitrous oxide isotopomers in the stratosphere.

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References

[20] MOLPRO is a package written by H.-J. Werner, P.J. Knowles, with contributions from J. Almlöf et al.