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Scalar and vector properties of the NO(v'=0) produced from the reaction O(¹D)+N₂O \rightarrow NO+NO

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We have measured the product state-selected differential cross-section (DCS), and the rotational angular momentum polarization, together with the energy distributions for the reaction $O(^{1}D)$ $+N_2O \rightarrow NO + NO$ by utilizing Doppler-resolved polarization spectroscopy. The reaction dynamics of the vibrational channel forming the product NO(v'=0) is discussed based on both the scalar and vector properties. The product rotational and center-of-mass translational energy distributions are described as Boltzmann distributions with $T_{\rm rot} \approx 10\,000\,{\rm K}$ and $T_{\rm tr} \approx 13\,000\,{\rm K}$, respectively. These energy distributions are close to statistical predictions. The product DCS has substantial intensities over the whole angular range with a slight preference for backward scattering. The product rotational angular momentum vector \mathbf{j}' does not have a noticeable angular correlation with either \mathbf{k} or \mathbf{k}' (the relative velocity vectors of the reactant and product, respectively). This nearly isotropic angular distribution of \mathbf{j}' indicates that both in-plane and out-of-plane motions of the collisional ONNO complex contribute to the product rotation to almost the same degree. Considering that this reaction has no potential well deep enough for the formation of a long-lived complex, these nearly statistical scalar and isotropic vector properties suggest that the energy redistribution among the internal modes of the collisional ONNO complex efficiently takes place. It implies that there are strong couplings among the internal modes. © 1999 American Institute of Physics. [S0021-9606(99)00226-3]

I. INTRODUCTION

The reaction of $O(^{1}D)$ with N₂O yielding two NO product molecules

$$O(^{1}D) + N_{2}O \rightarrow NO + NO \quad \Delta H^{0}(0) = -341 \text{ kJ/mol}, \qquad (1)$$

plays an important role in atmospheric chemistry and thus has been of great interest. With many kinetic studies showing large rate constants,^{1,2} the dynamics of this highly exothermic reaction has been investigated by measuring the product internal state distributions^{3–6} and recently by probing vector properties such as product recoil anisotropy and rotational angular momentum polarization.^{7,8}

Although the two NO products of this reaction are chemically identical species, they are generated from distinctly different origins. One is the "new" NO formed in the reaction and the other is the "old" NO present in the reactant N₂O molecule. An early study using isotopically labeled reagents showed almost symmetric energy partitioning among the two NO products in the low vibrational levels v'=0-2.³ From a traditional understanding, this result is expected to imply that this reaction proceeded via an intermediate complex.

As a possible intermediate species of this reaction, an *ab initio* calculation suggested a *cis*-planar ONNO structure.⁹ The binding energy of the *cis*-planar NO dimer was experimentally determined to be about 8.5 kJ/mol.¹⁰ Since this binding energy is negligibly small compared with the available energy of about 400 kJ/mol, this reaction is not likely to proceed via a long-lived complex.

Akagi *et al.*¹¹ recently observed the individual vibrational distributions of the two NO products in the range of vibrational levels v' = 0-18 under much lower pressure than in the previous study.³ The vibrational populations showed that the energy partitioning between the two NO products was more symmetric than that generally expected from a direct pathway although it was more asymmetric than that reported in Ref. 3. This result suggests that energy randomization occurs in spite of the fact that this reaction is not a typical statistical complex reaction with a deep potential well.

Brouard et al. recently examined the stereodynamics of the vibrational channel $O(^{1}D) + N_2O \rightarrow NO(v' = 16,17)$ +NO(v'=0) based on the product recoil anisotropy obtained by utilizing Doppler-resolved polarization spectroscopy.⁸ The product NO(v' = 16,17) was translationally hot and recoiled with the upper limit of the anisotropy parameter in the laboratory (LAB) frame, corresponding to the forward scattering in the center-of-mass (CM) frame, while the sister fragment NO(v'=0) had extremely low translational energy close to thermal energy. Furthermore, they found hot rotational distributions of NO(v' = 16,17) in contrast to a cold rotational distribution of NO(v'=0) almost identical to a thermal distribution. They consequently concluded that the vibrational channel forming NO(v'=16-18) + NO(v'=0)was dominated by a near-stripping mechanism where the old NO behaves as a spectator during the reaction. They also found relatively high rotational excitation of the NO(v') ≥ 1) products, remarkably different from that of the

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NO(v'=0).⁷ Thus, they suggested that the NO($1 \le v' \le 15$) products were formed via a short-lived complex in contrast to a direct stripping process for the formation of NO(v'=0,16-18). Such drastic change of the reaction dynamics, though not impossible, seems to be somewhat puzzling.

As opposed to the rotational distribution of NO(v'=0) reported by Brouard *et al.*,^{7,8} our unpublished preliminary works suggested that the rotational distribution of this level was more excited than those of NO($v' \ge 1$) products reported in Ref. 7. Furthermore, considering that the vibrational populations of the NO products monotonously decline with increasing vibrational quantum number,^{4,6,11} the formation of NO(v'=16-18) is estimated to be a minor channel. Thus, probing the channel forming the product NO(v'=0) is essential to clarify the dynamics dominant for this reaction and reexamine the large gap between the reaction dynamics for the formation of NO(v'=0) and NO($v'\ge 1$).

For examining the reaction dynamics in more detail, the measurement of vector properties as well as scalar properties is important. Several groups^{7,8,12–29} have recently measured vector properties for bimolecular reactions with fundamental importance so far and provided a better understanding of the reaction dynamics. We have measured the state-selected differential cross-section and the rotational angular momentum polarization of the product NO(v'=0) by utilizing Doppler-resolved polarization spectroscopy, as well as the rotational and translational energy distributions. In the present study, although the two NO products are not isotopically distinguished, the observed NO(v'=0) products are mainly considered as the old NO since the population of the old NO in v'=0 was found to be about four times larger than that of the new NO.¹¹

The observed scalar properties of NO(v'=0) shows that the NO(v'=0) is rotationally and translationally excited to the same degree as predicted by statistical models. The vector properties suggest the efficient energy redistribution among the internal modes of the short-lived collision complex.

II. EXPERIMENT

Experiments were carried out in a stainless steel vacuum chamber. Nitrous oxide (Showa Denko 99.999%) was used without further purification. This sample gas was introduced into the reaction chamber and the flow rate was controlled with stainless steel needle valve. The sample gas in the reaction chamber was continuously pumped by using a rotary pump. The pressure of N₂O was about 200 mTorr at 300 K. The electronically excited oxygen atom $O(^{1}D)$ was produced from the photodissociation of N₂O with 193 nm light generated by an ArF excimer laser (Lambda Physik EMG 53 MSC). At a delay time of 100 ns after the photolysis laser irradiation, a tunable UV light (223-227 nm) was introduced into the reaction chamber to probe the nascent NO(v'=0)with laser-induced fluorescence (LIF) via the NO $A^{2}\Sigma^{+} - X^{2}\Pi(0,0)$ excitation. The tunable UV light was generated by doubling the output of the dye laser (Lambda Physik SCANmate 2E, Coumarin 2) pumped by a XeCl excimer laser (Lambda Physik COMPex 102). For the measurement of Doppler profiles, the dye laser was equipped with an intracavity etalon and the bandwidth of the UV light used for probing the products was about 0.14 cm^{-1} in full width at half maximum (FWHM).

The fluorescence was collected by a synthetic silica lens and focused by another silica lens on a photomultiplier tube (Hamamatsu R928) mounted perpendicular to both the photolysis and probe laser beam axes. A long-pass filter (Corning CS9-54) was placed in front of the photomultiplier tube to eliminate the strong scattered light and emission arising from the photolysis laser. The LIF signal was amplified by a fast preamplifier (Comlinear CLC100) and gated by a boxcar integrator (Stanford Research System SR250). The gated signal was digitized by an A/D convertor (Stanford Research System SR245) and stored in a personal computer via a GPIB interface. The photolysis-probe experiments were performed at a repetition rate of 10 Hz. The timing of the laser system was adjusted by a digital pulse/delay generator (Stanford Research System DG535). Each laser power was monitored by a photodiode (Hamamatsu 1336-5BQ) for normalizing the LIF signal to correct for the fluctuations of the power.

The Doppler-resolved spectral line profiles were measured in several LIF excitation-detection geometries which were characterized by the combination of the directions of the polarization and propagation vectors of each laser. Incomplete horizontal polarization of the output of the probe laser was converted to higher horizontal linear polarization with a Glan laser prism (Meiritsu LAN-10-L). This horizontally polarized light was sent to a half-wave plate (New Focus 5540) to obtain a vertically polarized light (degree of polarization >0.99). Unpolarized ArF laser light was passed through a pile of plates consisting of 12 quartz plates in Brewster's angle to obtain vertically polarized light (degree of polarization >0.95). The polarization direction of the photolysis laser was alternately changed from vertical to horizontal in a shot-by-shot manner with a photoelastic modulator (Hinds PEM-90). The trigger pulses switching the two appropriate timings for the vertical and horizontal polarization were generated with homemade electronic devices. This shot-by-shot alternation of the polarization vector allows one to observe the polarization-dependent spectral line profiles in the two different LIF geometries in a single frequency scan. Such shot-by-shot alternate observation gave the rotational alignment $A_0^{(2)} = 0.00 \pm 0.02(1\sigma)$ for both of $P_1(34.5)$ and $Q_1 + {}^QP_{21}(34.5)$ which was used for the subsequent Doppler profile analysis. In order to improve the signal-to-noise ratio, 50-100 laser shots were averaged at each step of a frequency scan and the spectra obtained from 9-25 scans were summed up.

For extracting vector correlations, we measured Doppler profiles for the rotational branches of P_1 and $Q_1 + {}^{Q}P_{21}$ due to the A' and A'' Λ -doublet states, respectively, with assumption that these two Λ -doublet states have the same vector properties. The Doppler-resolved spectral line shapes did not show any appreciable changes at a delay time ranging from 50 to 100 ns at a pressure of 200 mTorr. Furthermore, we checked that the probe laser power was weak enough to avoid the saturation of the NO A ${}^{2}\Sigma^{+}-X {}^{2}\Pi(0,0)$ excitation.

III. ANALYSIS

Only the outline of Doppler profile analysis is given here since the details have been described elsewhere.³⁰ In recent years, Aoiz *et al.* have extended the Dixon's formulation for the Doppler analysis of the vector correlations in photodissociation processes³¹ to those in photo-initiated bimolecular reactions.^{32,33} They have developed a theoretical basis to extract the mutual angular correlations among the LAB velocity vectors of an atomic reagent (**v**) and product (**v**'), and the product rotational angular momentum vector (**j**') from the polarized Doppler-resolved line profiles. In case of a linearly polarized photolysis-probe experiment, the 1+1 LIF Doppler profile $D(\nu)$ as a function of the displaced frequency ν from the line center frequency ν_0 can be written by the Legendre polynomial expansion of $P_n(x)$ up to the second-order as

$$D(\nu) = \int_{\nu_p = |(\nu/\nu_0)c|}^{\infty} \frac{1}{2\nu'} \left[g_0(\nu') + g_2(\nu') P_2\left(\frac{\nu_p}{\nu'}\right) \right] d\nu'.$$
(2)

Here, $v_p = |(v/v_0)c|$ (*c*; the speed of light) represents the minimum product LAB speed giving the displaced frequency v as the Doppler shift proportional to the projection of \mathbf{v}' onto the propagation direction of the probe laser. The coefficients $g_0(v')$ and $g_2(v')$ in Eq. (2) are expressed by linear combinations of bipolar moments averaged over all the possible velocities of the reagents, $\overline{\beta_0^K(k_1,k_2;v')}$. The bipolar moments reflect the LAB frame vector correlations as a function of product LAB speed v'.

As shown by Docker,³⁴ an appropriate linear combination of the Doppler profiles measured in several LIF excitation-detection geometries for two different types of rotational transitions (*P* or *R* vs *Q*) gives the composite Doppler profile $D_0^K(k_1,k_2;\nu)$ which depends on a single bipolar moment $\overline{\beta_0^K(k_1,k_2;\nu)}$ in g_0 or g_2 . The composite Doppler profile $D_0^K(k_1,k_2;\nu)$ is expressed as³³

$$D_0^K(k_1,k_2;\nu) = \int_{\nu_p=|(\nu/\nu_0)c|}^{\infty} \frac{1}{2\nu'} \overline{\beta_0^K(k_1,k_2;\nu')} P_{k_1}\left(\frac{\nu_p}{\nu'}\right) d\nu'.$$
(3)

The composite Doppler profiles $D_0^0(0,0;\nu)$ and $D_0^2(2,0;\nu)$ are related to the LAB speed distribution (population) and $\mathbf{v}-\mathbf{v}'$ correlation (anisotropy), respectively. The other three composite Doppler profiles reflect the polarization of the product rotational angular momentum vector, \mathbf{j}' in the three correlations: $D_0^2(0,2;\nu)$ for $\mathbf{v}-\mathbf{j}'$, $D_0^0(2,2;\nu)$ for $\mathbf{v}'-\mathbf{j}'$, and $D_0^2(2,2;\nu)$ for $\mathbf{v}-\mathbf{v}'-\mathbf{j}'$ correlations.

To discuss the dynamics of collisional events, the LAB frame vector correlations described above need to be converted to those in the CM frame, that is, the angular correlations among the relative velocity vectors of the reactant (**k**) and product (**k**'), and the product rotational angular momentum vector (**j**'). Aoiz *et al.* have derived the relationship between the LAB frame vector correlations represented by $D_0^K(k_1,k_2;\nu)$ and those in the CM frame.³³ Based on their formalism, we obtained the CM frame vector correlations by



FIG. 1. LIF spectra of NO(${}^{2}\Pi_{1/2}$, v'=0) measured at the two different delay times and their difference in the reaction of O(${}^{1}D$) with N₂O in the region of $A {}^{2}\Sigma^{+}-X {}^{2}\Pi(0,0)$ band. (a) The probe laser is fired at 100 ns *after* the photolysis laser irradiation. (b) The probe laser is fired at 600 ns *before* the photolysis laser irradiation. (c) The difference spectrum (a)–(b). The spectrum corresponding to the nascent products shown in (c) is obtained by subtracting the background contamination of thermalized NO shown in (b) from the raw spectrum shown in (a).

using the least-squares fitting method for the observed composite Doppler profiles $D_0^K(k_1,k_2;\nu)$ with appropriate basis functions.

For preparing the basis functions, we used the recoil velocity distribution of $O(^{1}D)$ produced from the 193 nm photodissociation of N₂O which was reported by Felder et al.³⁵ In order to consider all the possible collisions, the velocity distribution of $O(^{1}D)$ was convoluted with the thermal motions of the precursor N₂O and the reactant N₂O as well as the angle between the velocity vectors of the reactants. The mean collision energy for the reaction of $O(^{1}D)$ with N₂O is 55 kJ/mol and the spread of the distribution is about 40 kJ/mol (FWHM). Felder et al. gave a single anisotropy parameter, $\beta_{\text{photo}} = 0.48$, without taking account of the recoil speed dependence of β_{photo} for their angle-resolved time-of-flight measurement.³⁵ On the other hand, Suzuki et al. showed the recoil speed dependence of β_{photo} for the 205 nm photodissociation with a two-dimensional imaging method.³⁶ Considering the latter results, we represented the distribution for the 193 nm photodissociation by using two components with different β_{photo} s (β_{photo} =0.0 for the broad component and β_{photo} =1.03 for the narrow component), so as to reproduce the average $\beta_{\text{photo}} = 0.48$.³⁵

IV. RESULTS

A. Scalar properties

Figure 1(a) shows the laser-induced fluorescence (LIF) spectrum of the NO(v'=0) products in the reaction of O(¹D) with N₂O which was measured at a time delay of 100 ns. The spectrum seems to consist of two components: strong peaks above 225.5 nm and numerous weak peaks below 225.5 nm. We also measured in the same region under another photolysis-probe delay time condition where the probe



FIG. 2. Rotational energy distribution of the product NO(${}^{2}\Pi_{1/2}, v'=0$). Solid and dotted lines represent Boltzmann fit ($T_{rot} \approx 10\ 000\ K$) and a prior distribution, respectively. The highly excited rotational distribution arises from the energy partitioning of the large available energy close to a statistical prediction.

laser was fired at 600 ns *before* the photolysis laser irradiation, and the spectrum is shown in Fig. 1(b) on the same scale as used in Fig. 1(a). The rotational lines observed at such reversed time delay definitely arise from the ''residual'' NO molecules present in the reaction chamber. Such thermalized NO products ($T_{rot} \approx 300$ K) always contribute especially to the spectrum of NO(v'=0) as the background peaks. Comparison between Figs. 1(a) and 1(b) clearly shows that the strong peaks above 225.5 nm in Fig. 1(a) are assigned to those arising from the residual NO molecules. Therefore, the weak peaks below 225.5 nm are assigned to those originating from the nascent NO products.

To separate the LIF signals of the nascent NO from those contaminated by the residual NO, a shot-to-shot subtraction was performed to minimize the effect of the time drift of the amount of the residual NO during the experiment. The devices used for alternating the laser polarization (see Sec. II) were utilized to the shot-by-shot alternation of the delay time. The LIF spectrum of the nascent NO products obtained by the shot-to-shot subtraction is shown in Fig. 1(c). The rotational energy distribution of the nascent NO(v'=0) is derived from the line intensities of P_1 and R_1 branches and is displayed in Fig. 2, plotted on a linear scale. This rotational distribution can be described as a Boltzmann distribution with $T_{\rm rot} \approx 10\,000$ K. As shown in Fig. 2, a comparison with a prior distribution shows that the rotational distribution of the nascent NO(v'=0) is close to the statistical distribution. This implies that the rotational distribution with $T_{\rm rot} \approx 10\,000$ K corresponds to a moderate rotational excitation resulting from a partitioning of the large available energy of this reaction.

The amount of the residual NO is estimated to be only 5% of the total NO molecules in v' = 0. However, as shown in Fig. 1(a), even such a small amount of the residual NO yields the spectrum in which thermalized NO molecules are emphasized because of the significant difference between the spreads of the rotational distributions with $T_{\rm rot} \approx 300$ K and $T_{\rm rot} \approx 10\,000$ K.

The rotational distribution of NO(v'=0) observed here is obviously different from that with $T_{rot} \approx 320$ K previously reported by Brouard *et al.*⁷ However, from the observation



FIG. 3. Observed composite Doppler profiles for the product NO(${}^{2}\Pi_{1/2}, v' = 0, j' = 34.5$). (a) $D_{0}^{0}(0,0;v)$ (population) (\bigcirc) and (b) $D_{0}^{2}(2,0;v)(\mathbf{v}-\mathbf{v}')$. Smooth solid lines in the two panels are best fits to these profiles.

described here, it could be possible that the thermalized residual NO contaminated the spectrum in the previous study.⁷

Figure 3 shows the observed composite Doppler profiles $D_0^0(0,0;\nu)$ and $D_0^2(2,0;\nu)$ for the NO(${}^2\Pi_{1/2}, \nu' = 0, j' = 34.5$), reflecting the LAB speed distribution and recoil anisotropy, respectively. The least-squares fitting to these profiles yields the product center-of-mass (CM) transitional energy distribution and differential cross-section (DCS). We carefully checked that the LIF signal arising from the residual NO was negligibly small and did not have any influence on the Doppler profiles for the nascent NO in the ob-



FIG. 4. Center-of-mass translational energy distribution given to the NO(${}^{2}\Pi_{1/2}$, v' = 0, j' = 34.5) and its sister fragment (\bullet). Solid and dotted lines represent Boltzmann fit ($T_{tr} \approx 13\,000$ K) and a prior distribution, respectively. Error bars correspond to $\pm 1\sigma$. The distribution is, though slightly colder, roughly close to a statistical prediction.



FIG. 5. Total DCS for the NO(${}^{2}\Pi_{1/2}$, v'=0, j'=34.5) averaged over the recoil energy. Error bars correspond to $\pm 1\sigma$. The DCS shows substantial intensities over the whole angular range with a slight preference for backward scattering.

served rotational level, j' = 34.5. Figure 4 shows the product CM translational energy distribution. This distribution can be described as a Boltzmann distribution with $T_{tr} \approx 13\,000$ K. The translational energy distribution is, though slightly colder, roughly close to the statistical prediction as observed for the rotational energy distribution. The wide spread of the translational energy distribution suggests that the sister products of the observed NO(v'=0) are populated over various rovibrational states.

Brouard *et al.* reported the nearly statistical excitation of rotational and translational degrees of freedom for the NO products in $v' \ge 1$ (Ref. 7) as observed for NO(v'=0) in this work. Since the population of the old NO is about four times larger than that of the new NO in the observed vibrational level v'=0,¹¹ the energy distributions obtained here are almost assigned to those of the old NO. Therefore, these results indicate that not all the old NO(v'=0) are produced from a near-stripping mechanism⁸ where the old NO almost behaves as a spectator.

B. Vector properties

The total DCS averaged over the recoil energy for the product NO(${}^{2}\Pi_{1/2}$, v' = 0, j' = 34.5) is shown in Fig. 5. The DCS shows substantial intensities over the whole angular range with a slight preference for backward scattering. In the analysis for extracting DCS, the variation in DCS with the product recoil energy was allowed. The DCS obtained for each recoil energy was not so much different.

Figure 6 shows the observed composite Doppler profiles $D_0^2(0,2;\nu)$, $D_0^2(2,2;\nu)$, and $D_0^2(2,2;\nu)$, reflecting the polarization of rotational angular momentum vector \mathbf{j}' of the observed NO. The least-squares fitting to these profiles yields the distribution function $P(\theta_r, \phi_r)$ representing the angular distribution of \mathbf{j}' with reference to the relative velocity vectors of the reactant (\mathbf{k}) and product (\mathbf{k}') as shown in Fig. 7(a). Here, θ_r and ϕ_r are the angle between \mathbf{k} and \mathbf{j}' , and the dihedral angle between \mathbf{k}' plane and $\mathbf{k}\mathbf{j}'$ plane. The nearly flat $P(\theta_r, \phi_r)$ shows that there is not a noticeable spatial correlation between \mathbf{j}' and the collision plane spanned by \mathbf{k} and \mathbf{k}' . In order to examine this weak spatial correlation between \mathbf{j}' and the collision plane in more detail, the distribution functions $P(\cos \theta_r)$ and $P(\cos \theta_{tr})$ representing the angle between the angle in the distribution between \mathbf{k}' and \mathbf{k}' .



FIG. 6. Observed composite Doppler profiles for the product NO(${}^{2}\Pi_{1/2}$, v'=0, j'=34.5). (a) $D_{0}^{2}(0,2;v)$ ($\mathbf{v}-\mathbf{j}'$ correlation), (b) $D_{0}^{0}(2,2;v)$ ($\mathbf{v}'-\mathbf{j}'$ correlation), and (c) $D_{0}^{2}(2,2;v)$ ($\mathbf{v}-\mathbf{v}'-\mathbf{j}'$ correlation). The smooth solid lines are the best fits to these profiles.

gular correlations of \mathbf{j}' with \mathbf{k} and \mathbf{k}' , respectively, are shown in Figs. 7(b), and (c), where θ_{tr} is the angle between \mathbf{j}' and \mathbf{k}' . These nearly flat distributions imply that \mathbf{j}' is almost isotropic with respect to both \mathbf{k} and \mathbf{k}' .

V. DISCUSSION

A. Origin of the nearly isotropic DCS

A nearly isotropic product DCS is ordinarily attributed to the lifetime of a collision complex comparable to or longer than its rotational period. If the intermediate of the reaction has a long lifetime, the observed nearly statistical energy distributions of the products are easily understood. However, since the $O(^{1}D) + N_{2}O$ reaction is known to have no deep potential well, the lifetime of the complex is not expected to be long. The quasiclassical trajectory (QCT) calculations on a London-Eyring-Polanyi-Sato surface accordingly suggested that the lifetime of the collision complex was at most 1 ps.³⁷ We estimated the rotational period of the possible intermediate of a *cis*-planar ONNO complex⁹ to be about 1.8 ps by using the rotational constants of cis-NO dimer³⁸ and the average orbital angular momentum ($\approx 50\hbar$) of the reactants. Thus, the lifetime of the collisional ONNO complex is about half of its rotational period and cannot fully explain the nearly isotropic DCS obtained here.

The spread of scattering angle distribution for the reaction not involving a long-lived complex is usually related to the spread of impact parameters. Since the total cross-section



FIG. 7. (a) Angular distribution function $P(\theta_r, \phi_r)$ representing the polarization of the rotational angular momentum vector, \mathbf{j}' for the NO(${}^{2}\Pi_{1/2}, v' = 0, j' = 34.5$). (b) Angular distribution $P(\cos \theta_r)$ representing the $\mathbf{k}-\mathbf{j}'$ correlation. (c) Angular distribution $P(\cos \theta_r)$ representing the $\mathbf{k}'-\mathbf{j}'$ correlation. The nearly flat angular distribution of \mathbf{j}' with respect to the collision plane shown in (a) arises from the isotropic angular distribution of \mathbf{j}' with respect to both \mathbf{k} and \mathbf{k}' shown in (b) and (c), respectively.

of this reaction was very large, the collisions with wide range of impact parameters can contribute to the reaction. Such wide spread of opacity function generally gives rise to the scattering of the products over wide angular range as also suggested in the QCT calculation for the reaction $O({}^{3}P)$ +CS \rightarrow CO+S.²⁹

Thus, we attribute the nearly isotropic DCS to both the wide range of impact parameters and the lifetime of the collision complex comparable to half of the rotational period.

B. Implication of the isotropic rotational angular momentum polarization

As described in Sec. IV A, we have found the nearly statistical rotational and translational energy distributions. In the recent study,^{6,11} the vibrational energy distribution of this reaction was shown to be closer to the statistical prediction than that expected from a direct process. To clarify the origin of these nearly statistical energy distributions, examining the rotational angular momentum polarization sensitive to reaction dynamics is advantageous.

As shown in Fig. 7(c), \mathbf{j}' is nearly isotropic with respect to \mathbf{k}' for this reaction. If the in-plane (out-of-plane) motion of the N–N–O moiety contributes primarily to the product rotation, \mathbf{j}' should be predominantly polarized perpendicular (parallel) to \mathbf{k}' . Therefore, the nearly isotropic $\mathbf{k}' - \mathbf{j}'$ corre-



FIG. 8. Angular distributions $P(\cos \theta_{tr})$ representing the $\mathbf{k}' - \mathbf{j}'$ correlations for forward and backward components. The almost isotropic $\mathbf{k}' - \mathbf{j}'$ correlations imply the contribution of both in-plane and out-of-plane motions to the product rotation irrespective of scattered hemispheres.

lation indicates that both the in-plane and out-of-plane motions of the N–N–O moiety contribute to the product rotation to almost the same degree. Nearly equivalent contribution of several modes to the product rotation most probably suggests that the energy redistribution among the internal modes of the collision complex is almost completed prior to its fragmentation and leads to the nearly statistical energy distributions even with the short lifetime of the complex.

As another origin of the nearly statistical distributions for the reaction not involving a long-lived complex, the spread of the impact parameters suggested from the DCS should be discussed. Even if each reactive collision with a specific range of impact parameters yields an unstatistical distribution, the seemingly statistical distributions would happen to be given by summing up the individual unstatistical distributions. For a direct reaction, it is known that there is a relatively tight correlation between impact parameters and scattering angles. The QCT calculation for this reaction indicated that the collisions with small and large impact parameters preferentially yielded the backward and forward scattering of the new NO, respectively.³⁷ Thus, the possibility that the observed statistical distributions originate from the spread of the impact parameters can be examined by the extent of the difference between the angular momentum polarization of the forward and backward components. Figure 8 shows the $\mathbf{k}' - \mathbf{j}'$ correlations of the products scattered into the forward and backward hemispheres. The correlations in both hemispheres are isotropic to almost the same degree. As mentioned in Sec. IV B, the product DCS was not found to significantly depend on the recoil energy, or the internal energy of the sister fragment. In other words, this implies that the energy distribution as well as the $\mathbf{k}' - \mathbf{j}'$ correlation does not have a significant dependence on scattering angles. These results indicate that the nearly statistical energy distributions observed here do not accidentally originate from a special superposition of individual reaction dynamics initiated by the collisions with specific impact parameters.

We can therefore conclude that the nearly statistical distributions observed for the $O(^{1}D) + N_{2}O$ reaction are attributed to the occurrence of almost complete energy randomization within the lifetime of the collision complex.

C. Origin of efficient energy redistribution

As mentioned in Sec. VA, the QCT calculation³⁷ suggested that an interaction time of this reaction was at most 1 ps. Whether or not such an interaction time of picosecond order is essential to yield the statistical energy partitioning can be examined by comparing with other bimolecular reac-For the bimolecular reactions $O(^{1}D) + CH_{4}$ tions. \rightarrow OH+CH₃^{12,39,40} and H(²S)+CO₂ \rightarrow OH+CO, ^{18,41-45} the real time pump-probe experiments utilizing ultrafast lasers showed that each reaction involved a complex with a lifetime of picosecond order exceeding the rotational period: 3 ps for the $O(^{1}D) + CH_{4}$ reaction⁴⁰ and 0.5–5 ps for the $H(^{2}S)$ + CO₂ reaction.⁴³⁻⁴⁵ These results imply that these two reactions are complex-mode reactions involving "long-lived" complexes. However, as opposed to a traditional expectation for complex-mode reactions, the energy distributions of the products deviated from the statistical predictions,^{39,41,42} and the product rotational angular momentum was polarized for both reactions.^{12,18} Therefore, a comparison of the three reactions involving intermediates with similar lifetimes of picosecond order suggests that the statistical energy distributions do not essentially depend on the absolute value of the lifetime of the collision complex.

Based on the above comparison, for the $O({}^{1}D) + N_{2}O$ reaction the redistribution of the available energy among the internal modes of the collision complex is expected to take place more efficiently than for the other two reactions. The efficient energy redistribution expected in this reaction suggests that there should be strong couplings among the internal modes of the collisional ONNO complex.

For considering such energy flow, the difference between normal mode and local mode characters will give an insight. For the molecules containing two equivalent bonds with a common vibrational frequency, the energy deposited in one bond flows into the other bond according to the strength of the coupling between the two bonds.⁴⁶ The molecules involving heavy atoms with light hydrogen atoms such as H₂O and H₂S have local mode characters, where the two equivalent modes are localized because of the relatively weak interbond coupling and the strong anharmonicity.⁴⁶ On the other hand, the molecules with heavy terminal atoms such as CO_2 and SO_2 have the large couplings and behave with normal mode characters. Since the normal mode character will be applied to the ONNO system due to its mass combination, the efficient energy redistribution in this system can be reasonably expected to occur.

One of the salient features of the $O({}^{1}D) + N_{2}O$ reaction as compared with other two reactions mentioned above is the absence of light hydrogen atoms. As is analyzed by Akagi *et al.*,⁴⁷ the presence of light atoms considerably reduces the momentum couplings among the vibrational modes and significantly retards the energy redistribution. In contrast, the collision complex composed of only heavy atoms possesses low-frequency vibrations to enhance the density of states and large momentum couplings to facilitate the energy randomization. Therefore, in the $O({}^{1}D) + N_{2}O$ reaction, the initial energy deposited between the approaching $O({}^{1}D)$ atom and the terminal N atom of the reactant N₂O can flow efficiently into the other vibrational modes.

VI. SUMMARY

We have measured scalar and vector properties of the product NO(v'=0) generated from the reaction O(¹D) + N₂O \rightarrow NO+NO. The observed rotational and translational energy distributions of the NO(v'=0) are considerably hot and described as Boltzmann distributions with $T_{\rm rot} \approx 10\,000$ K and $T_{\rm tr} \approx 13\,000$ K, respectively. These results indicate that the formation of all the old NO(v'=0) is not dominated by a stripping mechanism where the old NO behaves as a spectator during reaction. These energy distributions are close to the statistical predictions.

The DCS of the product NO(v'=0,j'=34.5) has a nearly isotropic distribution with a slight preference for backward scattering. The product angular momentum vector \mathbf{j}' is almost isotropic with respect to both \mathbf{k} and \mathbf{k}' (the relative velocity vectors of the reagents and products, respectively). This suggests that both the in-plane and out-of-plane motions of the collisional ONNO complex contribute to the product rotation to almost the same degree. Considering that this reaction has no potential well deep enough for the formation of a long-lived complex, the nearly statistical scalar and isotropic vector properties suggest that the energy redistribution efficiently takes place among the internal modes of the short-lived ONNO complex. It suggests that there are strong couplings among the internal modes of the complex.

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