The increased width of S_0 states does narrow the distribution of lifetimes about the average and generate a significant fraction of coincident lifetimes.

Vibronic Effects. For nearly isoenergetic levels, S_1 states with excitation in C–D stretch (ν_1 and ν_5) exhibit much slower decay rates than states with excitation in ν_2 and ν_4. Both 1^14^1 ($E_{\mathrm{vib}} = 2144\ \mathrm{cm}^{-1}$) and 5^1 ($E_{\mathrm{vib}} = 2239\ \mathrm{cm}^{-1}$) decay less rapidly than either 2^14^3 ($E_{\mathrm{vib}} = 1845\ \mathrm{cm}^{-1}$) or $2^14^26^1$ ($E_{\mathrm{vib}} = 2257\ \mathrm{cm}^{-1}$). In fact, 5^1 is almost isoenergetic with $2^14^26^1$, but the average decay rate in 5^1 is 3 times slower. Similarly 4^25^1 has 220 cm^{-1} more vibrational energy than 2^24^1 but decays 2.75 times less rapidly. This phenomenon is less obvious at vibrational energies greater than 2600 cm^{-1}.

As vibrational energy in S_1 is increased, the greater density of vibrational states makes the possibility of either Coriolis coupling or Fermi interactions more likely. The decay rates for bands 2^15^1 ($E_{\mathrm{vib}} = 3428\ \mathrm{cm}^{-1}$), 2^34^1 ($E_{\mathrm{vib}} = 3542\ \mathrm{cm}^{-1}$), $2^14^25^1$ ($E_{\mathrm{vib}} = 3797\ \mathrm{cm}^{-1}$), and $1^12^14^3$ ($E_{\mathrm{vib}} = 3917\ \mathrm{cm}^{-1}$) show only a slight trend of increasing decay rate with vibrational energy. One might expect 2^34^1 to decay more rapidly than either 2^15^1 or $2^14^25^1$; however, several of these bands are severely perturbed and almost certainly have mixed vibrational character. The fluorescence spectrum of 2^34^1 shows two almost equally intense rotational structures that have not been analyzed. The decay rate plotted in Figure 6 in part reflects the vibrational character of the perturbing band because the rate plotted is the median of the decay rates of all reasonably intense spectral lines. This median is therefore a lower limit to the decay rate of pure 2^34^1 since mixing with any other vibration would result in an equal or slower decay.[26] Both $2^14^25^1$ and $1^12^14^3$ are also perturbed, though not as extensively.[17,19] Vibrational mixing will cause these bands to decay more rapidly than the vibrationally pure states unless they are coupled to a vibration with poorer Franck–Condon overlap, e.g., ν_3.[26,27] The very short lifetimes observed for some states in these two bands may bias the median decay rates.

The dependence of τ_{fl} on Franck–Condon overlap between S_1 and S_0 has also been observed in H_2CO.[15] Here too, levels with excitation in ν_2 and ν_4 decay more rapidly than levels containing ν_5 or ν_1 excitation. Many of the states containing a quantum of ν_5 are also Coriolis coupled to states containing $\nu_1 + \nu_4$: $1^14^1/5^1$, $2^15^1/1^12^14^1$, and $2^25^1/1^12^24^1$, and the SVL lifetimes are longer than nearby combinations of ν_2 and ν_4. In the $1^14^1/5^1$ system, lifetimes for a very limited number of vibrationally pure rotational states were measured and indicate that lifetimes in the 1^14^1 states are actually short, which is puzzling since the ν_1 CH excitation should give smaller Franck–Condon factors.[28] In general, however, H_2CO and D_2CO nonradiative decay rates can be understood in terms of Franck–Condon overlap between S_1 and S_0.

Conclusion

At the energies studied, S_0 structure seems to exist on scales greater than 0.2 cm^{-1} but smaller than the difference in S_1 and S_0 rotational term values, <5 cm^{-1}. Although a slight trend in nonradiative decay rate with both J' and K'_a is observed, the predicted monotonic dependence on K' is not. Any systematic effect must be smaller than the observed erratic lifetime variation over $K' = 0$–3 for a given J', which is about a factor of 2 in $1^12^14^3$. One would hope that a systematic dependence of k_{nr} with K' would become clear at higher vibrational energy; however, vibrational mixing that could conceal this dependence becomes increasingly important as energy increases.

The previously unobserved dependence of D_2CO fluorescence decay rates on vibrational motion have finally been measured; states containing CD stretching motion (ν_1 and ν_5) decay more slowly than levels with ν_4 (out-of-plane bend) excited. As S_1 vibrational energy is increased, a higher incidence of vibrational perturbations (Coriolis coupling and Fermi interaction) degrades the integrity of vibrational levels, and this difference is no longer apparent.

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Registry No. D_2CO, 1664-98-8.

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Vibrational-State Distribution of O_2 Generated by Multiphoton Dissociation of NO_2 at 505 nm

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The internal state energy distribution of $O_2(X^3\Sigma_g^-, v''=20\text{–}25)$, produced by the multiphoton dissociation of NO_2 at 505 nm, was measured by pump–probe two-color experiments using a laser-induced fluorescence method. The vibrationally excited $O_2(v'')$ was generated by the reaction of $O^* + NO_2$, where O^* was an electronically excited oxygen atom. The vibrational distribution was broad over $v'' = 20$–24 but dropped at $v'' = 25$. The behavior of O^* in the presence of N_2 or NO was subject to the $O(^1S)$ kinetics in accordance with the recent result of Jusinski et al. (*J. Chem. Phys.* **1987**, *86*, 5509). The dynamics of the $O(^1S) + NO_2$ reaction is discussed on the basis of the state distribution of $O_2(v'')$.

Introduction

Electronically excited oxygen atoms, $O(^1D)$ and $O(^1S)$, have been known to play important roles in many photochemical reactions.[1,2] Information on the chemical reactions of $O(^1D)$ and $O(^1S)$ was listed by Schofield.[3] The physical quenching of $O(^1S)$ is in general much less effective than that of $O(^1D)$ because there are no adiabatic singlet pathways correlating reactants, including $O(^1S)$, with energetically accessible products.[4] The reactions of

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$O(^1D)$ have been extensively studied because of its importance in atmospheric chemistry.[5-7] Analysis of the internal energy distribution of products provides clue information on the intermediate potential surface on which the bimolecular reaction takes place.[8-13]

The production of $O(^1D)$ by the single-photon absorption of NO_2 was reported to occur in the region shorter than the threshold wavelength (244 nm).[14] The photodissociation of NO_2 in the region 106–162 nm was investigated by Lee and Chiang.[15] Instead of ultraviolet or vacuum ultraviolet light, visible laser light has been found to generate the metastable oxygen atoms from NO_2.[16-19] Multiphoton (four-photon) ionization of NO_2 by visible laser light takes place effectively via real states.[17] The multiphoton absorption processes of NO_2 could be strongly dependent upon the laser power.[20] Matsumi et al.[16a] first reported on a formation of vibrationally excited $O_2(v''=22\text{–}26)$ in the multiphoton absorption of NO_2. Two possible formation mechanisms were proposed: (1) Unimolecular elimination of $O_2(v'')$ out of NO_2^* in the highly excited state; (2) $O_2(v'')$ formation through the chemical reaction $O^* + NO_2$, where O^* is an electronically excited oxygen atom. Subsequently, Shibuya et al.[16b] carried out the isotopic experiments to check the formation mechanism and established that $O_2(v'')$ was formed through the chemical reaction $O^* + NO_2$. The same conclusion has been obtained by Jusinski et al.[18]

The question then becomes, what is the O^* intermediate, $O(^1D)$ and/or $O(^1S)$? Matsumi et al.[16a] originally proposed $O(^1S)$ as O^*, which was based on the energetical reason that the O_2 products generated were in the vibrational levels up to $v'' = 26$ ($E_{\text{vib}} = 32\,908$ cm^{-1}) and the excess energy of the reaction $O^* + NO_2$ must therefore exceed 394 kJ mol^{-1}:

$$O(^1S) + NO_2 \rightarrow O_2 + NO, \quad \Delta H = -597 \text{ kJ mol}^{-1} \quad (1)$$

The laser-power dependence was examined in the one-color experiments, and it was found that $O_2(v''=24,26)$ yields depended on the power indexes of 1.9 and 2.8, respectively. The difference in the power indexes implies that there are two or more source reactions to produce $O_2(v'')$. In the two-color experiments[16b] the laser flux was lowered by loosely focusing the pump laser beam, and then no signals originating from $O_2(v''=26)$ were detectable. Under those conditions the highest vibrational energy of the O_2 products was limited to 31 490 cm^{-1}, corresponding to $v'' = 26$ in the case of $^{18}O_2$, which gave at least 377 kJ mol^{-1} as the excess energy of the source reaction. Thus, we proposed that, instead of the reaction 1, $O_2(v'')$ was formed through

$$O(^1D) + NO_2 \rightarrow O_2 + NO, \quad \Delta H = -383 \text{ kJ mol}^{-1} \quad (2)$$

simply on the basis of the maximum internal energy of the product. The recent report of Fujimura et al.[19] supports the existence of the $O(^1D)$ intermediate in the multiphoton dissociation of NO_2 at laser wavelengths shorter than 490 nm. They proposed that NO^* in the $A(v'=0\text{–}3)$ state was generated through

$$O(^1D) + NO_2^* \rightarrow O_2 + NO(A), \quad \Delta H = -106 \text{ kJ mol}^{-1} \quad (3)$$

where NO_2^* is excited at 475 nm. In the two-photon dissociation of NO_2 at 450 nm, Bigio et al.[17d] also proposed the $O(^1D)$ production on the basis of the maximum vibrational energy of NO. Recently Jusinski et al.[18] have objected to our proposed $O(^1D)$ mechanism, reaction 2, to generate $O_2(v'')$. The reason is that upon N_2 addition the $O_2(v'')$ formation was not reduced to the extent expected for $O(^1D)$ as the O^* intermediate.

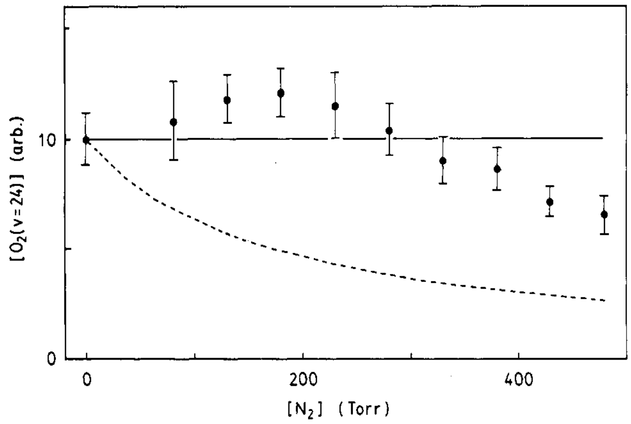

Figure 1. Dependence of N_2 pressure on the $O_2(v''=24)$ yield. The NO_2 pressure was kept at 34.7 Torr. The solid and broken lines are calculated by assuming $O(^1S)$ and $O(^1D)$ kinetics, respectively. See text.

In the present article we have reexamined the kinetic behavior of O^* in more detail and confirmed that not $O(^1D)$ but $O(^1S)$ is the intermediate responsible for the $O_2(v'')$ formation. We have further measured the partial vibrational-state distribution of $O_2(v''=20\text{–}25)$ to investigate the $O(^1S) + NO_2$ reaction. The vibrational distribution is broad over $v'' = 20\text{–}24$ but falls off at $v'' = 25$. The probable reaction dynamics of $O(^1S) + NO_2$ is discussed on the basis of the abnormal distribution.

Experimental Section

Experimental procedures are essentially the same as described before.[16b] Both pump and probe dye lasers (Lambda Physik FL-2002E) were simultaneously excited by the divided 308-nm laser beams from a XeCl excimer laser (Lambda Physik EMG-103E MSC) operated at 10 Hz. The focused beam ($f = 150$ mm lens) of the pump laser was used to photodecompose NO_2 in a quartz cell by the multiphoton absorption. The beam of the probe laser was then introduced into the NO_2 cell to monitor the O_2 molecules generated after the multiphoton absorption. Optical time delay was 3 ns, and a lens ($f = 250$ mm) was placed in front of the cell to compensate for the beam divergence of the probe laser. The dyes employed were coumarin 540A, coumarin 503, coumarin 480, coumarin 460, coumarin 440, and stilbene 420. The outputs of the pump and probe lasers were typically controlled at 1 and 0.1 mJ/pulse, respectively. The output energy of the probe laser pulse was continuously monitored by a photomultiplier (Hamamatsu R928) after the laser beam was split by a beam splitter. Attenuation of the laser intensity due to the absorption of NO_2 was corrected by standard procedures. The ultraviolet part (250–300 nm) of O_2 Schumann–Runge emission was detected by a solar-blind photomultiplier (Hamamatsu R166) through a band-pass filter (Corning 7-54). Most experiments were carried out at rather high pressures. More than 10 Torr of NO_2 was needed to obtain a sufficient signal of O_2 emission.

Research grade N_2 (Takachiho, 99.999%) and O_2 (Takachiho, 99.95%) were used without further purification. The NO_2 sample was prepared by the reaction of NO with O_2. The research grade O_2 was mixed with NO (Takachiho, 99.9%), and the mixture was kept overnight. The excess O_2 was then degassed at 77 K. The

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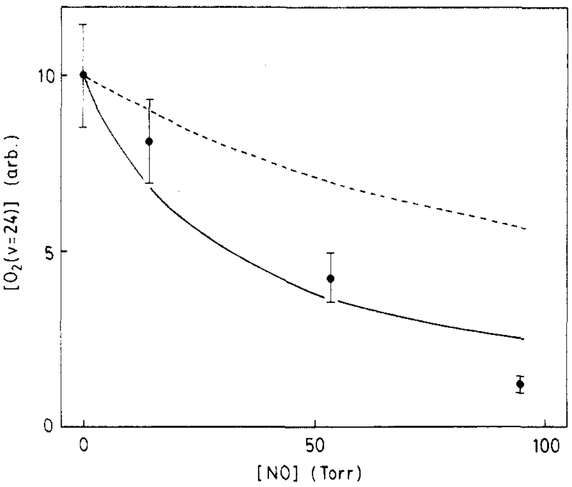

Figure 2. Dependence of NO pressure on the $O_2(v''=24)$ yield. The NO_2 pressure was kept at 35.3 Torr. The solid and broken lines are calculated by assuming $O(^1S)$ and $O(^1D)$ kinetics, respectively. See text.

frozen NO_2 was white and did not show any obvious visible discoloration due to impurities.

Results and Discussion

Electronically Excited Oxygen Atom Responsible for $O_2(v'')$ Formation. It has been established[16b,18] that $O_2(v'')$ is formed by a certain chemical reaction, most possibly by $O^* + NO_2$. As discussed in the Introduction, the electronically excited oxygen atoms could be $O(^1D)$ or $O(^1S)$. Jusinski et al.[18] have suggested that O^* is $O(^1S)$ because the $O_2(v'')$ yield decreases by a factor of only 1.5 upon the addition of 430 Torr of N_2 to 30 Torr of NO_2.[18] We reexamined the effect of the added foreign gases at various pressures (Figure 1). The foreign gas pressure effect on the $O_2(v'')$ yield is calculated by using reported rate constants[3] and also plotted in Figure 1. Comparison between experiment and calculation confirms that not $O(^1D)$ but $O(^1S)$ is a main precursor of $O_2(v'')$. There is a discrepancy between the pressure effect estimated from $O(^1S)$ kinetics and the measured $O_2(v'')$ yield. In the low-pressure region of N_2, the experimental yields are larger by a small amount than calculated, while the situation is reverse in the high-pressure region. To explain the helium pressure effect on the $O_2(v'')$ formation, we proposed the collision-enhanced O^* generation in our previous paper.[16b] Again we observed the enhancement of the $O_2(v'')$ yield in the low-pressure region of N_2. The reason for this observation is not clear yet. The apparent decrease of the $O_2(v'')$ formation was proposed by Jusinski et al.[18] as a result of vibrational relaxation of $O_2(v'')$ and/or electronic quenching of $O_2(B)$. Furthermore, we examined the effect of NO as an additive (Figure 2). $O(^1S)$ is quenched by NO more than 10 times as effectively as $O(^1D)$.[3] Again, the result fits with the $O(^1S)$ kinetics. The generation of $O(^1S)$ requires absorption of three photons by NO_2 at 509 nm (the threshold wavelength). Any increase in the $O_2(v'')$ production was not observed at wavelengths shorter than 509 nm.[16b] Possibly the $O(^1S)$ intermediate is prepared by sequential four-photon absorption of NO_2.

The plausible pathways to produce $O_2(v'')$, except the $O(^1S) + NO_2$ reaction, may be the interaction of $O(^1S)$ with vibrationally and electronically excited NO molecules, $NO(v'')$ and NO^*, respectively. It has been experimentally confirmed that there exist $NO(v''\leq 7)$[18] and $NO(A)$[19] in the visible multiphoton system similar to the present NO_2 system. Jusinski et al.[18] found that the spatial distribution of $O_2(v'')$ was different from that of $NO(v'')$. In their intense laser experiments, the $NO(v''\leq 7)$ molecules are formed in the bleaching volume directly by the two-photon absorption of NO_2. From their intense laser experiments one cannot accept the $O_2(v'')$ formation mechanism of $O(^1S) + NO(v'')$. In the multiphoton dissociation of NO_2 at wavelengths shorter than 490 nm, Fujimura et al.[19] have reported that NO(A) is formed through the $O(^1D) + NO_2{}^*$ reaction, where $O(^1D)$ is generated by two-photon absorption of NO_2 and $NO_2{}^*$ is the one-photon excited state. They found the quenching of $O(^1D)$ and $NO_2{}^*$ by N_2, but we did not observe the N_2 pressure effect on the $O_2(v'')$ formation. Thus, the $O(^1S)$ + NO(A) reaction is not responsible for the $O_2(v'')$ formation of interest. The remaining possibility is the $O(^1S) + NO_2$ reaction.

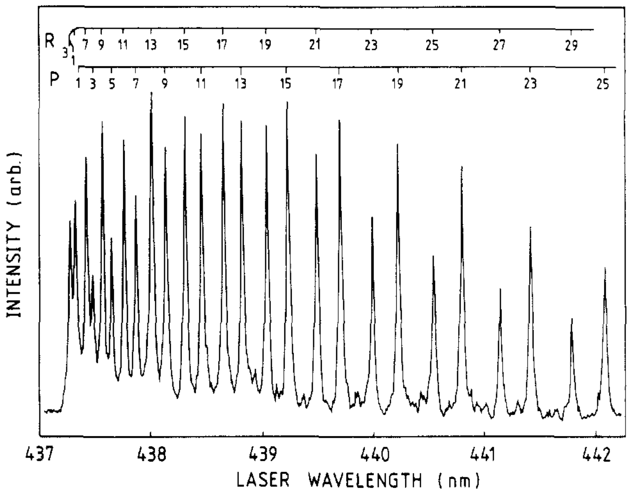

Figure 3. Typical LIF excitation spectrum of O_2. The $O_2(v'')$ products were generated after the multiphoton absorption of NO_2 at 505 nm. The transition probed is O_2 $B^3\Sigma_u{}^-(v'=2) - X^3\Sigma_g{}^-(v''=21)$.

Vibrational-State Distribution of $O_2(v'')$. To determine the internal state distribution of $O_2(X^3\Sigma_g{}^-(v''))$, we measured the laser-induced fluorescence (LIF) excitation spectra of O_2 in the region 400–560 nm, corresponding to O_2 $B^3\Sigma_u{}^-(v'=1,2) \leftarrow X^3\Sigma_g{}^-(v''=20\text{–}25)$ transitions. Transitions originating from $O_2(v''\geq 25)$ were not detected under the present experimental conditions. Transitions originating from $O_2(v''\leq 19)$ were not measured because probe laser wavelengths shorter than 400 nm were within the sensitive region of the filter/photomultiplier combination, and we could not get rid of the scattered light.

A typical LIF excitation spectrum of O_2 $B^3\Sigma_u{}^-(v'=2) \leftarrow X^3\Sigma_g{}^-(v''=21)$ is shown in Figure 3, where O_2 in the ground electronic state was generated after the pump-laser-induced multiphoton absorption at 505.0 nm. Vibrational and rotational assignments of the observed spectra corresponding to O_2 $B^3\Sigma_u{}^-(v') \leftarrow X^3\Sigma_g{}^-(v'')$ transitions were made by using the molecular constants reported by Creek and Nicholis.[21] Each vibrational band has rotational structure consisting of P and R branches. No electron spin structure was observed because the spin splitting of O_2 in the $B^3\Sigma_u{}^-$ state is smaller than the predissociative line width.[22] Each rotational level is well expressed by the rotational quantum number N. Rotational levels with even N are missing in the $X^3\Sigma_g{}^-$ state because of nuclear spin statistics.

Since the rotational distribution was of Boltzmann in O_2 $X^3\Sigma_g{}^-(v'')$, the population of the (v'',N'') level is expressed as[16b]

$$n(v'',N'') = n_{v'',0}(2N''+1)\exp(-E_{\mathrm{rot}}/kT_{\mathrm{rot}}) \qquad (4)$$

The population of a specific vibrational level can be calculated by

$$n(v'') = \sum_{N''} n(v'',N'') \qquad (5)$$

At least 10 Torr of NO_2 was necessary to obtain enough LIF intensity of O_2 Schumann–Runge bands for the qualitative analysis, but the rotational contours of neighboring vibronic bands overlapped each other because of the high rotational temperature of $O_2(v'')$, $T_{\mathrm{rot}} > 1000$ K. In the present experiment a rather high pressure of He (180 Torr) was added to NO_2 (12.9 Torr). The addition of He cooled the temperature to $T_{\mathrm{rot}} \sim 700$ K, so that

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TABLE I: Summary of Vibrational-State Distribution $n(v'')$ and Franck–Condon Factors $q_{v',v''}$ of O_2 Schumann–Runge Bands

v''	20	21	22	23	24	25
$q_{v'=2,v''}$	0.1111[a]	0.1257[a]	0.1008[b]	0.0618[b]	0.0294[b]	0.0108[b]
$n(v'')$ (arb)	0.190 (28)	0.195 (14)	0.158 (16)	0.197 (25)	0.237 (24)	≤0.06[c]
$q_{v'=1,v''}$	0.0806[a]	0.0459[a]	0.0210[b]	0.0079[b]	0.0024[b]	0.0006[b]
$n(v'')$ (arb)	0.207 (16)	0.216 (47)	0.120 (19)	nd[d]	nd[d]	nd[d]

[a] The Franck–Condon factors of O_2 $B^3\Sigma_u^-(v'\leq13) - X^3\Sigma_g^-(v''\leq21)$ were reported by Albritton et al.[24] [b] To analyze the present results, we calculated the Franck–Condon factors for O_2 $B^3\Sigma_u^-(v') - X^3\Sigma_g^-(v''\geq22)$. In our calculation $q_{v'=2,v''=20} = 0.1116$, $q_{v'=2,v''=21} = 0.1251$, $q_{v'=1,v''=20} = 0.0792$, and $q_{v'=1,v''=21} = 0.0451$, which accord with the values calculated by Albritton et al.[24] [c] Population of $n(v''=25)$ was estimated as the upper limit by assuming the 2–25 band intensity to be the detection limit of the present experiment. [d] Not determined.

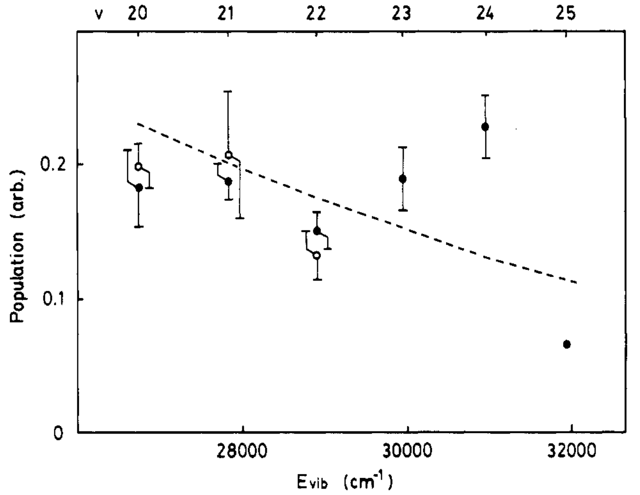

Figure 4. Vibrational-state distribution of $O_2(v'')$. The closed and open circles were obtained from the O_2 $B^2\Sigma_u^-(v'=2) - X^3\Sigma_g^-(v'')$ and $B^3\Sigma_u^-(v'=1) - X^3\Sigma_g^-(v'')$ progressions, respectively. The population of $O_2(v''=25)$ is the upper limit. The statistical distribution is calculated by eq 7 and indicated by the broken line.

we could determine $n(v'',N'')$ experimentally. The rotational distribution was not thermalized under the pressure conditions. The effect of vibrational relaxation was negligible, because vibrational relaxation takes place normally much slower than the rotational relaxation. The vibrational relaxation time (τ_v) at [He] = 180 Torr is estimated as 400 μs, by using τ_v[He] = 100 atm μs reported for O_2–He collisions at 300 K.[23] The vibrational relaxation by NO_2 was also neglected because the vibrational distributions at the NO_2 pressures of 12.9 and 30 Torr, corresponding to three and six hard collisions during a 20-ns delay time, respectively, were essentially the same within the estimated errors. The resultant populations of $n(v'')$ are listed in Table I and plotted in Figure 4. The distribution $n(v'')$ is rather broad over v'' = 20–24 but drops at v'' = 25. Here, the population at v'' = 25 gives the upper limit, because it was not detected by LIF under the present experimental conditions.

Energetically it is possible to generate $O_2(v''\leq25)$ from the $O(^1D) + NO_2$ reaction. But $O(^1D)$ is not important to generate $O_2(v'')$ as discussed before. Actually we did not observe the enhancement of the $O_2(v'')$ yield in the pump laser wavelength region shorter than 490 nm.[16b] It should be noted here that $O(^1D)$ is also generated in the multiphoton dissociation of NO_2 at 505 nm. We observed the background UV emission probably due to electronically excited NO in the $A^2\Sigma^+$ state as Fujimura et al.[19] established in the formation mechanism, $O(^1D) + NO_2^* \rightarrow NO(A) + O_2$. The background emission decreased on adding N_2 as expected for the $O(^1D)$ kinetics. Another chemical source of O_2 is $O(^3P) + NO_2$ reactions. The $O(^3P)$ atoms exist undoubtedly in the present system, but the $O(^3P)$ reaction gives only $O(v''\leq11)$. As far as the vibrational-state distribution of current interest is concerned, the contribution of $O(^3P)$ reaction can be neglected.

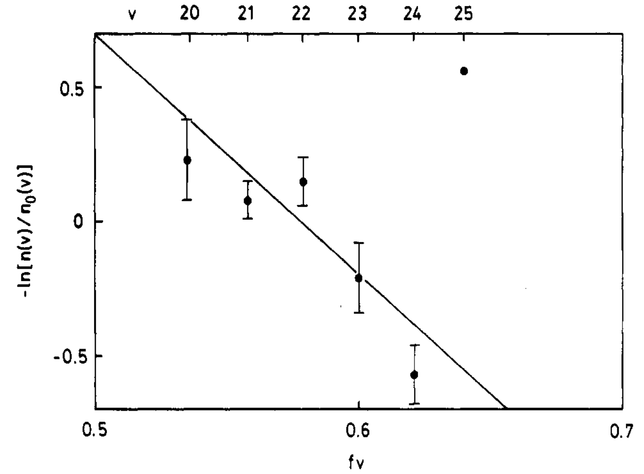

Figure 5. Surprisal plots of $-\ln[n(v)/n_0(v)]$. The linear relation over v'' = 20–24 gives λ_v = −9. The plot at v'' = 25 is the lower limit and deviates from the linear relation.

The vibrational distribution of O_2 can be estimated by a statistical model.[13] The model assumes the total available energy of the reaction was completely randomized among all degrees of freedom of the product molecules. The statistical distribution is obtained by counting all possible energy states of the product molecules under the energy conservation law. The product-state population in a particular rovibrational state is estimated by[13]

$$n_0(v'',N'') = (2N''+1)C_t\sum_{v,J}(2J+1)\{E^* - E_{NO}(v,J) - E_{vib}(v'') - E_{rot}(N'')\}^{1/2} \quad (6)$$

Here, $C_t = 4\pi(2\mu^3)^{1/2}/h^3$. As the available energy of E^*, the exothermicity of $O(^1S) + NO_2 \rightarrow O_2 + NO$ was included, but the translational and internal energies carried by the reactions were neglected. All the possible states of NO with the internal energy $E_{NO}(v,J)$ are considered by making the summation over v and J in eq 6. Thus, the vibrational-state distribution, $n_0(v'')$, is calculated by summing eq 6 over N'':

$$n_0(v'') = \sum_{N''} n_0(v'',N'') \quad (7)$$

The broken line of Figure 4 shows the calculated distribution of $n_0(v'')$. Surprisal plots of the vibrational distribution are shown in Figure 5. If the distribution determined experimentally follows the statistical model, the slope of the surprisal plots, $\lambda_v(O_2)$, is expected to be zero. The surprisal plots in v'' = 20–24 give a large negative $\lambda_v(O_2)$ value of −9, but one must keep in mind that the $f_v(O_2)$ region studied in the present experiments (0.53–0.64) covers only 11% of the total available energy. The result may imply that even if the collision complex of NO_3 exists during the $O(^1S) + NO_2$ reaction, it dissociates into O_2 + NO fast enough before the available energy is randomized among all the vibrational degrees of freedom. In many other abstraction reactions λ_v is negative, showing a preferential disposal of the reaction exothermicity into the product vibration.[25] The sampler reactions are $O(^1D) + NH_3$

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$\rightarrow OH(v'') + NH_2$ with $\lambda_v(OH) = -10$,[26] $F + H_2 \rightarrow HF(v'') + H$ with $\lambda_v(HF) = -6.9$,[27] $Cl + HI \rightarrow HCl(v'') + I$ with $\lambda_v(HCl) = -8.0$,[28] and so on.

In the photolysis of isotopic 1:1 mixture of $N^{16}O_2$ and $N^{18}O_2$,[16b] the branching ratio of $[^{16}O_2]:[^{16}O^{18}O]:[^{18}O_2]$ was determined to be 1:1.4:0.5. On the basis of the measured ratio of $[^{16}O_2]:[^{18}O_2]$, the relative $[^{16}O^{18}O]$ yield can be estimated for two limiting reaction cases (an abstraction mechanism and a long-lived complex formation mechanism) to be $[^{16}O_2] + [^{18}O_2] = 1.5$ and $\{[^{16}O_2] + [^{18}O_2]\}/2 = 0.75$, respectively. Thus, the isotopic mixture experiments also suggest that the $O(^1S) + NO_2$ reaction proceeds to generate the $O_2(v'')$ products through an abstraction mechanism.

The remaining question is why the $O_2(v''=25)$ yield is so low and deviates from the expected yield as recognized in Figure 5. Possible reaction dynamics can be speculated as follows. Probably $O(^1S)$ attacks one of the O atoms of NO_2, and most of the internal energy of the unstable and short-lived collision complex (NO_3) will be localized in the vibration of a newly formed O–O bond. The fragmentation takes place through an early barrier to generate $O_2(v'')$ and NO, which results in a high excitation of the O_2 vibration. Near the exit channel the $O_2(v''=25)$–NO pair crosses over from the $O_2\ X^3\Sigma_g^-$–NO $X^2\Pi$ potential surface, responsible for the $O_2(v''=20–24)$ formation, to the other excited O_2^*–NO $X^2\Pi$ surface. On the basis of the energetical reason that $O_2(v''=25)$ with $E_{vib} = 31\,953$ cm^{-1} was not observed, O_2^* could be the $c^1\Sigma_u^-$ state ($T_{00} = 32\,664$ cm^{-1}). As a result of the dynamical effect the $O_2(v''=25)$ yield becomes much lower than the yield extrapolated from the data in $O_2(v''=20–24)$.

Registry No. O_2, 7782-44-7; NO_2, 10102-44-0; O, 17778-80-2.

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Laser Ionization Spectroscopy of Diazabicyclo[3.3.3]undecane[†]

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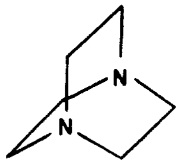
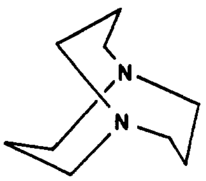
Two-photon resonant multiphoton ionization of diazabicyclo[3.3.3]undecane (DABCU) vapor is reported over the 4–6-eV range. Transitions from the symmetric and antisymmetric combination of nitrogen lone-pair orbitals to several molecular Rydberg states are detected. Comparison with the optical spectrum allows assignment of the lowest excited singlet electronic states and a confirmation of the ground-state orbital ordering. A single-center term value approach is used in the analysis of the Rydberg states of DABCU and the closely related diazabicyclo[2.2.2]octane (DABCO).

Introduction

Hoffmann[1] introduced through-bond, through-space (TBTS) coupling almost two decades ago for understanding the interaction of localized sets of orbitals in polyatomic molecules. A particularly successful application of TBTS coupling theory involves the nitrogen lone-pair orbitals in the symmetric caged amines diazabicyclo[2.2.2]octane (DABCO) and diazabicyclo[3.3.3]undecane (DABCU).



DABCO



DABCU

Through-space coupling predicts the molecular orbital corresponding to the symmetric combination of lone-pair orbitals, n(+), will fall lower in energy than n(−), the antisymmetric lone-pair combination. Hoffmann argued that mixing with other σ bonds (through-bond interaction) should overwhelm through-space coupling in DABCO, leaving n(+) as the HOMO. In DABCU symmetry considerations reverse the direction of through-bond coupling, supporting along with through-space coupling n(−) as the HOMO. Heilbronner and Muszkat[2] confirmed that the first ionization of DABCO corresponds to removal of an electron from the n(+) orbital by analysis of the vibrational fine structure of the photoelectron spectrum. Alder et al.[3] have investigated in detail the photoelectron spectra and proton affinities of a series of larger bicyclic [*n*,*l*,*m*] amines, including DABCU, where *n*, *l*, *m* = 2, 3, or 4, and found good agreement with TBTS predictions of the lone-pair molecular orbital ordering.

Similar arguments have been used in the past[4-7] for the LUMOs of DABCO and DABCU, which would then correspond to symmetric or antisymmetric combinations of 3s, $3p_{xy}$, $3p_z$, and 3d atomic orbitals. On the basis of a large body of experimental evidence for "double molecules", especially diones, Robin[8] suggests the use of only single-center molecular Rydberg states, thus only the symmetric (+) combination of excited atomic orbitals. This approach explains the similar term values for the excited states of DABCO and the monoaza analogue ABCO[4] and produces only half the number of the excited electronic states compared to the two-center approach, which is in better agreement with the observed spectra. We follow the single-center approach in this paper.

[†] Dedicated to the memory of Edward K. C. Lee.

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