

The Schumann-Runge O₂ Emission, Following Visible Multiphoton Excitation of NO₂

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The Schumann-Runge emission ($B^3\Sigma_u^- - X^3\Sigma_g^-$) of oxygen was observed in the wavelength range of 220–300 nm, when NO₂ was irradiated with a focused visible laser (470–580 nm). The excitation spectrum of the emission also showed the Schumann-Runge transition from highly excited vibrational levels ($v'' = 22-26$) of the X state to the $v' = 1-3$ levels of the B state of oxygen. The highly vibrationally excited O₂ ($E_{vib} \approx 30000 \text{ cm}^{-1}$) is once produced through a multiphoton process of NO₂ and then absorbs one more photon. The resulting excited state of O₂ emits fluorescence in the UV region. Even at 40 torr of NO₂, no rotational-vibrational relaxation in the B state was observed. The mechanism of the multiphoton process is discussed.

INTRODUCTION

Recent developments of lasers have demonstrated the importance of multiphoton processes. The multiphoton excitation processes of polyatomic molecules with visible-ultraviolet laser light have been investigated a great deal with respect to the emission from the simultaneous two-photon excited state¹ and the multiphoton ionization through the intermediate resonance state.² The dissociation processes from highly excited states by multiphoton excitation have been studied mainly by using high-power ultraviolet lasers such as excimer lasers.³ The new processes arising from a high-lying electronically excited state of a simple molecule produced by sequential multiphoton excitation can be studied. This has not been performed with

single-photon excitation, since the Franck-Condon factors and/or the selection rules of transitions for both symmetry and multiple-electron excitation are different from those in single-photon excitation.

In the long wavelength region of 320 to 1000 nm, the NO₂ molecule has a complex congested absorption band, which was partly assigned and has not been perfectly analyzed.⁴ The *ab initio* calculation of electronic states of NO₂ was carried out by Gillispie *et al.*⁵ Reeves and coworkers⁶ observed a multiphoton-induced emission from NO₂ in the region of 380 to 440 nm, using 694 nm ruby laser excitation. Morrison *et al.*⁷ reported the MPI spectrum of NO₂ in the region of 420 to 520 nm under a condition of moderate pressure (2 torr) in a static cell and that of low pressure with mass resolution in both a flow system and a supersonic beam. They observed the resonance-enhanced MPI spectrum, due to the 3sσ Rydberg state of NO₂ and the MPI spectrum of nascent NO, resulting from the two-photon photodissociation of NO₂. Radhakrishnan *et al.*⁸ also observed the MPI of NO resulting from the photodissociation of NO₂ in a one-color experiment.

The oxygen molecule has a very strong absorption in the range of 175 to 205 nm, corresponding to the B³Σ_u⁻ - X³Σ_g⁻ transition, which is called the Schumann-Runge band system. The B³Σ_u⁻ state has been known to predissociate with maximum efficiency at the v' = 4 level.⁹ The *ab initio* calculation showed that the predissociation is attributed to the perturbation mainly by the ⁵Π_u repulsive state.¹⁰ Thus far the emission of the Schumann-Runge band has been observed in the discharge arc through atmospheric pressure oxygen.¹¹⁻¹³ Recently Shibuya and Stuhl¹⁴ observed resonance fluorescence from the B state, using an intense ArF excimer laser (193 nm).

Here is reported the ultraviolet emission which is obtained with a visible dye laser focused on NO₂ vapor. This emission is assigned to the Schumann-Runge band system of oxygen molecules, and the excitation spectrum of the UV emission reveals an excitation profile of v' = 1-3 ← v'' = 22-26 of the Schumann-Runge system. This indicates that highly excited vibrational states (E_{vib} ≈ 30000 cm⁻¹) of oxygen are produced through the multiphoton absorption process in NO₂.

EXPERIMENTAL

Figure 1 shows a schematic diagram of the experimental apparatus. A flash-pumped dye laser (0.8 μs, ~ 2mJ/pulse, 5-8 Hz, 0.1 nm) was used

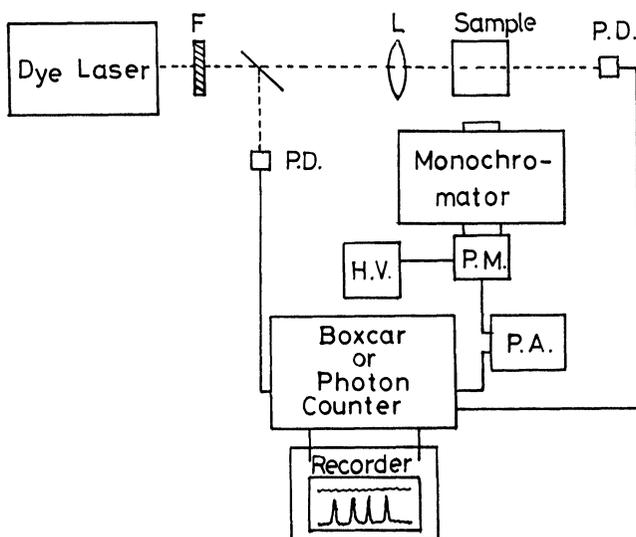


FIGURE 1 Schematic diagram of experimental apparatus. F = short-cut filter, L = lens, P.D. = photodiode, P.M. = photomultiplier, P.A. = preamplifier, H.V. = high voltage power supply, Dye laser = flash-pumped or nitrogen-pumped dye laser.

with coumarin-504, LD-473, and sodium fluorescein (Exciton) dyes, by which a wavelength region of 470–580 nm was covered. The laser pulses were focused with a lens ($f = 70$ mm) into a quartz cell ($l = 50$ mm, $d = 50$ mm) containing NO₂ gas. When excitation spectra were taken, the UV emission was detected at right angles to the laser beam by an R166 photomultiplier (Hamamatsu) with a UV filter (Corning CS 7-54). This combination allows the detection of light between a wavelength of 250 and 300 nm. The signal of the photomultiplier was averaged by a PAR model 164 gated integrator. The laser power was kept nearly constant during scanning in the wavelength range of each dye by the feedback system to the pumping flash voltage. The emission spectra were dispersed by a monochromator (JY HR1000 or Nikon P250) equipped with the R166 photomultiplier. A photon-counting detection system was used. The combination of a single and a rotatable double Fresnel rhombs was used to examine the influence of polarization on the laser light. The latter gave linearly or circularly polarized light depending on the polarization angle of the incident light beam.

A nitrogen-pumped dye laser (Molelectron DL 14, 5–6 ns) was also used

instead of the flash-pumped dye laser for studying the influence of time width of the laser pulse.

NO₂ was prepared by the reaction of NO with O₂. NO (Takachiho Chem. Co.) was distilled at 113 K. Oxygen of research grade (Takachiho) was added to NO. The excess O₂ was degassed at 77 K, and frozen NO₂ was white with no detectable impurity discoloration. ¹⁴N¹⁸O₂ was prepared by the photochemical migration between ¹⁴N¹⁶O₂ and ¹⁸O₂ (Prochem.). The isotopic purity of ¹⁴N¹⁸O₂ was measured to be 70% by a mass spectrometer.

RESULTS

Typical excitation and emission spectra of the UV emission are shown in Figures 2 and 3, respectively, when NO₂ vapor is irradiated by the visible flash-pumped dye laser. As can be seen in Figure 2, the spectrum obtained exhibits very sharp band structures in contrast to the complexity of the single photon absorption and fluorescence excitation spectra of NO₂ in the visible wavelength region. Similar bands were observed in the excitation spectra of the UV emission in the wavelength range of 480–580 nm. When the laser was unfocused, the UV emission was not observed. In order to elucidate the emitting species, the isotope effects on the excitation and emission spectra of UV emission were examined. No difference was observed in the spectra between ¹⁵N¹⁶O₂ and ¹⁴N¹⁶O₂, though the isotope effect was expected to appear within the limit of spectral resolution, assuming that the emitting species was NO₂. Then ¹⁴N¹⁸O₂ was examined. Definite isotope shifts were observed in the emission and excitation spectra of the UV emission, as shown in Figures 3 and 4, respectively. These results suggested that the UV emission should be attributed to an excited molecule containing no nitrogen atom. Since pure oxygen vapor hardly has absorption in the wavelength range of 470–580 nm, it seemed to be difficult to analyze the excitation spectra. The emission spectrum in Figure 3 could be assigned to the transition from the $v' = 2$ level of the B³Σ_u⁻ state of oxygen molecules to the $v'' = 5-11$ level of the X³Σ_g⁻ state for both ¹⁴N¹⁶O₂ and ¹⁴N¹⁸O₂. Herman *et al.*¹² observed the emission of the Schumann-Runge band (B³Σ_u⁻ – X³Σ_g⁻) in a high-frequency discharge through flowing oxygen at atmospheric pressure and analyzed the vibrational and rotational bands up to 570 nm. The excitation spectrum shown in Figure 2 is in agreement with their observed emission, terminating to the high vibrational levels of the X³Σ_g⁻ state. It is concluded that the highly

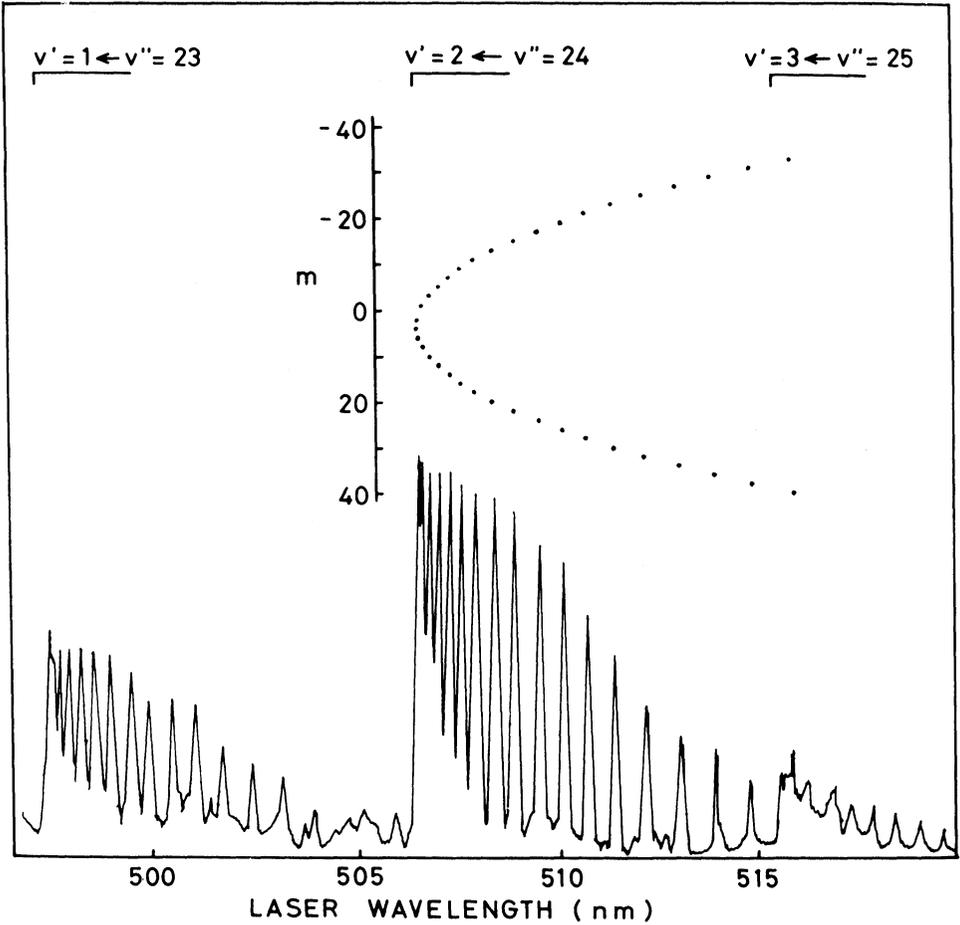


FIGURE 2 Excitation spectrum of the UV emission when NO₂ (P = 40 torr) was irradiated with the flash-pumped dye laser. The lines were identical with those of the Schumann-Runge emission ($B^3\Sigma_u^- - X^3\Sigma_g^-$) in the discharge arc of oxygen reported by Herman *et al.*¹² Assignments were taken from Ref. 12.

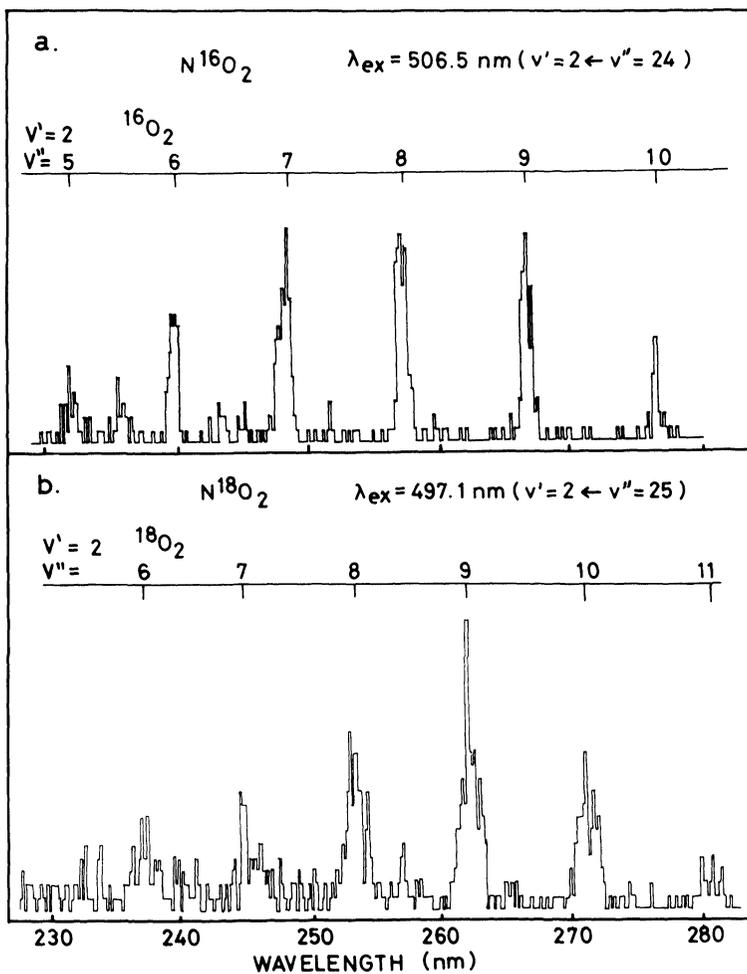


FIGURE 3 Emission spectra in UV wavelength region following irradiation of (a) $^{14}N^{16}O_2$ (40 torr) and (b) $^{14}N^{18}O_2$ (40 torr) with a visible laser. Spectroscopic constants in Ref. 13 and expression (1) in the text were used for vibrational band assignments.

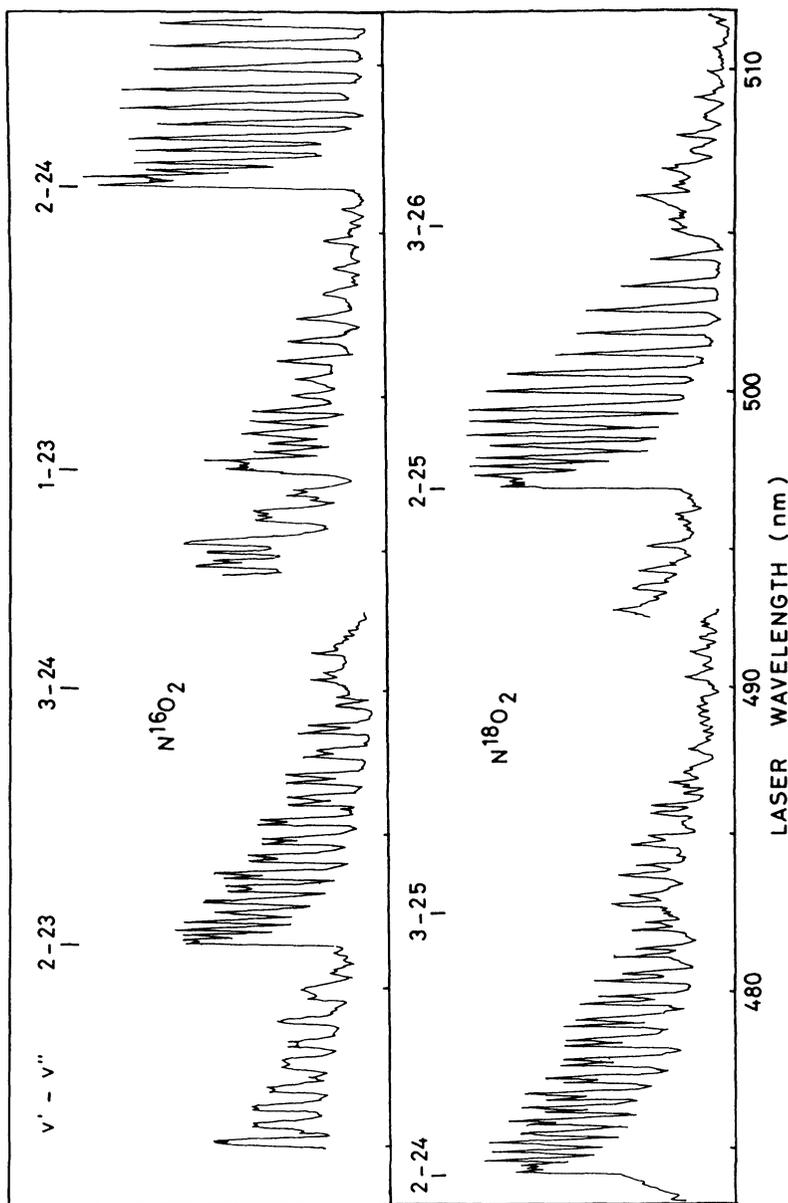


FIGURE 4 Excitation spectrum of the UV emission when (a) ¹⁴N¹⁶O₂ (P = 40 torr) and (b) ¹⁴N¹⁸O₂ (P = 40 torr) were irradiated with the flash-pumped dye laser. The lines were assigned to the Schumann-Runge system ($B^3\Sigma_u^- - X^3\Sigma_g^-$). Spectroscopic data in Ref. 13 and expression (1) in text were used for the vibrational band assignments.

vibrationally excited oxygen molecule in the electronically ground state is produced through the multiphoton excitation process of NO_2 and then absorbs one more photon. The resulting excited state of oxygen emits fluorescence in the UV wavelength region. It is worth noting that the excitation spectrum reflects predominantly the transition to the B state from the highly vibrationally excited O_2 in the X state. Though the ${}^3\Sigma_u^- - {}^3\Sigma_g^-$ transition accompanies six branches (three R- and three P-branches), no spin triplet structure is resolved within the bandwidth (4 cm^{-1}) of the laser. Since the nuclear spin of oxygen is zero, lines with even N value are all missing. Table I lists the vibrational bands of the Schumann-Runge system in the excitation spectrum of the UV emission, which is observed with the visible laser focused on NO_2 vapor. In the case of ${}^{14}\text{N}^{18}\text{O}_2$, the vibrational band was assigned by using the following expression,¹⁵

$$\nu^j = (\rho\omega_e - \rho^2\omega_e x_e)\nu - \rho^2\omega_e x_e \nu^2 \quad (1)$$

where ρ is $(\mu/\mu_i)^{1/2}$, with the vibrational constants for ${}^{16}\text{O}_2$ taken from Ref. 13. The progression with excitation to the $\nu' = 2$ level was most

TABLE I

Observed vibrational bands of the Schumann-Runge system of O_2 in the excitation spectra of the UV emission following irradiation of (a) ${}^{14}\text{N}^{16}\text{O}_2$ and (b) ${}^{14}\text{N}^{18}\text{O}_2$ by a visible laser

(a). ${}^{16}\text{O}_2$ (nm)			
$\nu'' \setminus \nu'$	1	2	3
22	473.1	458.8	
23	497.8	481.4	
24	524.4	506.5	490.2
25	553.0	532.9	515.5
26		561.7	542.0
(b). ${}^{18}\text{O}_2$ (nm)			
$\nu'' \setminus \nu'$	1	2	3
24		474.3	
25	512.9	497.1	482.5
26		521.6	505.3

intense, as shown in Figure 2. The band involving $v' = 4$ or more quanta of upper vibration was not observed in the excitation spectrum.

The excitation wavelengths of the emission spectra in Figure 3 were set at the bandheads of the $v' = 2 \leftarrow v'' = 24$ band for $^{14}\text{N}^{16}\text{O}_2$ and $v' = 2 \leftarrow v'' = 25$ for $^{14}\text{N}^{18}\text{O}_2$ in Figure 4. As can be seen in Figure 3, only the emission from the directly excited vibrational level in the $\text{B}^3\Sigma_u^-$ state was observed, that is, vibrational relaxation did not occur during its emission lifetime. Figure 5 shows the parts of the emission spectra, where the laser wavelengths were tuned onto the various rotational transitions of the $v' = 2 \leftarrow v'' = 24$ band system. Single rotational-vibrational level (SRVL) fluorescence spectra were obtained. It can be seen from Figure 5 that only the emission originated from the excited rotational level was observed, that is, the rotational relaxation did not occur even at the pressure of 40 torr.

The intensity of UV emission was examined as a function of the laser power. The power law exponents are 1.9 for 506.5 nm and 2.8 for 561.7 nm. These power indices are lower than expected because more than five photons are required energetically for the UV emission, as described later. The UV emission is, therefore, released through sequential multiphoton processes with saturation.

Inoue et al.¹⁶ observed the visible emission from NO_2^* formed in the photodissociation of N_2O_4 with irradiation of the near UV laser light. At room temperature N_2O_4 equilibrates with NO_2 , while at 463 K the fraction of N_2O_4 is less than 0.001%. The participation of N_2O_4 in this multiphoton process was examined by comparing the intensity of the UV emission at room temperature and 463 K. As a result, the intensity was very little dependent on temperature, suggesting that N_2O_4 was not concerned with the UV emission.

The influence of the incident light polarization on the rate of the photon absorption process was also investigated. The polarization effects on multiphoton absorption provide information about the symmetry of the states concerned with the simultaneous multiphoton absorption.¹⁷⁻²⁰ In this study the UV emission intensity was independent of the polarization of the laser light. The ratio of the absorptivity for the corotating circularly polarized laser light to that of the parallel linearly polarized light was close to unity. In the multiphoton process of NO_2 this result should suggest that the simultaneous multiphoton process is not included in the excitation process.

When the nitrogen-pumped dye laser (time width: 5–6 ns) was used instead of the flash-pumped dye laser (time width $\sim 0.8 \mu\text{s}$), a similar excitation spectrum was obtained, which is shown in Figure 6.

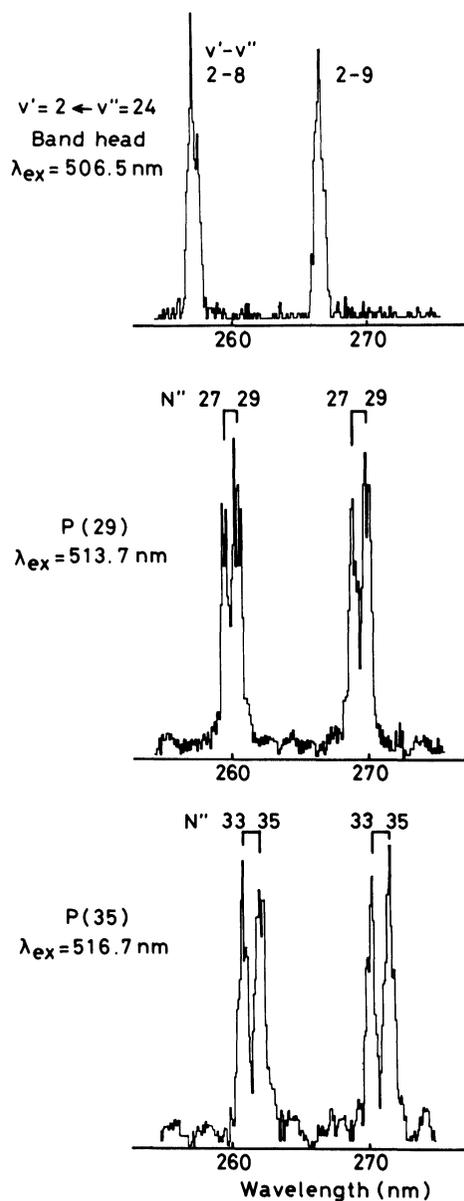


FIGURE 5 Single rotational level fluorescence spectra of Schumann-Runge system of $^{16}\text{O}_2$ following irradiation of $^{14}\text{N}^{16}\text{O}_2$ with a visible laser. The pressure of NO_2 was 40 torr. The excitation wavelengths and rotational lines are shown on the left.

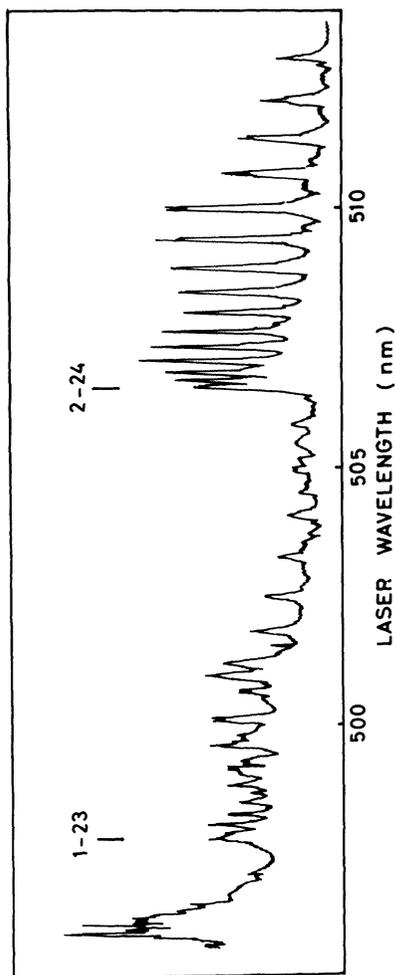


FIGURE 6 Excitation spectra of the UV emission when a nitrogen-pumped dye laser (time width: 5 ns) was used instead of the flash-pumped dye laser (time width: 800 ns). The pressure of $^{14}\text{N}^{16}\text{O}_2$ was 40 torr.

DISCUSSION

Laser-induced fluorescence of the Schumann-Runge system of O₂

Thus far the emission of the Schumann-Runge system has been predominantly observed in the discharge arc of oxygen.¹¹⁻¹³ It is difficult to excite the thermal O₂ molecule optically to the low vibrational levels of the B state due to the large difference of the equilibrium nuclear distance between the B and X states of O₂. Recently Shibuya and Stuhl¹⁴ observed resonance fluorescence from the $v' = 4$ level of the B state using a 193 nm ArF excimer laser. They observed no vibrational relaxation in the pressure region of up to 760 torr. In the present study, since the oxygen molecules in the $v'' = 22-26$ levels of the X state are produced, they can be efficiently excited to the $v' = 1-3$ levels of the B state by the dye laser due to larger Franck-Condon (F-C) factors than those from low vibrational levels in the X state. According to the calculation by Ory *et al.*,²¹ the F-C factors of the Schumann-Runge band system for the transition from $v'' = 0$ are less than 5×10^{-5} , while those from $v'' = 22-25$ to $v' = 2$ are in the range of $10^{-2}-10^{-1}$. As can be seen in Figure 4, the vibrational bands terminating to the $v' = 2$ level were strong in the excitation spectrum. The spectral intensity depends on both the F-C factor and the fluorescence quantum yield. The emission from the $v' \geq 4$ levels in the B state could not be observed, which may be due to a small fluorescence quantum yield because of the fast predissociation. It can be seen in Figure 5 that neither vibrational nor rotational relaxation in the $v' = 2$ level in the B state occurs at the NO₂ pressure of 40 torr. This is reasonable because the linewidth of the $v' = 2$ level observed in the absorption spectrum⁹ was about 0.3 cm⁻¹ and its lifetime is estimated to be of the order of 10⁻¹¹ sec.

As shown in Figure 4, the structure of the excitation spectrum for the UV emission hardly reflects the production processes of the highly vibrationally excited O₂ from NO₂, but well reveals the excitation band structure of the B-X Schumann-Runge system of O₂. The excitation spectrum for the formation of the highly vibrationally excited O₂ could be concealed under the Schumann-Runge system by the saturation of the photoexcitation processes necessary to produce the excited O₂.

Morrison *et al.*⁷ have reported the MPI spectrum of NO₂ in the region of 520 to 420 nm. Above 500 nm, many narrow lines rose out of the

background in the MPI spectrum of NO₂ and were attributed to the resonance enhancement due to the 3sσ Rydberg state of NO₂ at the level of the third photon. Below 490 nm they observed the MPI spectrum of nascent NO resulting from the two-photon dissociation of NO₂. No notable resemblance was found between their MPI spectrum and our excitation spectrum of the UV emission in the same wavelength region. This indicates that the production of the highly excited O₂ undergoes a different multiphoton excitation mechanism from that of multiphoton ionization.

Production mechanism of highly vibrationally excited O₂

The production process of the highly vibrationally excited O₂ molecule from NO₂ under the irradiation of the focused dye laser is possibly interpreted by the following two mechanisms. One is that NO₂ is excited to a high-lying electronic state through multiphoton processes and dissociates to the excited O₂ and N atom. The other is that the excited O₂ is produced by chemical reaction involving the oxygen atom as one of the dissociation products from NO₂ through multiphoton excitation.

The highest vibrational level of the observed O₂ molecule is $v'' = 26$, which corresponds to vibrational energy $E_{vib} = 32908 \text{ cm}^{-1}$ (94.0 kcal mol⁻¹). Figure 7 shows energy diagrams of NO₂ and O₂ with the laser wavelength of 561.7 nm (17803 cm⁻¹, 50.9 kcal mol⁻¹) tuned on the $v' = 2 - v'' = 26$ transition of the B-X system of O₂. The potential curves of O₂ are combined to the energy levels of NO₂ so that the lowest energy level of the ground state of O₂ is adjusted to the dissociation energy of NO₂ to N(⁴S) + O₂(X³Σ_g⁻).

The dissociation energies of NO₂ to various fragments are listed in Table II. Vacuum UV photodissociation experiments were performed by Welge²² and by Lenzi and Okabe.²³ They observed the production of A and B states of NO through the processes (G) and (H) listed in Table II. In the present study emission from electronically excited NO could not be observed. Uselman and Lee^{24,25} investigated wavelength dependence of the production of O(³P) and O(¹D) near the threshold of the photodissociation processes (A) and (C), respectively. In the absorption spectrum of the 2²B₂ - \tilde{X}^2 A₁ system of NO₂, line broadening starts at 249.1 nm, which is longer than the wavelength corresponding to the threshold energy of the process (C).²⁶ It was attributed to the dissociation process (A) and/or (B),²⁵ although the experimental evidence of the process (B) is not available. Not only the process (B) but also electronic excitation of O₂ to the A or

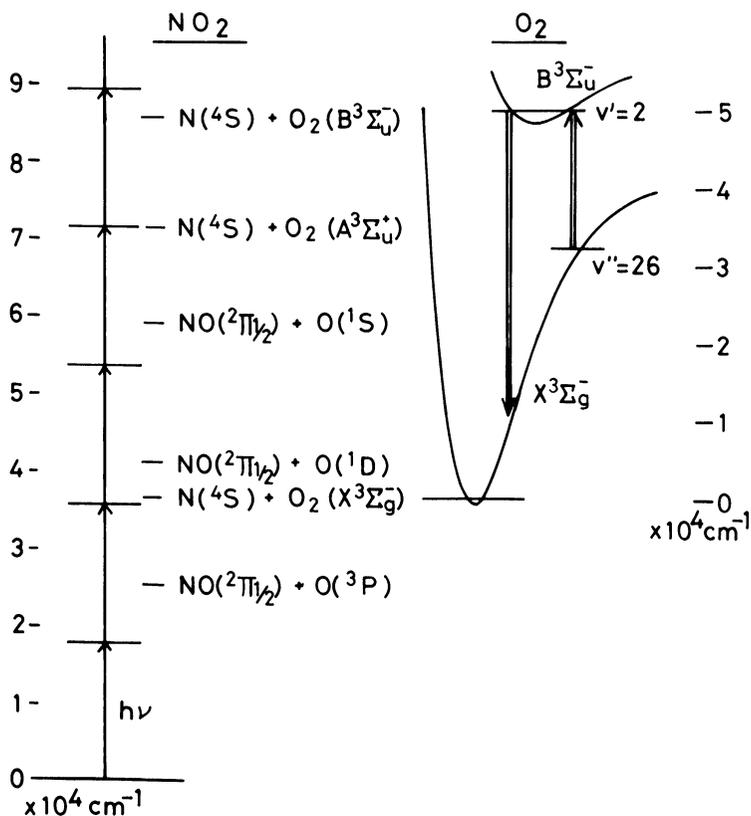


FIGURE 7 Energy diagram of NO_2 and O_2 molecules. Excitation energy was set at 561.7 nm (17800 cm^{-1}), which corresponded to the $v' = 2 \leftarrow v'' = 26$ band of the Schumann-Runge system of O_2 .

B state through the process (E) or (F) followed by the collisional transfer to the highly excited vibrational state of the X state is highly possible. In these mechanisms more than four photons are energetically required to produce the excited O_2 , as illustrated in Figure 7. If the above multiphoton processes occur, the molecular energy exceeds the dissociation energy of the process (A) in the second photoexcitation step. The subsequent absorption of a photon may take place before the dissociation or the multiphoton excitation may proceed *via* a non-dissociating state. Since the nuclear distance of oxygen atoms in the excited NO_2 is considerably dif-

TABLE II
Dissociation energies of NO₂ into various fragments

Reactions	Threshold energies (cm ⁻¹)
(A) NO ₂ → O(³ P) + NO(² Π _{1/2})	25105 ± 10 ^a
(B) → N(⁴ S) + O ₂ (X ³ Σ _g ⁻)	36320 ± 60 ^a
(C) → O(¹ D) + NO(X ² Π _{1/2})	40973 ± 10 ^a
(D) → O(¹ S) + NO(X ² Π _{1/2})	58893 ^b
(E) → N(⁴ S) + O ₂ (A ³ Σ _u ⁺)	71327 ^b
(F) → N(⁴ S) + O ₂ (B ³ Σ _u ⁻)	85678 ^b
(G) → O(³ P) + NO(A ² Σ ⁺)	69305 ^b
(H) → O(³ P) + NO(B ² Π)	70587 ^b

^aTaken from Ref. 29.

^bCalculated using values in Refs. 29 and 30.

ferent from that in the O₂ molecule, it is probable that the O₂ molecule dissociated from the excited NO₂ is highly vibrationally excited.

The alternative mechanism is that the excited O₂ is produced by chemical reaction during the laser irradiation. Since the vibrationally excited O₂ absorbs one more photon and then emits fluorescence in the UV wavelength region, the chemical reaction concerned must take place within the time width of the laser which is 5–6 ns in the case of the nitrogen-pumped dye laser. Zavelovich *et al.*²⁷ reported that NO in the excited D (v = 1, 5) and E (v = 0) states is generated from N₂O during irradiation with a 193 nm excimer laser in three sequential steps involving photodissociation, chemical reaction, and photoexcitation. Even if the reaction between one-photon excited NO₂ molecules produces an excited O₂ molecule, a high vibrational state such as v'' = 26 is not available. Therefore, the multiphoton dissociation is necessarily followed by chemical reaction involving the oxygen atom.

The oxygen atom formed by multiphoton dissociation of NO₂ should be a precursor of the excited O₂ molecule. The following multiphoton dissociation processes provide oxygen atoms as can be seen in Figure 7.

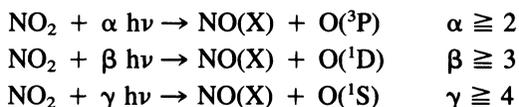


TABLE III

Heat of reaction and rate constant between the oxygen atom in the various states and NO₂

Reactions	ΔH (kcal mol ⁻¹)	Rate Const. (cm ³ molecule ⁻¹ sec ⁻¹)
(I) O(³ P) + NO ₂ → NO + O ₂	-46.1	9.3 × 10 ^{-12a}
(J) O(¹ D) + NO ₂ → (NO + O ₂)	-91.5	(2.8 ± 0.5) × 10 ^{-10b}
(K) O(¹ S) + NO ₂ → (NO + O ₂)	-142.7	5 × 10 ^{-10c}

^aFrom Ref. 31.^bFrom Ref. 32.^cFrom Ref. 28. Quenching rate constant of O(¹S - ¹D) emission by NO₂.

In the MPI experiments the spectrum of nascent NO resulting from the two-photon dissociation of NO₂ was observed,⁷ and the pressure and wavelength dependence of the spectrum was explained by the partitioning between competing photodissociation channels producing NO(X²II) + O(³P) and NO(X²II) + O(¹D). The reactions of these O atoms with NO₂ which may take place are listed in Table III. The highest vibrational energy of the observed excited O₂ was 32908 cm⁻¹, so that the excess energy of the reaction must exceed 94.0 kcal mol⁻¹. Only the reaction (K) in Table III satisfies the energetic requirement. The rate constant of the reaction (K) in Table III shows the quenching rate constant of the atomic emission from O(¹S), which was reported by Filseth *et al.*²⁸

Since the decay rate of O(¹S) is estimated from this rate constant to be 10 ns at 10 torr of NO₂, it is not impossible for this reaction to occur within the pulse width of 5 ns of the nitrogen-pumped dye laser. However, it is more likely that the electronic relaxation predominates over chemical reaction in the quenching of O(¹S). Moreover, even if the reaction takes place, it is improbable that most of the excess energy in the reaction (O(¹S) + NO₂) is partitioned to the vibrational energy of the O₂ molecule produced. Therefore the O₂ molecule would not be formed efficiently in the highly excited vibrational state through chemical reactions. The former mechanism, that is, the molecular dissociation to the highly vibrationally excited O₂ via a multiphoton excitation of NO₂ seems to be preferable for the interpretation of present experimental results.

CONCLUSION

When NO₂ is irradiated with the focused dye laser in the wavelength region of 470–580 nm, the oxygen molecules in the $v'' = 22$ –26 levels of the $X^3\Sigma_g^-$ state are produced. Then they are efficiently excited to the $v' = 1$ –3 levels of the $B^3\Sigma_u^-$ state of oxygen with the aid of the visible laser radiation, owing to their large F-C factors. The resulting oxygen molecules in the B state emit the fluorescence in the UV region. The highly vibrationally excited oxygen molecules are generated through molecular elimination from the high-lying electronic state of the NO₂ molecule, which is excited by the multiphoton process.

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References

1. D. M. Friedrich and W. M. McClain, *Ann. Rev. Phys. Chem.* **31**, 559 (1980).
2. P. M. Johnson, *Acc. Chem. Res.* **13**, 20 (1980).
3. For example, C. Fotakis, *Chem. Phys. Letters* **82**, 68 (1981); K. C. Kim, M. Reisfeld, and D. Seits, *J. Chem. Phys.* **73**, 5605 (1980); W. W. Rice, F. B. Wampler, R. C. Oldenberg, W. B. Lewis, J. J. Tiee, and R. T. Pack, *J. Chem. Phys.* **72**, 2948 (1980).
4. D. K. Hsu, D. L. Monts, and R. N. Zare, *Spectral Atlas of Nitrogen Dioxide* (Academic, New York, 1978).
5. G. D. Gillispie, A. U. Khan, A. C. Wahl, R. P. Hosteny, and M. Krauss, *J. Chem. Phys.* **63**, 3425 (1975); G. D. Gillispie and A. U. Khan, *J. Chem. Phys.* **65**, 1624 (1976).
6. J. Gerstmayr, P. Harteck, and R. R. Reeves, *J. Phys. Chem.* **76**, 474 (1972); D. Hakala, P. Harteck, and R. R. Reeves, *J. Phys. Chem.* **78**, 1583 (1974); D. Hakala and R. R. Reeves, *Chem. Phys. Letters* **38**, 510 (1976).
7. R. J. S. Morrison, B. H. Rockney, and E. R. Grant, *J. Chem. Phys.* **75**, 2643 (1981).
8. G. Radhakrishnan, D. Ng, and R. C. Estler, *Chem. Phys. Letters* **84**, 260 (1981).
9. M. Ackerman and F. Biaume, *J. Mol. Spectrosc.* **35**, 73 (1970); R. D. Hudson and S. H. Mahle, *J. Geophys. Res.* **77**, 2902 (1972).
10. P. S. Julienne and M. Krauss, *J. Mol. Spectrosc.* **56**, 270 (1975).
11. M. W. Feast, *Proc. Phys. Soc. A.* **63**, 36 (1950).
12. P. L. Herman, M. R. Herman and D. Rakotoarjimy, *J. Phys. Radium* **22**, 1 (1961).

13. D. M. Greek and R. W. Nicholls, *Proc. R. Soc. Lond. A*, **341**, 517 (1975).
14. K. Shibuya and F. Stuhl, *J. Chem. Phys.* **76**, 1184 (1982).
15. G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (Van Nostrand, New York, 1950), p. 143.
16. G. Inoue, Y. Nakata, Y. Usui, H. Akimoto, and M. Okuda, *J. Chem. Phys.* **70**, 3689 (1979).
17. K. Kasatani, Y. Tanaka, K. Shibuya, M. Kawasaki, K. Obi, H. Sato, and I. Tanaka, *J. Chem. Phys.* **74**, 895 (1981).
18. W. M. McClain and R. A. Harris, *Excited States Vol. 3* (Academic, New York, 1977) pp. 1-56.
19. D. H. Parker, R. Pandolfi, P. R. Stannard, and M. A. El-Sayed, *Chem. Phys.* **45**, 27 (1980).
20. K. Kasatani, M. Kawasaki, H. Sato, Y. Murasawa, K. Obi, and I. Tanaka, *J. Chem. Phys.* **74**, 3164 (1981).
21. H. A. Ory and A. P. Gittlemann, *Astrophys. J.* **139**, 357 (1964).
22. K. H. Welge, *J. Chem. Phys.* **45**, 1113 (1966).
23. M. Lenzi and H. Okabe, *Ber. Bunsenges. Phys. Chem.* **72**, 168 (1968).
24. W. M. Uselman and E. K. C. Lee, *J. Chem. Phys.* **64**, 3457 (1976).
25. W. M. Uselman and E. K. C. Lee, *J. Chem. Phys.* **65**, 1948 (1976).
26. K.-E. J. Hallin and A. J. Merer, *Can. J. Phys.* **54**, 1157 (1976).
27. J. Zavelovich, M. Rothschild, W. Gornik, and C. K. Rhodes, *J. Chem. Phys.* **74**, 6787 (1981).
28. S. V. Filseth, F. Stuhl, and K. H. Welge, *J. Chem. Phys.* **52**, 239 (1970).
29. A. E. Douglas and K. P. Huber, *Can. J. Phys.* **43**, 74 (1965).
30. K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van Nostrand, New York, 1979).
31. D. L. Baulch, R. A. Cox, R. F. Hampson Jr, J. A. Kerr, J. Troe, and R. T. Watson, *J. Phys. Chem. Ref. Data* **9**, 295 (1980).
32. R. F. Hampson and D. Garvin, *Natl. Bur. Stand. Tech. Note* **866**, (1975).