Journal of Photochemistry, 17 (1981) 487–494

SEQUENTIAL MULTIPHOTON EXCITATION OF SIMPLE MOLECULES*

IKUZO TANAKA

Department of Chemistry, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo (Japan)

Summary

Iodine vapour was irradiated by a focused dye laser pulse in the range 420 - 510 nm. The effect of polarization of the laser light indicates that the simultaneous multiphoton excitation process becomes gradually dominant at $\lambda_{ex} \leqq$ 450 nm, whereas the sequential excitation proceeds through dissociative states up to 450 nm, above the dissociation limit of the B state.

The emission in the UV region was observed by excitation of NO_2 with a focused tunable dye laser. The UV emission was attributed to the Schumann–Runge bands resulting from laser excitation of the highly vibrationally excited O_2 (v'' = 22 - 26) which was produced by multiphoton excitation of NO_2.

1. Introduction

One of the most prominent characteristics of visible multiphoton absorption is the generation of visible and UV emission from new excited states of parent molecules or fragments after intense laser irradiation in the visible region.

Multiphoton excitation processes can be classified into two types: sequential excitation which proceeds through real intermediate states and simultaneous excitation which proceeds through virtual intermediate states.

First, I shall discuss the case of excitation at the intermediate level, just above the dissociation limit. By measuring the excitation spectra, the emission spectra and the effect of the polarization of the incident laser radiation on the absorptivity, it is possible to determine which of the excitation processes, sequential multiphoton excitation or simultaneous multiphoton excitation, is dominant. In order to investigate the role of the dissociative states as intermediate levels, iodine vapour was irradiated by laser radiation in the range 420 - 510 nm, because the dissociation limit of the B state occurs at 498.9 nm.

Secondly, I wish to emphasize that 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 never previously been attempted using single-photon excitation.

Extensive studies have been performed on the visible and near-IR fluorescences and photodecompositions of electronically excited NO_2. Thus the UV

---

* Paper presented at the Xth International Conference on Photochemistry, Iraklion, Crete, Greece, September 6 - 12, 1981.

0047-2670/81/0000-0000/$02.50

emission caused by sequential multiphoton excitation of NO_2 was observed and analysed in detail.

2. Experimental details

The experimental set-up is similar to that described previously [1, 2]. The light sources used were a flash-pumped dye laser (0.8 μs; 10 mJ pulse^{-1}; 10 Hz; 0.1 nm bandwidth), a nitrogen-laser-pumped dye laser (Molectron DL 200) and a delayed two-pulse excitation system generated by nitrogen-laser-pumped dye lasers.

To determine the polarization effect of the laser radiation, the combination of a rotatable double Fresnel rhomb and a single Fresnel rhomb was used. This combination gave linearly or circularly polarized light depending on the polarization angle of the incident light beam [3].

The laser pulses were focused with a lens into a quartz cell. The signal intensity was measured with a gated integrator (Ortec 9301/9302/9815/9820 or PAR 162/164) with a photomultiplier (HTV R585, HTV R166, HTV IP28 or HTV R636) and the laser power was measured with a PIN photodiode (HTV S1188). The monochromators were JT DH-20A, JYH-20, Nikon 250 and Nikon 500.

3. Results and discussion

3.1. I_2

In a previous paper [2] experiments are reported for iodine vapour irradiated by flash-pumped dye laser radiation in the range 450 - 610 nm. When the energy of the laser radiation was above the dissociation limit of the B state at 498.9 nm, the emission intensity decreased drastically but was still observed. No effect of polarization of the laser radiation (circular or linear) was observed in the range 450 - 610 nm, indicating that the multiphoton excitation is sequential excitation through dissociative states.

In the present experiment iodine vapour was irradiated by the nitrogen-pumped dye laser in the range 420 - 490 nm, above the dissociation limit of the B state. When the energy of the laser radiation was above the dissociation limit, the emission intensity decreased drastically; however, the UV emission could be measured quantitatively in the region 250 - 320 nm. The intensity of emission around the 290 nm band decreased with decreasing excitation wavelength (down to 450 nm) but increased again with shorter excitation wavelengths. The 290 nm band appeared also in the discharge of I_2 diluted with argon, and it was assigned to a transition originating from an excited state near $T_e \approx 47\,000$ cm^{-1}, the electronic designation of which was unknown [4]. However, since the intensity of the 290 nm band is strongest in UV emission, the power dependence of the emission intensity and the polarization ratio of the laser radiation were investigated by measuring the 290 nm band.

The power dependence of the emission intensity gave $n = 2$ for $\lambda_{ex} = 425$ nm and $\lambda_{ex} = 435$ nm where n is the power index in $I_{ex} \propto I_L^n$. The saturation effect for the intermediate level was not observed in these cases.

The influence of the incident light polarization on the rate of photon absorption was studied. The polarization ratios observed for iodine vapour are presented in Table 1 for various excitation wavelengths.

TABLE 1

The polarization ratio Ω of the absorptivity for two co-rotating circularly polarized photons to the absorptivity for two parallel linearly polarized photons

λ_{ex} (nm)	Ω	
	35 °C	*88 °C*
420	0.89	0.89
425	0.78	
435	0.67	
440	0.74	0.82
445	0.75	
470	0.98	
480	1.02	
490	1.12	

The value of Ω was found to be 1.0 within the limits of experimental error at a laser wavelength longer than 470 nm. This value is coincident with that obtained in the range 450 - 510 nm both below and above the dissociation limit of the B state using the flash-pumped dye laser as described previously [2]. In contrast, the value of Ω was less than 1.0 at laser wavelengths shorter than 450 nm.

The sequential two-photon excitation is given by the product of two one-photon absorptions. The one-photon absorption coefficient $\langle\varepsilon\rangle$ averaged over all orientations is expressed by $\langle\varepsilon\rangle \propto \frac{1}{3}(\hat{\lambda}\cdot\hat{\lambda}^*)(\hat{\mu}_{of}\cdot\hat{\mu}_{of}^*)$. Since $\hat{\lambda}\cdot\hat{\lambda}^* = 1$ for linear and circular polarizations, $\langle\varepsilon\rangle$ is independent of polarization. The sequential two-photon absorption is also independent of polarization. The observed values of the polarization ratio were close to unity at excitation wavelengths longer than 450 nm. This experimental result indicates that the excitation process in this region must be a sequential multiphoton absorption.

In addition to the above-mentioned sequential two-photon excitation, simultaneous two-photon excitation can be another plausible mechanism. The polarization ratio Ω in simultaneous two-photon excitation is expressed as follows [5]:

$$\Omega = \frac{\langle\delta_{cc}\rangle}{\langle\delta_{ll}\rangle} = \frac{-2\delta_F + 6\delta_G}{2\delta_F + 4\delta_G}$$

where $\langle\delta_{cc}\rangle$ and $\langle\delta_{ll}\rangle$ are the simultaneous two-photon absorptivities averaged over all orientations for co-rotatory circularly polarized light and parallel linearly polarized light respectively. δ_F and δ_G refer to specific sums of squares of the tensor components. Since the polarization ratios are less than 1.0 at excitation wavelengths shorter than 450 nm, δ_F should not be zero, as would be expected for totally symmetric upper states Σ^+ in simultaneous two-photon excitation.

Figure 1 shows the potential curves and absorption spectrum of I_2 [6, 7] from which the ratio $P(^1\Pi/\mathrm{B}\ ^3\Pi)$ of absorption probabilities from X $^1\Sigma_g{}^+$ to $^1\Pi$ and B $^3\Pi$ was determined. The $^1\Pi$ state in fact makes a larger contribution to the pure continuum absorption than does B $^3\Pi$, and the extinction coefficient of the continuum absorption decreases rapidly with decreasing wavelength. From these experimental results it can be concluded that the simultaneous multiphoton excitation process gradually becomes dominant at $\lambda_{ex} \leqq 450$ nm.

For Cl_2, focused laser irradiation in the range 481 - 514 nm gave rise to UV emission by multiphoton excitation through the discrete B $^3\Pi$ state. All levels with $v' \leqslant 13$ of Cl_2(B) are known to predissociate strongly owing to the repulsive state and to converge to two ground state $Cl(^2P_{3/2})$ atoms [8]. The UV emission excited above this predissociation limit ($D_0{}^0 \approx 20\ 000$ cm^{-1}) showed the band around 260 nm predominantly, while excitation below the predissociation limit changed the emission profile drastically with the appearance of emission at longer wavelengths up to 310 nm. Through the sequential multiphoton excitation process, the Franck–Condon factor may become favourable for transition to another emitting state for excitation below the predissociation limit.

3.2. NO_2

Extensive studies have been performed on the fluorescence and quenching of electronically excited NO_2 [9, 10]. The excitation of NO_2 at a wavelength longer than 398 nm yields the well-known visible and near-IR emissions, but no emission has been reported on excitation at a wavelength shorter than 398 nm because of dissociation [11, 12].

The emission in the UV region was observed when NO_2 at relatively high pressure or a mixture of NO_2 (0.5 - 10 Torr) and argon at high pressure was irradiated with a flash-pumped dye laser. We never observed the same emission and excitation spectra using NO, N_2O, N_2O_4, N_2 or O_2 under the same conditions instead of NO_2.

We have now confirmed the observation that the highly vibrationally excited O_2 ($v'' = 22$ - 26) is surprisingly produced by multiphoton excitation of NO_2, and the emission is attributed to the Schumann–Runge bands from B $^3\Sigma_u{}^-$ ($v' = 1, 2, 3$) formed by laser excitation of the highly vibrationally excited O_2.

Figure 2 shows a part of the laser excitation spectrum of the UV emission when the flash-pumped dye laser was focused into a cell containing 10 Torr of NO_2 and 100 Torr of argon. Although the excitation spectrum of the visible–near-IR emission of NO_2 was much congested, this spectrum had very distinct band heads and structures. The excitation spectrum showed no isotope effect between $^{14}N^{16}O_2$ and $^{15}N^{16}O_2$, while distinct differences were observed between the spectra of $^{14}N^{16}O_2$ and $^{14}N^{18}O_2$.

We found that the excitation spectrum is entirely in agreement with the analysis of the emission from the O_2 Schumann–Runge system in a high voltage arc reported by Herman *et al.* [13]. Since the nuclear spin of oxygen is zero, all the even *N* value rotational lines are missing. At the laser bandwidth used here

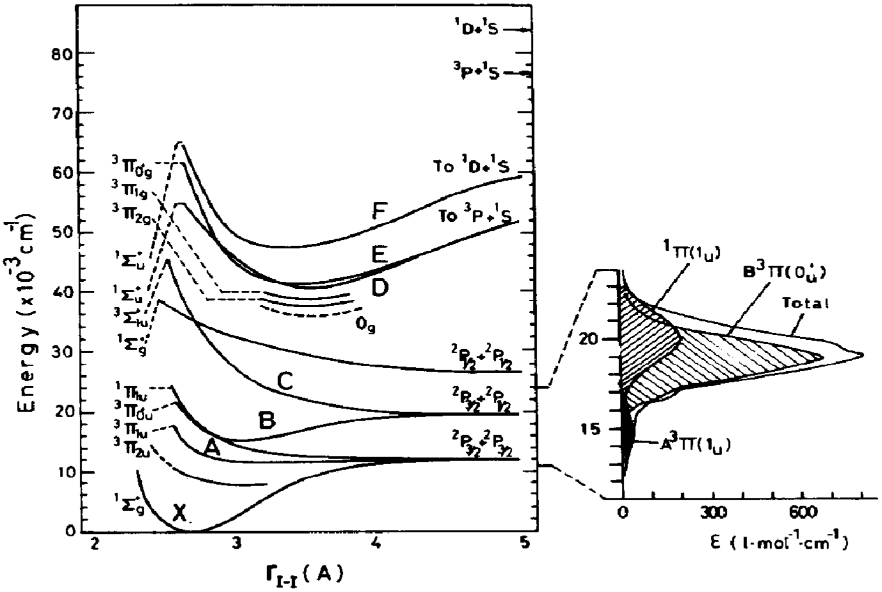


Fig. 1. The potential curves and absorption spectrum of I_2.

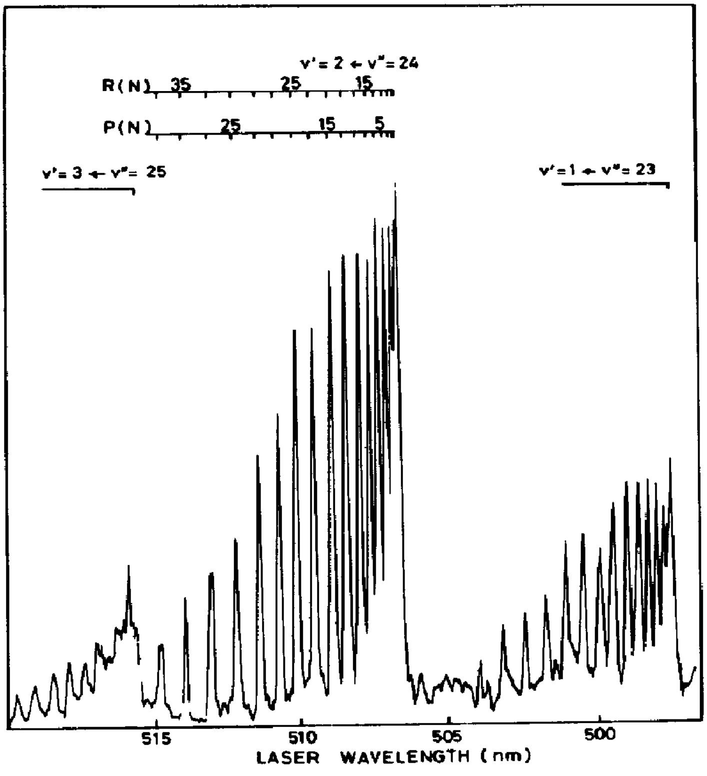
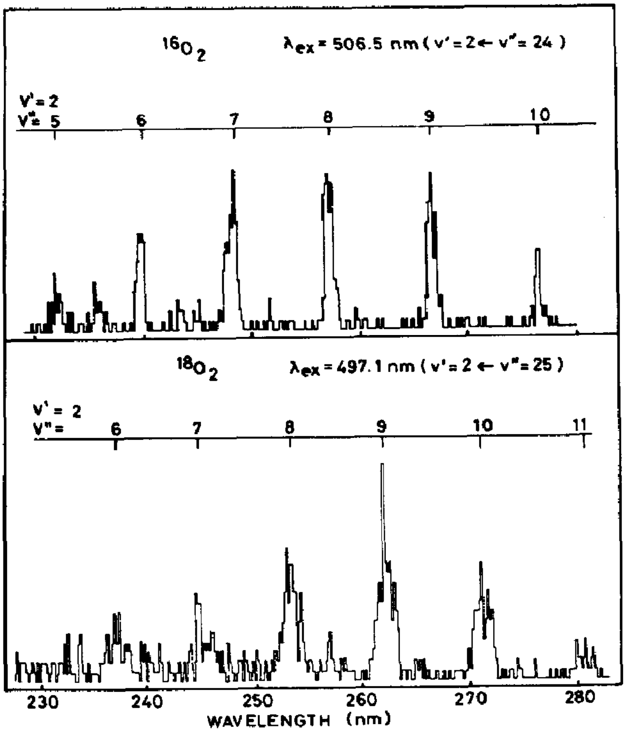


Fig. 2. The laser excitation spectrum of 40 Torr of NO_2 and 100 Torr of argon for UV emission.

TABLE 2
All the vibronic bands of the Schumann–Runge system observed in the multiphoton excitation of $^{14}N^{16}O_2$ and $^{14}N^{18}O_2$

v''	$v'=1$	$v'=2$	$v'=3$
$^{16}O_2$			
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
$^{18}O_2$			
24		474.3	
25	512.9	497.1	482.5
26		521.6	505.3



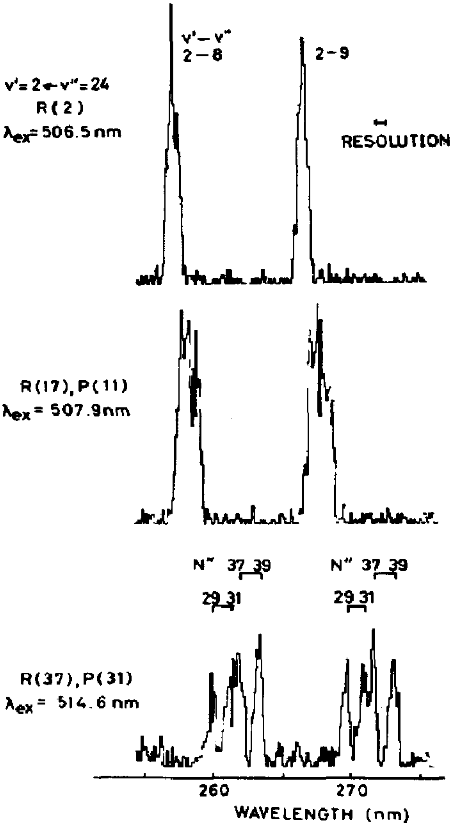


Fig. 3. Emission spectra caused by the multiphoton excitation of $^{14}N^{16}O_2$ and $^{14}N^{18}O_2$. These bands are the same as the Schumann–Runge bands of $^{16}O_2$ and $^{18}O_2$.

Fig. 4. Emission spectra from excitation of individual rotational lines of the $v' = 2 \leftarrow v'' = 24$ band shown in Fig. 2.

the spin triplets are not resolved and in the (2, 24) band the P(*N*) and R(*N*+6) lines overlap.

Two points are worth noting in this spectrum: (1) the extremely high vibrational states of O_2 ($E_{\mathrm{vib}} \geqq 30\ 000\ \mathrm{cm}^{-1}$) produced by the multiphoton process on NO_2; (2) the fact that the excitation spectra are quite different from those of the visible–IR emission of NO_2. The spectra seem to reflect only the final step, *i.e.* the laser excitation process on the highly vibrational states of O_2; nevertheless at least four photons are required to produce the highly vibrationally excited O_2 ($v'' = 22 - 26$) from NO_2. All the vibronic bands of the Schumann–Runge system observed in the multiphoton excitation of $^{14}N^{16}O_2$ and $^{14}N^{18}O_2$ are recorded in Table 2:

Figure 3 shows the emission spectrum of the O_2 Schumann–Runge bands caused by the multiphoton process on $^{14}N^{16}O_2$ and $^{14}N^{18}O_2$. The NO_2 pressures were 40 Torr.

Figure 4 also shows the emission spectrum when the individual rotational lines of the $v' = 2 \leftarrow v'' = 24$ band as shown in Fig. 2 are excited. Since the P(*N*) and R(*N*+6) lines overlap, two rotational states are simultaneously excited. However, as can be seen in Fig. 4, only the emission from the excited rotational levels is observed, *i.e.* rotational relaxation does not occur during the fluorescence lifetimes. This is reasonable because the lifetime of the $v' = 2$ level of the B $^3\Sigma_u^-$ state, estimated from the linewidth, is 2×10^{-11} s [14].

An energy diagram for the dissociation processes of NO_2 corresponding to the multiphoton excitation of 17 803 cm^{-1} (561.7 nm) and transitions involved in the production of the Schumann–Runge bands of O_2 is given in Fig. 5.

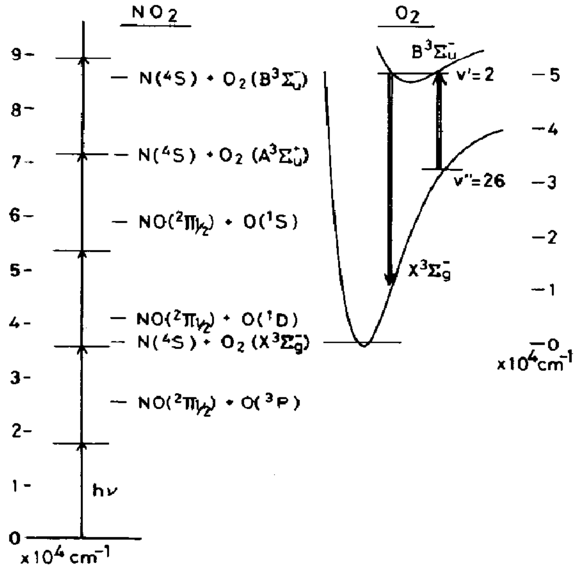


Fig. 5. A correlation energy diagram for multiphoton excitation of NO_2 and the production of O_2 in the B $^3\Sigma_u^-$ state.

The formation of O(^{3}P) and O(^{1}D) atoms cannot contribute to the Schumann–Runge bands because O_2 produced from the O(^{3}P or ^{1}D) + NO_2 reaction contains much less vibrational energy than 32 908 cm^{-1} for $v'' = 26$.

The reaction rate of O_2 formation from the O(^{1}S) + NO_2 reaction has not yet been measured except for the quenching rate of O(^{1}S) by NO_2 [15] so we cannot judge whether O(^{1}S) formation is important for producing the highly vibrationally excited O_2.

The direct formation of O_2(X $^3\Sigma_g^-$), O_2(A $^3\Sigma_u^+$) or O_2(B $^3\Sigma_u^-$) as a dissociation process of NO_2 by multiphoton excitation may play an important role in giving the Schumann–Runge emission. The threshold energy for the production of O_2(X) in the vibrational state $v'' = 26$ is almost equal to the energy of four photons of 17 803 cm^{-1}. Also we cannot neglect the possibility that the production of O_2(X) in a high vibrational state is due to the collision-induced internal conversion of O_2(A) or O_2(B).

References

1 M. Kawasaki, K. Tsukiyama, M. Kuwana, K. Obi and I. Tanaka, *Chem. Phys. Lett., 67* (1979) 365.
2 K. Kasatani, Y. Tanaka, K. Shibuya, M. Kawasaki, K. Obi, H. Sato and I. Tanaka, *J. Chem. Phys., 74* (1981) 895.
3 B. Rossi, *Optics,* Addison-Wesley, Reading, MA, 1965, p. 379.
4 K. Wieland, J. Tellinghuisen and A. Nobs, *J. Mol. Spectrosc., 41* (1972) 60.
A.L. Guy, K.S. Viswanathan, A. Sur and J. Tellinghuisen, *Chem. Phys. Lett., 73* (1980) 582.
5 W.M. McClain, *J. Chem. Phys., 55* (1971) 2789.
6 J.A. Coxon, *Mol. Spectrosc., 1* (1973) 191.
7 J. Tellinghuisen, *J. Chem. Phys., 58* (1973) 2821.
8 M.A.A. Clyne and I.S. McDermid, *J. Chem. Soc., Faraday Trans. II, 75* (1979) 1677.
9 D.L. Monts, B. Soep and R.N. Zare, *J. Mol. Spectrosc., 77* (1979) 402.
10 V.M. Donnelly, D.G. Keil and F. Kaufman, *J. Chem. Phys., 71* (1979) 659.
11 W.M. Uselman and E.K.C. Lee, *J. Chem. Phys., 64* (1976) 3457.
12 I.T.N. Jones and K.D. Bayes, *J. Chem. Phys., 59* (1976) 483b.
13 P.L. Herman, M.R. Herman and D. Rakotarijimy, *J. Phys. Radium, 22* (1961) 1.
14 R.D. Hudson and S.H. Mahle, *J. Geophys. Res., 77* (1972) 2902.
15 S.V. Filseth, F. Stuhl and K.H. Welge, *J. Chem. Phys., 52* (1970) 239.