

EMISSION AND RELAXATION OF ELECTRONICALLY EXCITED O₂ DOPED IN A LOW TEMPERATURE N₂ CRYSTAL

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Oxygen molecules doped in a low temperature N₂ crystal were irradiated at 240–260 nm. Two emission band systems were observed, one from the $v' = 0$ level of A' $^3\Delta_u$ state to X $^3\Sigma_g^-$ state, and the other, from the $v' = 0$ level of c' Σ_u^- state to a' Δ_g state, independent on the excitation wavelength. The latter emission grew together with the decay of the former emission at around the same rate after the pulsed laser excitation, which implies that the vibrational levels of c state lying below the $v' = 0$ level of $\Omega = 3$ of A' state are populated from the $v' = 0$ level of A' state, though some additional mechanism for populating the c state may exist. The rate was found to become larger with the increase of the crystal temperature. It was also found that the excitation spectrum obtained by monitoring the A'–X emission was the same as that obtained by the c–a emission. The progress of vibrational relaxation, coupling with the intersystem crossing between the Herzberg states, will be discussed.

KEY WORDS: Excited O₂, N₂ crystal, Emission spectroscopy, Low temperature spectroscopy, Relaxation dynamics, Photophysics

INTRODUCTION

Since the pioneering work by Schoen and Broida on the emission of O₂ in N₂ and rare gas matrices,¹ the electronic spectroscopy and relaxation dynamics of the low-lying A $^3\Sigma_u^+$, A $^3\Delta_u$, and c' Σ_u^- states of O₂ in low temperature solids have been studied extensively as reviewed in the feature article by Slinger and Cosby.² Goodman and Brus³ have measured the 190–240 nm excitation spectra of O₂ in solid N₂ and rare gases using laser excitation of specific levels, primarily in A' state, and have shown that vibrational relaxation within both singlet and triplet excited states is fast in N₂, Ar and Xe solids. The relaxation mechanism through the nesting vibronic levels of Herzberg electronic states at higher energies are, however, still not fully understood.

Goodman and Brus³ have observed the A'–X emission of $^{16}\text{O}_2$ and $^{16-18}\text{O}_2$, and the c–a emission of $^{18}\text{O}_2$ in solid N₂. Later, Rossetti and Brus⁴ extensively studied the cross relaxation (intersystem crossing) from A' state to c state in the case of $^{16-18}\text{O}_2$

in Ar and Kr matrices observing the A'-X and c-a emissions simultaneously. However, the c-a emission has not ever been detected in $^{16}\text{O}_2$ in N_2 solid. Thus the existence of the cross relaxation in the case of $^{16}\text{O}_2$ is not clear.

In the present paper, we observed for the first time the c-a emission of $^{16}\text{O}_2$ in addition to the A'-X transition in N_2 solids, which evidenced the existence of cross relaxation from A' state to c state. The excitation spectroscopy and the dispersed fluorescence study in 245–260 nm region did not show any dependence on the excitation energy, meaning of which will be discussed.

EXPERIMENTAL

A free-standing N_2 crystal containing a small concentration of O_2 (concentration range 0.7–1.0%) of a circular column structure of around 1 cm^3 was prepared according to the method of Schwentner and co-workers,⁵ using the same cryostat system which was previously employed in our laboratory.⁶ The purity of N_2 gas obtained commercially was more than 99.9999%. The required amount of O_2 was mixed to the gaseous N_2 in advance. The employed N_2 pressure in the cryostat at crystallization was 20–30 Torr and the crystallization rate was ca. $2.2 \times 10^{-3}\text{ mol min}^{-1}$.

The sample held at a given temperature (between 17 K and 35 K) was irradiated by a KrF excimer laser (pulse energy, 2.1–4.9 mJ pulse⁻¹/4 mm²; repetition rate, 10–15 Hz) or a dye laser (spectral width, 0.1 cm⁻¹; typical pulse energy, 0.01 mJ pulse⁻¹/1 mm²; repetition rate, 10–15 Hz) through a quartz window of the vacuum chamber. The resultant emission from the irradiated crystal was collected by quartz lenses and resolved by a monochromator (Nikon P-250) and detected by an appropriate photomultiplier (Hamamatsu Photonics R928, detection range: 220–800 nm). The output from the photomultiplier was treated appropriately, depending what kind of measurement was necessary, with a boxcar averager (EG&G 4121B) and/or a digital oscilloscope (Tektronix 2440).

We also measured the emission from liquid state N_2 containing O_2 . In these measurements, we used a high pressure cell of $1 \times 1 \times 1\text{ cm}^3$ size possessing four windows of quartz which was settled inside of the vacuum cryostat chamber.

RESULTS

Observation of Emission Spectrum At Several Different Temperatures

When the N_2 crystal containing a small concentration of O_2 was irradiated by a KrF laser or a dye laser in 245–260 nm region, two band systems were observed. At lower temperatures, the well known A'-X emission was observed. When the temperature was increased, the intensity of the A'-X transition gradually decreased. But keeping pace with this decrease, a new band system appeared and increased its intensity. On the basis of the vibrational spacing of the emission, and the wavelength values also, the band system was identified to be the $v' = 0$ progression of c-a transition of $^{16}\text{O}_2$.

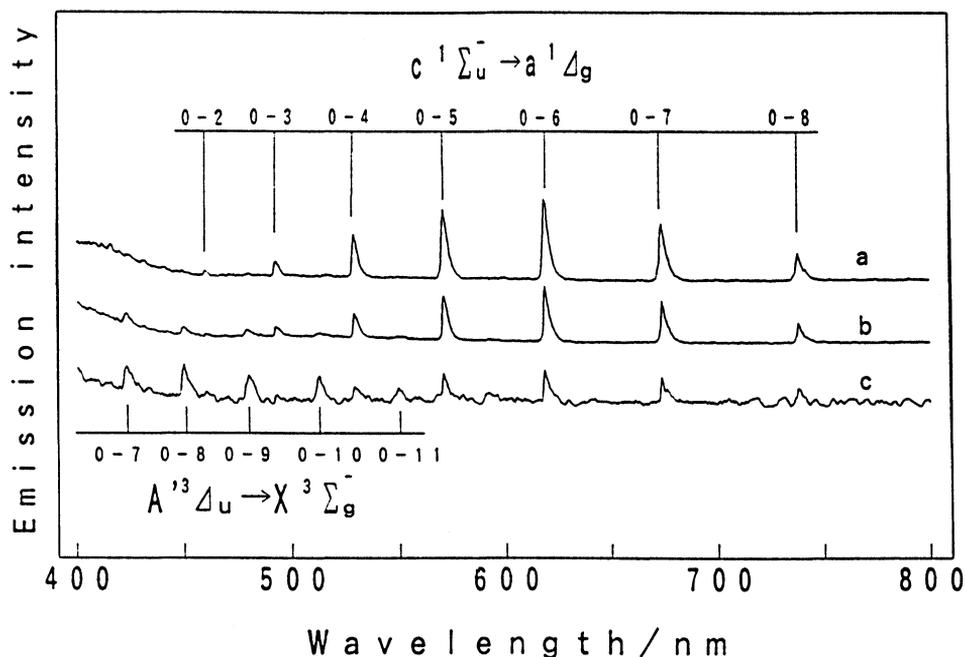


Figure 1 Emission spectra under different temperatures. Excitation, 248 nm; band path width, 0.3 nm; Boxcar gate, 0.1–1.1 μ s. Temperature: a, 35 K; b, 29 K; c, 24 K.

Figure 1 illustrates the emission at different temperatures. The A'–X and c–a systems were observed using a gate between 0.1 and 1.1 μ s. The c–a transition was observed even in the liquid state, though the intensity was relatively weak. Because this is the first case of the observation of the c–a transition in N₂ crystal, the values of the wavelength of the progression are tabulated in Table 1. The spectroscopic constants of a¹ Δ_g state obtained in terms of a Birge-Sponer plot are summarized in Table 2.

Table 1 Energy Difference in emission lines for the c¹ $\Sigma_u^-(v' = 0)$ – a¹ Δ_g Transition

| Band (v' , v'') | Gas ^{a)} $\nu(\text{cm}^{-1})$ | In N ₂ ^{b)} $\nu(\text{cm}^{-1})$ | $\Delta E^c)$ $\nu(\text{cm}^{-1})$ |
|--------------------------|--|--|--|
| (0, 2) | 21834 | 21715 | –119 |
| (0, 3) | 20403 | 20276 | –126 |
| (0, 4) | 18997 | 18885 | –112 |
| (0, 5) | 17619 | 17518 | –100 |
| (0, 6) | 16267 | 16170 | – 96 |
| (0, 7) | 14942 | 14844 | – 97 |
| (0, 8) | 13644 | 13555 | – 89 |
| (0, 9) | 12374 | 12285 | – 89 |

a) T. G. Slinger, J. Chem. Phys., **69**, 4779 (1978) and Ref. No. 2)

b) present work

c) energy (in N₂) – energy (gas phase)

Table 2 Spectroscopic Constants of $a^1\Delta_g$ State

| | Gas | Xe ³⁾ | Solid Ar ⁴⁾ | N ₂ ⁵⁾ |
|-----------------|-----------------------|------------------|---------------------------|------------------------------|
| T ₀₀ | 24782 ¹⁾ | 24552 | — | 24649 |
| ω_e | 1509.76 ²⁾ | 1507 | 1512.0 | 1507.5 |
| $\omega_e x_e$ | 13.065 ²⁾ | 13.8 | 13.67 | 13.4 |

unit cm⁻¹. T₀₀ is the energy difference between the $v = 0$ level of c and that of a state.

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- 5) present work

Excitation Spectrum And Dispersed Spectrum

Figure 2 shows the excitation spectra obtained by monitoring the $A'-X(0, 8)$ or $c-a(0, 6)$ transitions. The spectrum is completely the same for the different monitoring

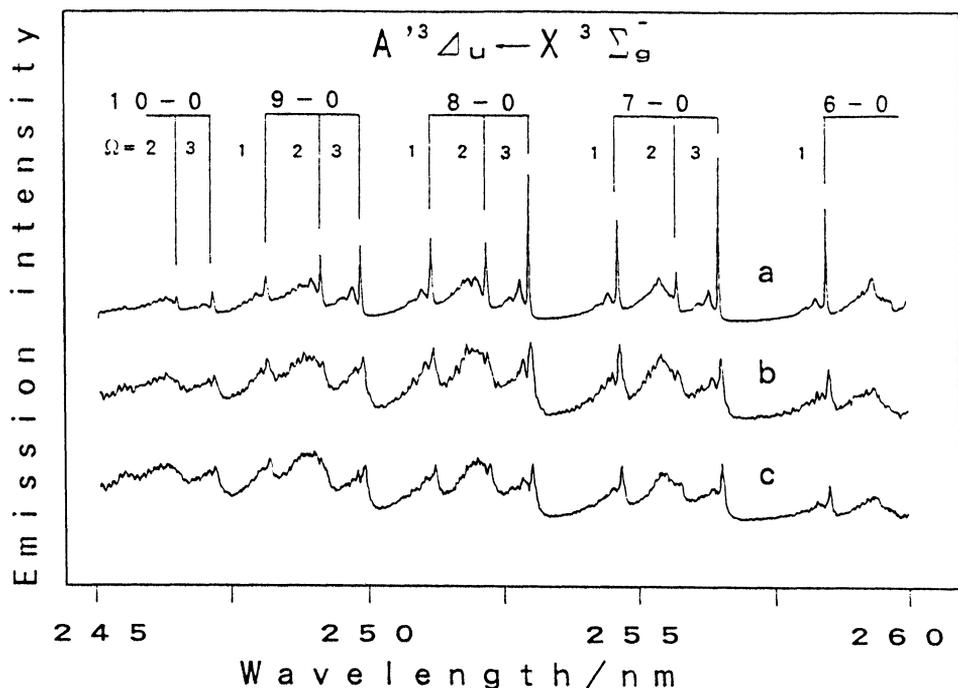


Figure 2 Excitation spectra obtained by monitoring different emissions. a, obtained by monitoring $A'-X(0, 8)$ emission at 14.9 K. b, obtained by monitoring $c-a(0, 6)$ emission at 22.5 K. c, obtained by monitoring $A'-X(0, 8)$ emission at 22.5 K. The assignment of the absorption $A'-X$ is designated in the figure.

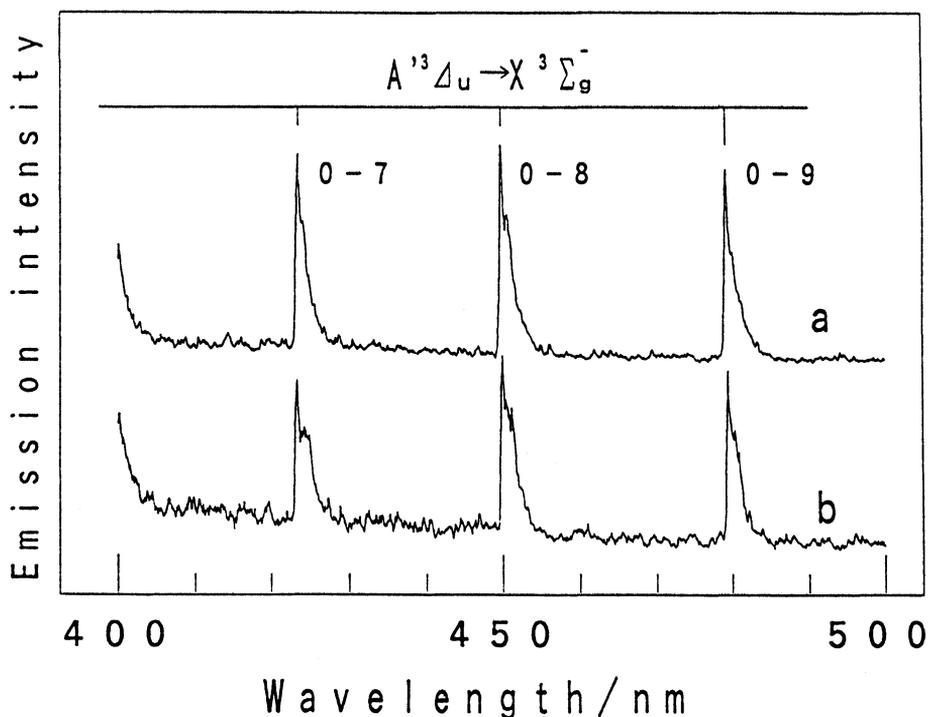


Figure 3 Dispersed spectra excited at different wavelength. Temperature, 14.9 K; band path width = 0.3 nm; Boxcar gate, 0–0.5 μ s. a, at 251.19 nm (not corrected for reference, but checked relatively to Fig. 2), excitation to $v = 8$, $\Omega = 2$, A' state. b, at 251.84 nm, excitation to $v = 7$, A state.

emissions. On the other hand, Figure 3 shows the comparison between the dispersed spectrum at two different excitation wavelengths. One of the excitation wavelengths corresponds to the excitation to the $v = 8$ level of $\Omega = 2$ of $A' \ ^3\Delta_u$ state and the other, to the $v = 7$ level of $A \ ^3\Sigma_u^+$ state, according to Goodman and Brus.³ The observed A' – X emission spectra seem not to be dependent on the excitation wavelength. These two informations imply that the history of the excitation is lost before the final emitting level is populated.

Relationship Between The A' – X And c – a Emissions

In order to check the correlation between the A' – X and c – a emissions, the dispersed emission spectra were measured with changing the gating time as shown in Figure 4. This figure clearly shows that the c – a transition makes its appearance with the decrease of the A' – X transition.

In order to conduct quantitative analysis, the time behaviors of the two emissions were measured at two different emission wavelengths; one corresponding to A' – X and the other, to c – a . The typical time profiles of the emission are shown in Figure 5. The decay of the A' – X emission has been found to obey a single exponential

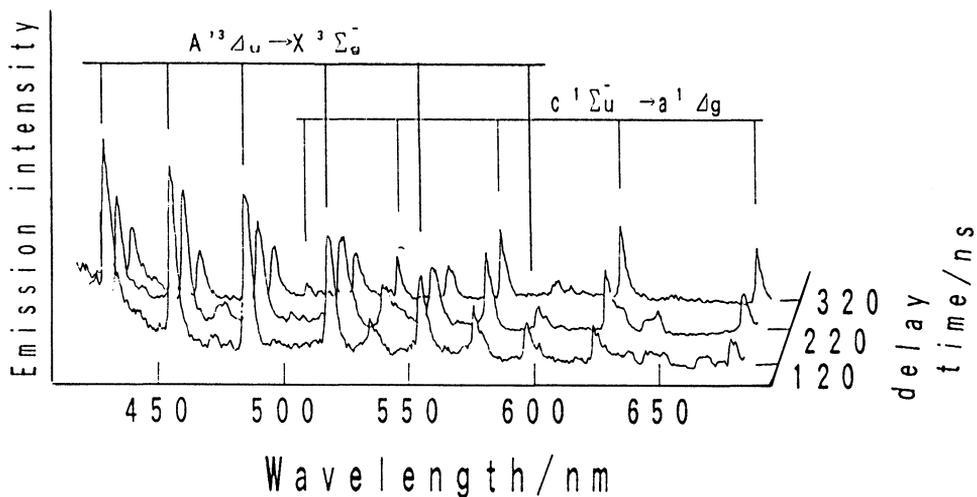


Figure 4 Change of the dispersed emission spectra with the delay of the observation. Temperature, 26 K; excitation at 248 nm; band path width, 0.3 nm. The delay time corresponds to the mean time of the observation gate after the excitation (gate width 100 ns).

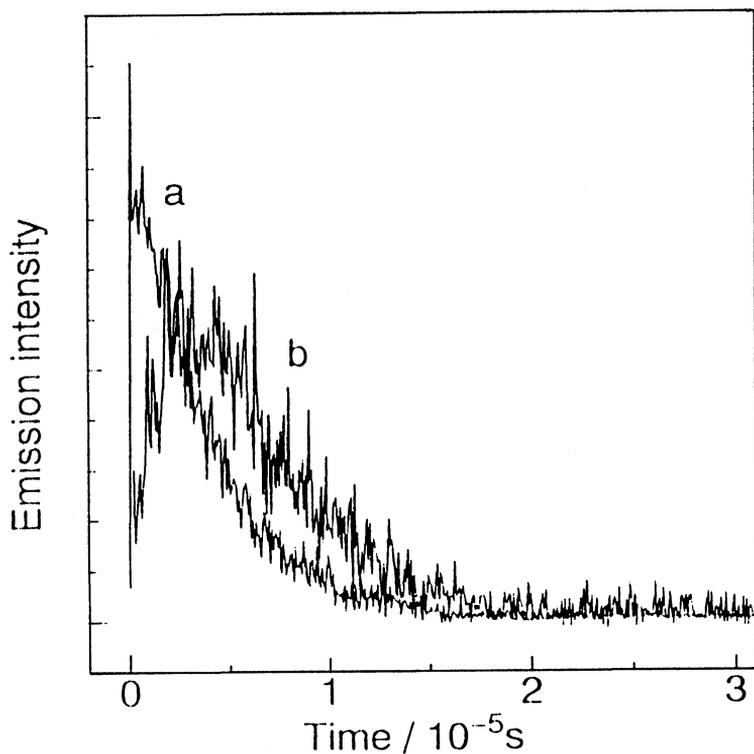


Figure 5 Relationship between the A'-X (0, 8) and c-a (0, 6) emissions. Temperature, 22.5 K; excitation at 248 nm; band path width, 0.3 nm. a: A'-X (0, 8), decay time constant = 3.9 μ s. b: c-a (0, 6), rise time constant = 1.8 μ s, decay time constant = 4.1 μ s.

decay, while the time profile of the c–a emission can be analyzed on the basis of an exponential rise and decay mechanism. The rate constants have been determined by logarithmically plotting the decay curves against the elapsed time as tabulated in Table 3. The decay rate constant of the A'–X emission has been found to be somewhat smaller than the rise rate constant of the c–a emission.

Table 3 The decay rate constants of A'–X emission, rise and decay rate constants of c–a emission, and the relative k_2 values at various temperatures

| T /K | $k_{decay}(A'-X)$ /s ⁻¹ | $k_2(\text{relative})$ | $k_{rise}(c-a)$ /s ⁻¹ | $k_{decay}(c-a)$ /s ⁻¹ |
|-----------|---------------------------------------|------------------------|-------------------------------------|--------------------------------------|
| 15.5 | 9.5×10^3 | — | — | — |
| 18.0 | 2.9×10^4 | — | — | — |
| 21.0 | 1.1×10^5 | 1 | 4.0×10^5 | 1.6×10^5 |
| 22.5 | 2.6×10^5 | 3.2 | 5.7×10^5 | 2.3×10^5 |
| 27.0 | 3.7×10^6 | — | 1.3×10^7 | 4.5×10^5 |

The decay rate constant of A'–X emission and the rise rate constant of c–a emission correspond to $k_1 + k_2 + k_3$, and the decay rate constant of c–a emission corresponds to $k_4 + k_5$, according to the model described in text.

It was also confirmed that the emission intensity of A'–X transition decreased monotonously with the temperature, while the intensity of c–a transition was found to be larger at 22.5 K than at 21.0 K.

DISCUSSION

Property of The Excited States And Relaxation

According to the previous work of Goodman and Brus,³ the 290–240 nm absorption of O₂ in solid is dominated by the A' ³Δ_u – X³Σ_g⁻ transition, though in the gas phase, the dominant transition is that one to A³Σ_u⁺ state. However, the A' state is perturbed by the near lying A state. And A state itself also directly absorbs light and appears as a broad spectrum with a negligible zero phonon line.

We have noticed that the excitation spectra are independent on the observation wavelength corresponding to different electronic states. And also, the emission spectrum is the same for the two excitation wavelengths, one of which corresponds to the $v = 8$ level of $\Omega = 2$ of A' state, and the other, to the $v = 7$ level of A state. These findings support the view proposed by Goodman and Brus;³ they claimed that levels which are predominantly A and A' both feed the $v = 0$ level of A' state. The situation is that there is a fast vibrational relaxation down through the A and A' manifolds, and any population which reaches the $v = 0$ level of A state, appears to quickly cross back and feed the $v = 0$ level of A' state.

Relation Between Energy Levels

Our finding is that the c–a transition is observable in the case of ¹⁶O₂ at higher temperatures, and the c–a emission grows with the rise rate constant which is in the same order of the decay rate constant of the A'–X emission.

The simplest model for describing the rise and decay behaviour of the c state is: A' state decays through radiative, intersystem crossing to c state, and some other nonradiative processes with the rate constant k_1 , k_2 and k_3 , respectively. The c state is populated through the intersystem crossing and decays through radiative and non-radiative process, with the rate constant k_4 and k_5 , respectively. Accordingly, the concentration of A' and c state can be described by

$$[A'] = [A']_0 \exp \{-(k_1 + k_2 + k_3)t\},$$

$$[c] = [k_2[A']_0 / \{(k_1 + k_2 + k_3) - (k_4 + k_5)\}] [\exp\{-(k_4 + k_5)t\} - \exp\{-(k_1 + k_2 + k_3)t\}],$$

where the suffix 0 means the initial value. According to this model, the decay rate constant of A' -X emission is equal to the rise rate constant of c -a emission. The experiment has shown that the former constant is somewhat smaller than the latter constant, though they are in the same order, which may imply that the main mechanism of populating the c state is the intersystem crossing from the $v = 0$ level of A' state, but that some other mechanism to populate the c state may exist in parallel. Unfortunately, any direct evidence for the latter mechanism could not be obtained by means of the present emission spectroscopy.

The ratio $k_2/(k_1 + k_2 + k_3)$ can not be determined because the proportional constants between the concentration and emission intensity are considered not to be common for the two emissions. However, the temperature dependence of k_2 can be estimated from the comparison of the time profiles obtained at 21.0 and 22.5 K, assuming that the ratio of radiative and nonradiative rate constant, k_4/k_5 , is the same between the two temperatures. The relative k_2 values are shown in Table 3. The temperature dependence of the decay rate constant of the A' -X emission and of the relative k_2 value are visualized in Fig. 6 in the form of Arrhenius plot.

In the gas phase, the $v = 2$ level of c state locates below the $v = 0$ level of $\Omega = 3$ of A' state by 60.17 cm^{-1} .¹ In Ar matrix, Rossetti and Brus⁴ observed the c -a emission from $^{16-18}\text{O}_2$ and $^{18}\text{O}_2$,⁴ but not from $^{16}\text{O}_2$. They argued that in the case of $^{16}\text{O}_2$, the crossing to the $v = 2$ level of c state is endothermic at least by 15 cm^{-1} . If c state is populated through the crossing, the $v = 2$ level is primarily populated, and the system relaxes rapidly to the $v = 0$ level and emits the c -a emission.

In N_2 matrix, the c -a emission is observable only for $^{18}\text{O}_2$ at low temperatures according to Goodman and Brus.³ Thus, the $v = 2$ level of c state is considered to be located lower than the $v = 0$ level of $\Omega = 3$ of A' state in $^{18}\text{O}_2$, but not in the case of $^{16-18}\text{O}_2$ and $^{16}\text{O}_2$ in N_2 solid. The present study has shown that the c -a emission appears at higher temperatures in the case of $^{16}\text{O}_2$. The apparent activation energy for the decay rate constant of A' -X emission is ca. 130 cm^{-1} from Figure 6, and the temperature dependence of k_2 may not be so much different from this value. Interestingly, the temperature dependence of the decay rate of A' state and/or the intersystem crossing rate is much larger than that in $^{16-18}\text{O}_2$ in Ar crystal observed by Rossetti and Brus.⁴ It is not clear whether the activation energy exactly corresponds to the energy difference between the $v = 2$ level of c state and the $v = 0$ level of A' state, it is certain that the former level locates higher than the latter level.

In the case of the relaxation of c state manifold of $^{16-18}\text{O}_2$ in Ar crystal, the intermediate vibrational levels, $v = 2$ and 1, were detected via the emission from the

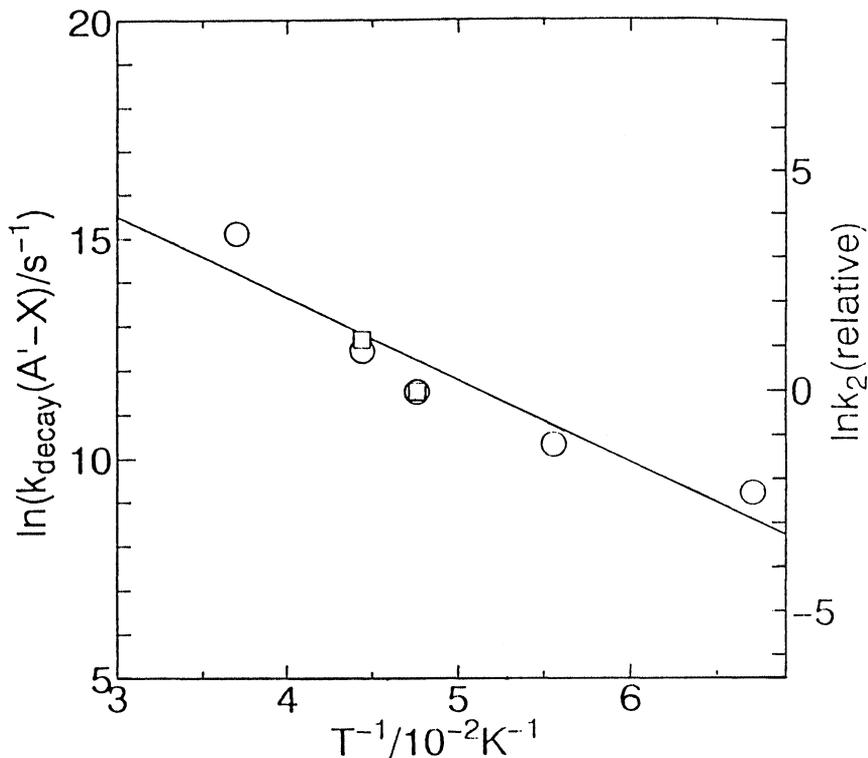


Figure 6 Arrhenius plots of the decay rate constant of A'-X emission and the relative k_2 value. The straight line corresponds to the activation energy of 130 cm^{-1} , circles: the decay rate constant, squares: relative k_2 values.

corresponding levels⁴. In the present study, such emissions have not been observed. However, this failure may not contradict with the above idea that the $v = 2$ level of c state is primarily populated via the $v = 0$ level of A' state, considering that the fast vibrational relaxation in the singlet c state manifold in N₂ solid is common for ¹⁸O₂³ and ¹⁶O₂.

In conclusion, the present findings strongly suggest that the main relaxation mechanism of O₂ in N₂ crystal is the intersystem crossing from the $v = 0$ level of $\Omega = 3$ of A' state to c state which is followed by the vibrational relaxation from $v = 2$ through $v = 0$ in c state, though some unknown mechanism may contribute to populate c state to some extent.

Acknowledgements

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