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Decay Kinetics of N(^{2}P or ^{2}D) + N$_2$(X$^1\Sigma_g^+$, v'') in Low Temperature Solid Nitrogen[†]

Kenji Takizawa,[‡] Akinori Takami, and Seiichiro Koda*

Department of Chemical System Engineering, School of Engineering, The University of Tokyo, Hongo 7-3-1, Bunkyo-ku, Tokyo 113-8656, Japan

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Under the irradiation of free-standing nitrogen crystal at low temperature with focused KrF excimer laser light, the system of N(^{2}P or ^{2}D) + N_2(X$^1\Sigma_g^+$, v'') has been prepared through the energy transfer between N(^{4}S) and N_2(A$^3\Sigma_u^+$). The decay processes have been monitored by observing α'' emission which corresponds to the transition N(^{2}D) + N_2(X, v'') → N(^{4}S) + N_2(X, $v'' - 1$) and δ'' emission which corresponds to the transition N(^{2}P) + N_2(X, v'') → N(^{2}D) + N_2(X, $v'' - 1$). The observed lifetimes for the α'' emissions for individual v'' are on the order of several seconds, and those for the δ'' emissions, on the order of several milliseconds. It is concluded that the α'' transitions are affected by the multiphonon assisted V−V (vibration to vibration) relaxation, and the δ'' transitions are mostly radiatively controlled.

Introduction

The knowledge concerning the energy transfer and relaxation processes from electronically and/or vibrationally excited molecules is very important in order to understand chemical reactions and to control reaction progresses. These processes are well studied for isolated and/or gas-phase molecules,[1,2] but are insufficiently done for molecules in condensed phases and/or those doped in solids[3,4] where the molecules are mutually affected by surroundings.

In a previous report,[5] we observed a strong emission from ^{2}D excited N atoms in a low-temperature nitrogen crystal under irradiation with a focused KrF excimer laser at 248 nm. Based on the kinetics and laser power dependence, it was concluded that N atoms and N_2 molecules in the A$^3\Sigma_u^+$ state are produced through multiphoton processes and that an efficient energy transfer occurs between these two kinds of species to yield excited N atoms. At the same time, several weaker emissions were observed which could be identified as the atomic transitions accompanied by N_2 molecular vibrational transitions. The emission named α'' is one of them, which corresponds to the transition, N(^{2}D) + N_2(X, v'') → N(^{4}S) + N_2(X, $v'' - 1$). Later we have also observed the emission named δ'', which corresponds to the transition, N(^{2}P) + N_2(X, v'') → N(^{2}D) + N_2(X, $v'' - 1$) as has been reported for the first time by Oehler et al.[6] These emissions, α'' and δ'', were originally observed from solid nitrogen excited by gas discharge[7] and electron bombardment.[6,8] However, the relaxation kinetics are not sufficiently studied. Laser excitation is expected to be superior to the gas discharge and electron bombardment due to its high energy and time resolution.

Considering the importance of understanding the relaxation mechanism in solid states, we have studied the behavior of these two bands, particularly addressing our interest to the vibrational relaxation of ground-state diatomic N_2 molecules.

Experimental Section

The experimental apparatus and the sample preparation are the same as described previously.[5] Briefly, the nitrogen solid is prepared according to the method proposed by Schwentner et al.[9] in a vacuum chamber as a free-standing crystal, which is of ca. 10 × 10 × 10 mm^3 size consisting of grains of several tenths of mm size. In a typical procedure a bottomless cup equipped with a gas inlet tube is pressed against the head of a copper cryotip, which is kept at a temperature lower than 20 K by a closed-cycle refrigerator in a vacuum chamber. The crystal is grown in the cup for several tens of minutes under 20−30 Torr. When the deposition is completed, the glass cup is removed upward and a free-standing crystal remains on the head of the cryotip.

In the study of photophysics, the crystal is irradiated by a focused KrF excimer laser (Lambda Physik, EMG101MSC) through a quartz lens of $f = 5$ cm. Typical irradiation conditions are: repetition rate, 3 Hz; fluence at the focal point, 5 J cm^{-2}. During and/or after the laser irradiation, the α'' emission is observed along the parallel direction to the irradiation laser beam, dispersed by using a monochromator (JASCO, NRS-2000) and detected by a liquid nitrogen cooled CCD detector attached to the monochromator. The δ'' emission is simultaneously observed along the perpendicular direction to the laser beam, dispersed by a monochromator (HAMAMATSU, C5095), and detected by an ICCD detector (HAMAMATSU, PMA-100). For the measurement of time evolution, relatively long gate widths are adopted, typically 1.5 s and 1 ms for the measurements of α'' and δ'' emissions, respectively.

Results

α'' and δ'' Emissions Under and After the Laser Irradiation. When the nitrogen crystal was irradiated, the atomic N(^{2}D) → N(^{4}S) emission was observed and the time behavior and dependence on experimental conditions such as laser pulse energy were in complete agreement with that found in the previous report.[5] Together with the atomic emission, α''- and δ''-banded emissions were observed as shown in Figures 1 and 2, respectively. The structures of the δ'' emission are much better resolved than any previous studies.[6] The assignments of these emissions are already established by the previous studies.[5,6] The α''-banded emissions are believed to be atomic ^{2}D → ^{4}S transitions accompanied by the simultaneous $v \rightarrow v - 1$ vibrational change of the N_2(X) molecule adjacent to the excited

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[*] To whom correspondence should be addressed. Tel: +81-3-5841-7327. Fax: +81-3-5841-7255. E-mail: koda@chemsys.t.u-tokyo.ac.jp.

[‡] E-mail: chenchei@kodalab.t.u-tokyo.ac.jp.

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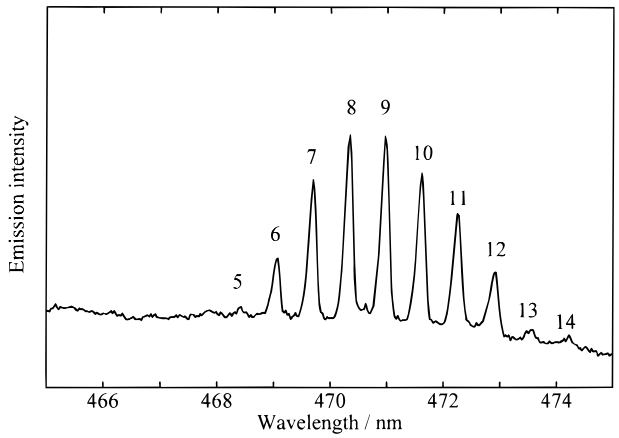

Figure 1. α″ emission of the nitrogen crystal under 248 nm irradiation. The crystal temperature is 16.0 K and the laser fluence is ca. 5 J cm^{-2}. Band path width is 0.05 nm. The numbers drawn in the figure correspond to the initial vibrational levels of the X state.

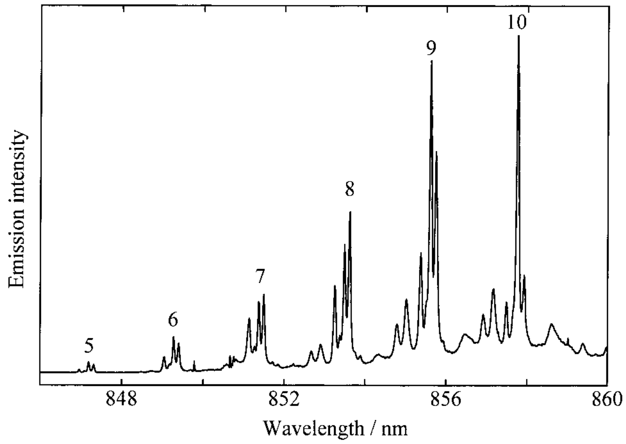

Figure 2. δ'' emission of the nitrogen crystal under 248 nm irradiation. The crystal temperature is 15.6 K and the laser fluence is ca. 5 J cm^{-2}. Band path width is 0.03 nm. The numbers drawn in the figure correspond to the initial vibrational levels of the X state.

N(^{2}D) atom, while the δ''-banded emissions represent the atomic transition from ^{2}P to ^{2}D accompanied by the adjacent N_2(X) vibrational change from v to $v - 1$. The process which populates high vibrational levels of N_2 adjacent to the excited N atom has been proposed[5,6] to be the energy transfer between the N_2($A^3\Sigma_u^+$) molecule and the N(^{4}S) atom, namely,

$$N_2(A^3\Sigma_u^+, v' = 0) + N(^4S) \rightarrow N_2(X, v'') + N(^2D) \quad (1a)$$

$$N_2(A^3\Sigma_u^+, v' = 0, 1) + N(^4S) \rightarrow N_2(X, v'') + N(^2P) \quad (1b)$$

The creation of N(^{2}D) atoms via reaction 1a is exothermic up to $v'' = 14$, while the creation of N(^{2}P) via reaction 1b is exothermic up to $v'' = 9$, or up to $v'' = 10$, if $v' = 1$ is available. There is a cutoff above $v'' = 10$ in the δ'' emission. The previous experiments have shown that the Vegard−Kaplan emission ($A^3\Sigma_u^+ \rightarrow X$) in pure solid nitrogen is observed only from $v' =$ 0 and 1,[5,10] although in rare gas matrices the bands are observed up to $v' = 6$.[11−13]

The pure atomic "δ emission" corresponding to the $^2P \rightarrow {}^2D$ transition could not be detected because the sensitive wavelength range of the present system is shorter than this atomic transition, which should appear at around 1040 nm.[6] Peyron and coworkers observed the $^2P \rightarrow {}^4S$ emission at 348 nm,[7,14] but we could not observe this transition due to its weakness. Other possible emissions to be observed are those from N_3 radicals. In solid nitrogen, a UV absorption peak at 272 nm[15] and IR spectra[16] of N_3 are reported. In gas phase, Beaman et al.[17] reported the laser-induced fluorescence of N_3, which has the lifetime of <20 ns. We tried to measure these absorptions and emissions without success. We conclude that the concentration of N_3 is lower than our detection limit and it may play a very minor role in our experiments.

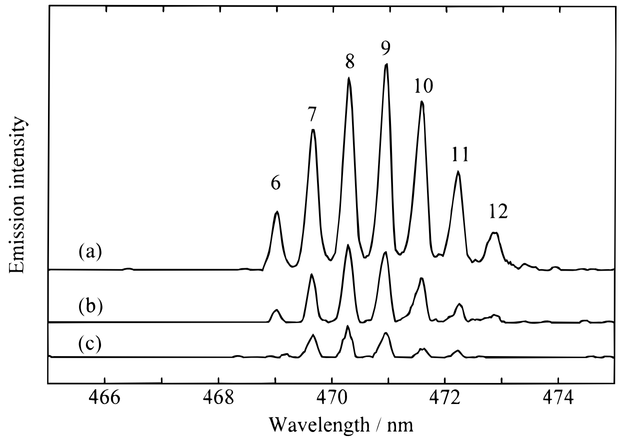

Figure 3. Time evolution of the α″ emission spectra at 16.0 K. The gate time is (a) from 0 to 1.5 s, (b) from 6.4 to 7.9 s, and (c) from 12.8 to 14.3 s after laser interruption. Band path width is 0.05 nm. The numbers drawn in the figure correspond to the initial vibrational levels of the X state.

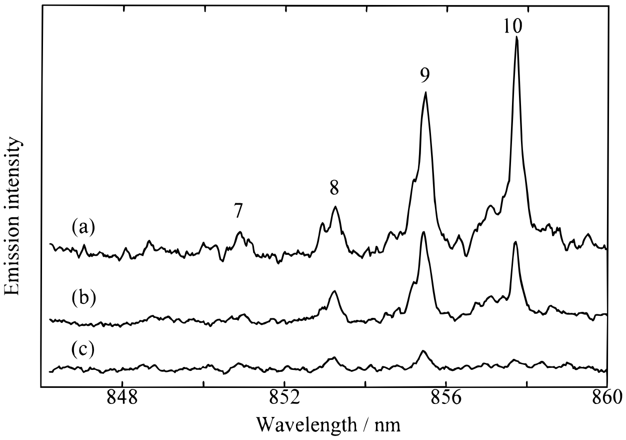

Figure 4. Time evolution of the δ'' emission spectra at 15.6 K. The gate time is (a) from 0 to 1.0 ms, (b) from 3.0 to 4.0 ms, and (c) from 9.0 to 10.0 ms after laser interruption. Band path width is 0.1 nm. The numbers drawn in the figure correspond to the initial vibrational levels of the X state.

The structure observed in the δ'' emission is much more complex compared with that in the α″ emission. Each δ'' band corresponding to the N_2(X) vibrational transition from v to $v - 1$ ($v = 10 \sim 5$) consists of several peaks. These structures of component peaks are similar, independent of the v levels. These component peaks are expected to be due to the crystal field splitting, whose analysis will be reported in the future.

The observed spectra using time gates after the interruption of laser irradiation are shown in Figures 3 and 4 for the α″ and δ'' emissions, respectively. By comparing the relative intensities of these bands we notice changes in the spectral profile, which imply different time behaviors corresponding to individual N_2(X) vibrational levels. Roughly speaking, the peaks corresponding to the higher vibrational levels seem to decrease faster than the lower vibrational levels. At the same time, it is important to notice that lifetimes for the individual δ'' emissions are much

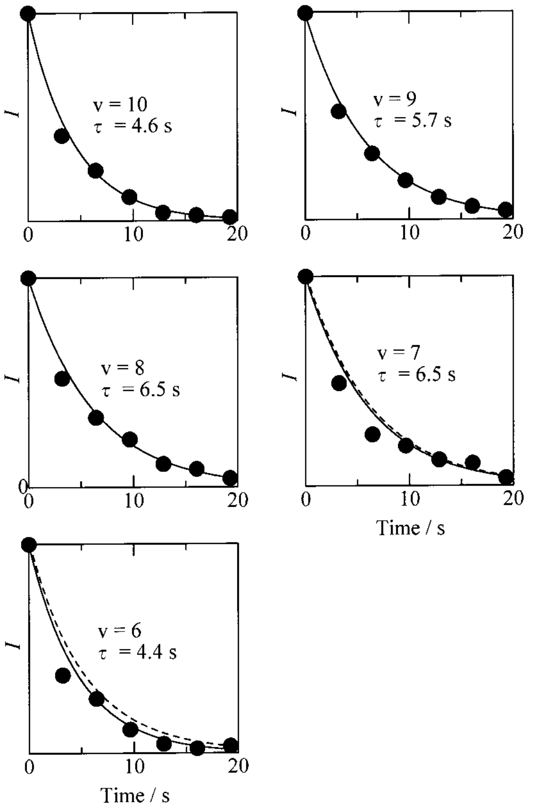

Figure 5. Decay plots of the α″ emissions at 16.0 K. The filled circles indicate the relative emission intensities. The solid lines represent the single exponential fits to the data and the dotted lines represent the double exponential curves based on eq 4 in the text. The individual lifetime τ is estimated from the single exponential fitting.

shorter than those for the α″ emissions. More detailed analysis of the time evolutions will be described in the following section.

Lifetimes of Individual Vibrational States. The time evolutions at individual peak intensities corresponding to different v levels are shown in Figure 5 for the α″ emission at 16.0 K. The time evolution of each peak is mostly a single-exponential decay, and the lifetime has been estimated by a single-exponential fitting as shown by the solid line in Figure 5.

The time evolutions at individual peaks representing individual vibrational N$_2$(X) levels are shown in Figure 6 for the δ'' emission at 15.6 K. The time evolution is mostly a single-exponential decay. The corresponding lifetimes are thus estimated in the same way as the α″ emission.

Discussion

We will model the relevant relaxation processes as follows. There should be two processes in parallel, which will be expressed by the following equations:

$$\mathrm{N}(^2\mathrm{D})\cdots\mathrm{N}_2(\mathrm{X},\, v = n) \rightarrow \mathrm{N}(^4\mathrm{S})\cdots\mathrm{N}_2\,(\mathrm{X},\, v = n - 1) + h\nu(\alpha'') \quad (2a)$$

$$\mathrm{N}(^2\mathrm{D})\cdots\mathrm{N}_2(\mathrm{X},\, v = n) \xrightarrow{\text{nonradiative}} \mathrm{N}(^2\mathrm{D})\cdots\mathrm{N}_2(\mathrm{X},\, v = n - 1) \rightarrow \mathrm{N}(^4\mathrm{S})\cdots\mathrm{N}_2(\mathrm{X},\, v = n - 2) + h\nu(\alpha'') \quad (2b)$$

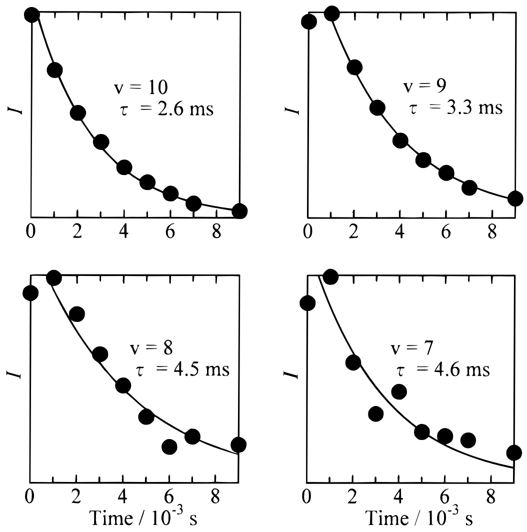

Figure 6. Decay plots of the δ'' emissions at 15.6 K. The filled circles indicate the relative emission intensities. The solid lines represent the single exponential fits to the data. The individual lifetime τ is estimated from the single exponential fitting.

The process described by eq 2a is the radiative decay accompanying the vibrational quantum number change. The other process described by eq 2b is the vibrational relaxation of ground state N$_2$ molecules in the first step, which is followed by the second radiative step. In the nonradiative decay process, only down-conversion of N$_2$(X, $v = n$) is taken into account. The reason up-conversion is not taken into account will be described later. Taking these two processes (2a and 2b) together, the population change of vibrationally excited N$_2$(X), N_v, should follow eq 3

$$\mathrm{d}N_v/\mathrm{d}t = -(k_v^{\mathrm{rad}} + k_v^{\mathrm{nrad}})N_v + k_{v+1}^{\mathrm{nrad}}\,N_{v+1} \quad (3)$$

where $k_v{}^{\mathrm{rad}}$ and $k_v{}^{\mathrm{nrad}}$ correspond to eq 2a and the first step of eq 2b, respectively. The time dependence is obtained via integration and is described by eq 4, assuming that the nonradiative transition from $v + 2$ and/or higher levels has negligible influence on the population of v level, N_v,

$$N_v = \left(\frac{k_{v+1}^{\mathrm{nrad}}\,N_{v+1,0}}{(k_{v+1}^{\mathrm{rad}} + k_{v+1}^{\mathrm{nrad}}) - (k_v^{\mathrm{rad}} + k_v^{\mathrm{nrad}})} + N_{v,0}\right) \times \exp(-(k_v^{\mathrm{rad}} + k_v^{\mathrm{nrad}})t) - \frac{k_{v+1}^{\mathrm{nrad}}\,N_{v+1,0}}{(k_{v+1}^{\mathrm{rad}} + k_{v+1}^{\mathrm{nrad}}) - (k_v^{\mathrm{rad}} + k_v^{\mathrm{nrad}})} \times \exp(-(k_{v+1}^{\mathrm{rad}} + k_{v+1}^{\mathrm{nrad}})t) \quad (4)$$

Here $N_{v,0}$ and N_v denote the number of vibrationally excited molecules just after the laser interruption and t seconds after the laser interruption. If the second exponential term in eq 4 is relatively large, the time profile of α″ should appear double exponentially. But the experimental result shows that the time evolution of each peak is eventually single exponential and that the contribution of the second term in eq 4 seems to be very small. Thus, we could determine only the sum of $k_v{}^{\mathrm{rad}}$ and $k_v{}^{\mathrm{nrad}}$ by comparing the experimental decay with the model prediction.

The radiative decay may be proportional to $v\nu_v{}^4$ as once discussed by Crepin et al.[18] Here ν_v is the transition frequency. The dependence of the decay rate on the vibrational quantum number may be compared with the experimental result, though the absolute value cannot be estimated. On the other hand, Zumofen[19] dealt with the phonon-assisted V−V (vibration to vibration) transfers among CO and N$_2$ molecules in nitrogen matrices that we will borrow. According to his study, the inverse lifetime is described as shown in eq 5; that is, the multiphonon relaxation lifetime τ is related to the energy gap Δ, number of the relevant phonons η, and the mean phonon frequency $\langle\Omega\rangle$ as

$$\tau^{-1}_{\mathrm{v}''\rightarrow \mathrm{v}''-1} = \frac{4\pi^2\, c \times 12\langle A^2\rangle v S^{\eta}}{\eta!\,\eta\langle\Omega\rangle}\, \mathrm{e}^{-hc\Delta/kT} \qquad (5)$$

where $\langle A^2\rangle$ is the averaged square of the exchange matrix element corresponding to an initial and final phononic ground state. The adopted values are $\langle A^2\rangle = 1.2 \times 10^{-3}$ cm^{-2} and $\langle\Omega\rangle = 45$ cm^{-1}, which are the same values as Zumofen estimated.[19] The Stokes shift S is considered to be the range of 0.1 to 1 according to his study. We will adopt $S = 1$, the upper bound. Also, $\eta = \Delta/\langle\Omega\rangle$ and $\Delta = (v - 1) \times 2\omega_e\chi_e$ are adopted, where $\omega_e\chi_e$ is 14.5 cm^{-1} from the present measurements, assuming that the vibrational relaxation occurs via V$-$V energy transfer according to the following mechanism:

$$\mathrm{N}_2(v) + \mathrm{N}_2(v = 0) \rightarrow \mathrm{N}_2(v - 1) + \mathrm{N}_2(v = 1) \qquad (6)$$

If the number of vibrationally excited molecules $\mathrm{N}_2(v \geq 1)$ surrounding the excited N atom is larger than one, the following up-conversion process may occur:

$$\mathrm{N}_2(v) + \mathrm{N}_2(v') \rightarrow \mathrm{N}_2(v + 1) + \mathrm{N}_2(v' - 1) \qquad (7)$$

However, the possibility that the number of $\mathrm{N}_2(v \geq 1)$ adjacent to the excited N atom is larger than one is negligibly small according to the excitation mechanism described by eqs 1a and 1b. Therefore, the vibrational energy transfer is limited to the down-conversion as written by eq 6. The total energy difference between v and $v - 1$ must be balanced by the phonon number change, which decreases with the decrease of the vibrational quantum number. In due course, the energy mismatch that should be balanced by phonon number change becomes smaller with the decrease of vibrational quantum number. Thus, the vibrational relaxation rate constants increase steeply with the decrease of vibrational quantum number.

As discussed above, the radiative decay model and the phonon-assisted decay model predict the opposite tendency of vibrational quantum numbers of N$_2$. The former predicts the lower vibrational states to decay slower, and the latter predicts the higher vibrational states to decay slower. We discuss which decay model is to be applicable by comparing them with the present experimental data.

We have plotted the experimental decay rate constants for α″ and δ'' bands as a function of the vibrational quantum number as shown in Figure 7. The prediction for radiative transition and for multiphonon relaxation adopting $S = 1$ is also drawn in this figure. The predicted radiative decay rates are moved only in parallel so as to give the best fit between the experiments and the prediction based on the assumption that vibrational relaxation with high vibrational quantum numbers must be dominated by radiative decay. The lifetime of atomic $^2\mathrm{D}\rightarrow{}^4\mathrm{S}$ transition in nitrogen solid is measured to be 42 s,[5] while the lifetime of $^2\mathrm{P}\rightarrow{}^2\mathrm{D}$ is mentioned to be 3 ms,[20] although the precise value for the latter is not reported. The wide difference between the two dashed curves in Figure 7 roughly reflects the difference between the lifetimes of ^{2}D and ^{2}P states. From the comparison between the experiments and predictions, it is concluded that δ'' transitions are explained mostly by the radiative decay process, while α″ transitions are influenced by the multiphonon relaxation to some extent. However, the quantitative difference between experimental data and the prediction by eq 5 with $S = 1$ is very large. This is caused mainly by the estimation of S to be unity. When we adopt the value of S to be 1 order of magnitude smaller, the rate constants of eq 5 are shifted, as drawn in Figure 7. The experimental rate constants with small v's are within these predictions using $S = 1$ and 0.1, which implies that the multiphonon relaxation model is appropriate to explain the present experiments in the small v region.

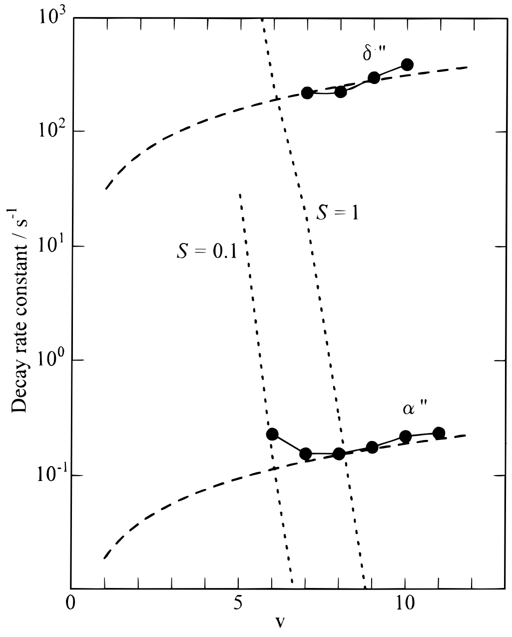

Figure 7. The v dependence of decay rate constants for α″ and δ'' bands. The filled circles and open circles are experimental data of α″ and δ'' transitions, respectively. The dotted curves are the predictions for the multiphonon relaxation at 16.0 K by eq 5 in the text adopting $S = 1$ and $S = 0.1$. The dashed curves are the predictions for the radiative transitions extrapolated from high v in the experimental data for α″ and δ'' transitions.

If the contribution of $k_\mathrm{v}^{\mathrm{nrad}}$ is noticeable, the decay curve may manifest its effect. Thus, we have recalculated the time profiles of α″ emissions, including the contribution of the V$-$V energy transfer, according to eq 4. For the calculation, the $N_{\mathrm{v},0}$ distribution is approximated to be the N_v distribution experimentally observed within 1.5 s after the laser interruption. Here we estimated N_v distribution from the α″ emission intensities I_v by the following relationship:

$$I_\mathrm{v} \propto N_\mathrm{v} v \qquad (8)$$

The re-estimated time evolutions are also drawn by dotted curves in Figure 5, which are eventually not different from the previous prediction based on the single exponential decay. This fact shows that the degree of contribution of the V$-$V transfer cannot be determined precisely, though the contribution is strongly suggested.

Concluding Remarks

The relaxation of vibrationally excited N$_2$(X) molecules, which are prepared via multiphoton excitation by KrF excimer laser light, is studied. The dipole transition for these molecules is forbidden when they are isolated. However, the radiative decay eventually occurs as dipole radiation induced by the neighboring excited atoms. Thus, we have measured emission spectra of atomic N transition accompanied by simultaneous $v \rightarrow v - 1$ vibrational change of the N$_2$(X) molecule. The time evolution of the vibrational populations is obtained based on these spectra, from which we have estimated the lifetime of

N_2(X) molecule adjacent to the excited N(^{2}D) atom and/or excited N(^{2}P) atom. The decay rates obtained in this way can be explained qualitatively by two kinds of relaxation mechanisms, i.e., the radiative decay and nonradiative multiphonon relaxation. In the small v region, where the energy mismatch of V−V transfer between the change from $N_2(v)$ to $N_2(v-1)$ and from $N_2(v=0)$ to $N_2(v=1)$ is small, the multiphonon relaxation is contributing to appreciable extent in α″ transitions. In the large v region, where this energy mismatch becomes larger, the multiphonon relaxation becomes less effective and the relaxation occurs exclusively through the radiative decay.

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