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TIME-RESOLVED FLUORESCENCE SPECTRA OF NITROGEN DIOXIDE EXCITED AT 450.4 NM BY A 4-METHYLUMBELLIFERONE LASER

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The fluorescence spectra of nitrogen dioxide at 0.1 torr were measured (gate time; 0-150 μsec, 0-100 nsec, 5-15 μsec). The short-lived discrete emission and the long-lived continuum emission were resolved by using the pulse-gated photon counting method.

The radiative lifetime of nitrogen dioxide is anomalously long compared with the value calculated from integrated absorption coefficients.[1] The double exponential decay and the single exponential decay of the fluorescence were observed under identical conditions except for a slight change in excitation wavelength,[2] and the shorter lifetime was determined to be 33 ± 4 μsec.[3] Butler et. al. have recently suggested that the source of the continuum emission is longer-lived than the source of the discrete emission from the spacially resolved fluorescence experiment.[4] In our study the time-resolved fluorescence spectrum of nitrogen dioxide was investigated in order to resolve the emissions from the short-lived species and from the long-lived species.

The fluorescence intensity of nitrogen dioxide is relatively small, and the fluorescence was measured for a specific duration by a pulse-gated photon counter. The experimental apparatus is shown in Fig. 1. A 4-methylumbelliferone dye laser, the exciting source, was operated at the repetition rate of about 13-20 Hz. The sample cell with two Brewster windows was placed between the multi-reflection mirrors in order to increase the fluorescence intensity. The fluorescence was measured by a JASCO CT-100 monochromator with the 0.4 mm slit (resolution 0.3 nm) and detected by a HTV R212UH photomultiplier. The signal was amplified and gated simultaneously by a video-amplifier. The fast response photodiode, LSD 39A, was used for the trigger circuit. The electronic pulses were counted by a NF 545A photon counter

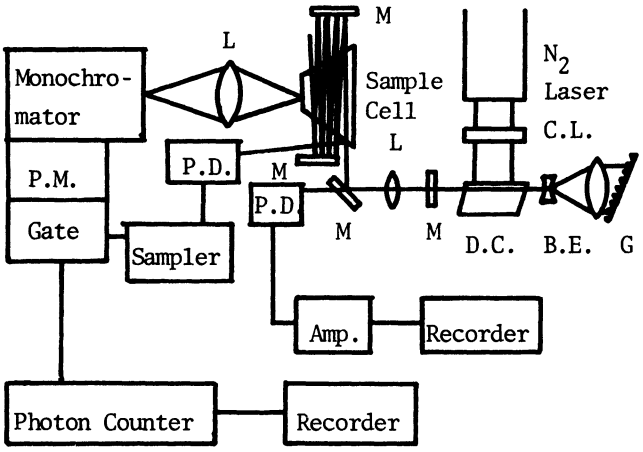

Fig. 1. Experimental Apparatus
G; Grating, B.E.; Beam Expander, M; Mirror
L; Lens, D.C.; Dye Cell, C.L.; Cylindrical Lens, P.M.; Photomultiplier, P.D.; Photodiode

(10^7 cps). The pressure of the nitrogen dioxide was measured by an oil manometer.

The wavelength of the laser emission was adjusted to 450.4 nm (the linewidth; 0.3 nm); around 450.0 nm, this wavelength gave the most intense discrete fluorescence ($\Delta\nu_2 = -1$). The pulse width of a photon was 20 nsec, and the minimum gate width was 30 nsec, which were measured by a synchroscope (IWATSU SS-6200,200 MHz). The initial time, 0 nsec, was determined by measuring the scattered light of the exciting dye laser. The background counts of the photomultiplier and the noise from the nitrogen laser were 0 pulse/50 sec. Those of the stray light and the fluorescence from the sample cell were below 10 pulse/50 sec, and they could be negligible in our study.

The time-resolved fluorescence spectrum of nitrogen dioxide at 0.1 torr are shown in Fig. 2. In the fluorescence spectrum (a), in which the observation aperture is adjusted to monitor the first 150 μsec of the fluorescence, a few relatively intense discrete bands superimpose on an apparent continuum emission. The ratio of the intensities of the discrete emission to the continuum emission depends on the linewidth of the laser source. The narrower laser gives more intense discrete emission. The fluorescence intensity excited by a laser of 1 GHz linewidth was reported to decrease by roughly a factor of ten when the monochromator was tuned away from the sharp fluorescence ($\Delta\nu_2 = -1$ band).[3] The bands at 466.2, 478.9, and 483.0 nm were assigned to the emissions to the ν_2, ν_1, and $2\nu_2$ levels of the ground state.[5] The discrete ν_2 band was assigned to the transition from the $^2B_1$ state.[3] The $2\nu_2$ band appeared more intense than the ν_3 band did; the latter was more intense when the nitrogen dioxide was excited at 457.9 nm by an argon ion laser;[5] in this case the transition was assigned to $^2B_2 \leftarrow {}^2A_1$. Most of the photoemission can be detected in this gate time, since the radiative lifetime of the long-lived species of the nitrogen dioxide is 70-82 μsec.[7] The continuum emission increases as the emission wavelength increases as reported by Sakurai and Broida.[5]

The fluorescence spectrum (b) was measured with the gate time of 0-100 nsec. Maximum counting rate in the spectrum is 0.35 photoelectron per a laser pulse, and no correction for the two-photoelectron process is necessary. The same vibrational bands appeared in this spectrum with the spectrum (a), and no noticeable change in the relative intensity is observed. However, the relative intensity of the discrete emission to the continuum emission is considerably large. The increase of the discrete structure shows that the source of the discrete emission has a shorter lifetime than that of the continuum one. This is consistent with the lifetime measurement recently reported.[3]

In the fluorescence spectrum (c) (gate time, 5-15 μsec), few discrete structures were observed and the intensity of the continuum emission increases as the wavelength increases as in the case of the spectrum (a). The source of the continuum emission is confirmed to have a longer lifetime. The continuum emission was observed in the near collision-free condition (pressure, 0.1 torr; gate width, 100 nsec; the probability of the collision, 0.15 times/molecule), thus it originates either in a unimolecular process or in an efficient collisional process. The ratio of the discrete band intensity to the total intensity have been reported to be independent of the pressure from the magnetic quenching result.[4] This fact supports that the continuum emission appeared through the noncollisional process.

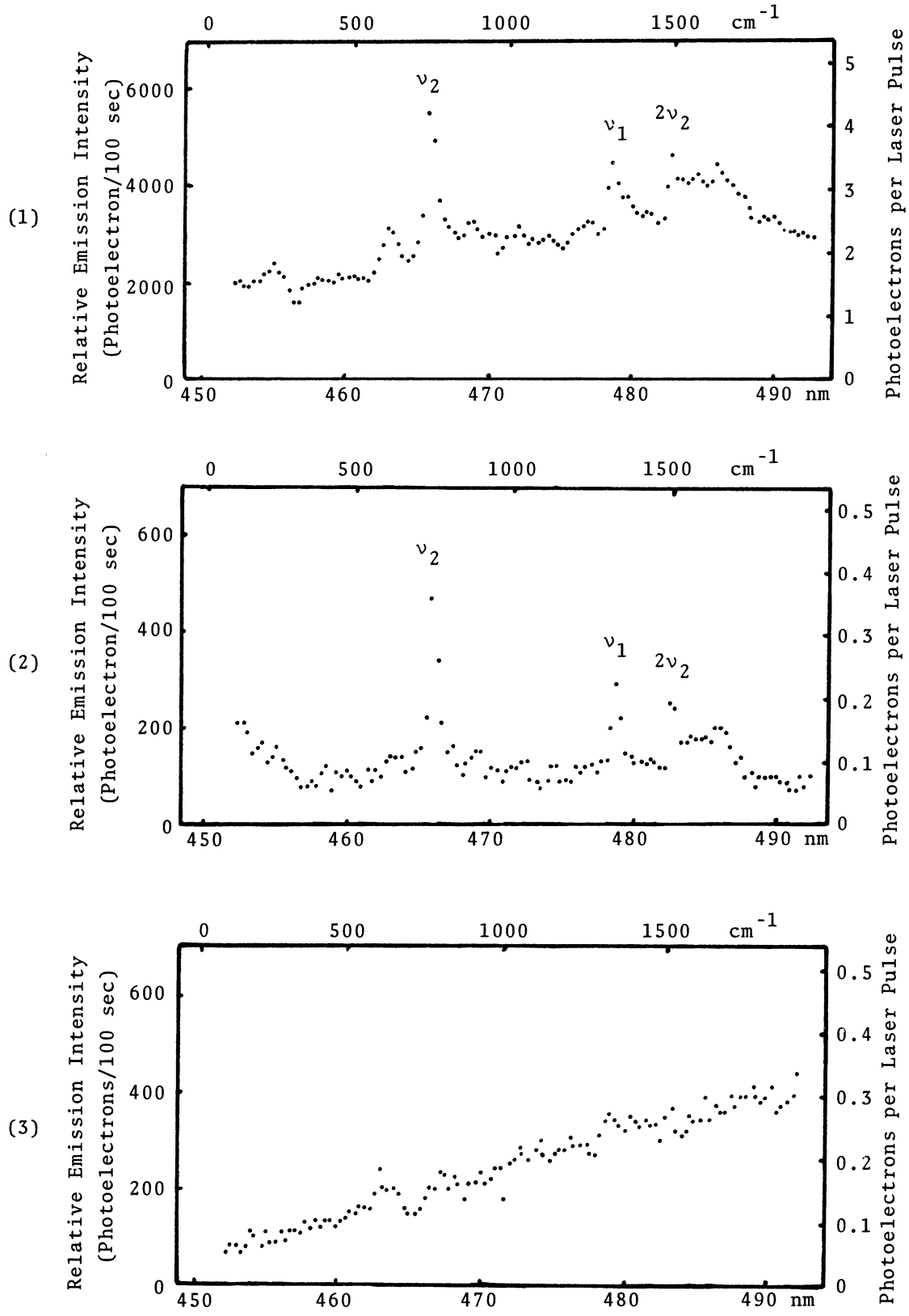

Fig. 2. The time-resolved emission spectrum of nitrogen dioxide at 0.1 torr. Gate time; (1) 0-150 μsec, (2) 0-100 nsec, (3) 5-15 μsec.

The excited species of nitrogen dioxide, which has the reasonably long lifetime, diffuses some distance from the region of the exciting line. Thus, in the measurement of the time-resolved fluorescence from the nitrogen dioxide, the photoemission from the region of the exciting line has to be measured infallibly, since the diffused species are long-lived and give a continuum emission.[4] It was confirmed that the collecting mirror was in a position to give the maximum intensity of the ν_2 sharp band (the short-lived species) with the gate time of 0-100 nsec before and after the measurements.

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