

ANALYSIS OF POLYATOMIC SPECTRA USING TUNABLE LASER-INDUCED FLUORESCENCE: APPLICATIONS TO THE NO₂ VISIBLE BAND SYSTEM*

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By exciting NO₂ with a narrow band, pulsed, dye laser in the region between 5934 and 5940 Å, we have obtained a partial rotational analysis of a $K = 0$ sub-band of a ${}^2B_2 \leftarrow {}^2A_1$ transition. In addition, we find evidence for a ${}^2B_1 \leftarrow {}^2A_1$ transition in this region. By measuring the decay of resolved fluorescence features, we have determined the lifetimes of these two states, and find that they are markedly different.

1. Introduction

Despite rapid progress in the rotational analysis of the electronic transitions of small polyatomic molecules, the successes have been largely limited to transitions between "well behaved" states, i.e., states whose rotational energy levels correspond closely to near rigid rotors [1]. However, there are certain molecular band systems that have defied analysis by traditional means; a situation that arises whenever extensive near-resonant interactions disrupt the regularity of the line positions. Prime examples of this behavior are the visible band system of NO₂ and the near UV band systems of CS₂ and SO₂. In addition, these molecular band systems exhibit "anomalously long lifetimes", i.e., lifetimes that are longer by one or more orders of magnitude than estimates based on integrated absorption coefficient measurements [2].

We report a technique for investigating highly perturbed molecular band systems by monitoring the fluorescence under high resolution following excitation by a narrow-band, tunable laser. By tuning the excitation frequency from line to line, the rotational quantum numbers as well as vibronic symmetries can be as-

signed in a way that is *independent* of the location of other members of branch or sub-band. We have applied this technique to the visible spectrum of the NO₂ molecule for which we obtain a partial rotational analysis in the vicinity of 5935 Å. By measuring the radiative decay rate of the energy-resolved fluorescence, lifetimes are also assigned to the fluorescence features.

2. Experimental

Fig. 1 shows a block diagram of the experimental set-up[†]. A rhodamine 6G/methanol dye solution circulates through a quartz cell and is excited by a xenon flashlamp (0.1 μsec risetime, 1.0 μsec pulse duration). The laser cavity is terminated at one end by a totally reflecting dielectric-coated mirror and at the other by an echelle grating (316 lines/mm) operating in eighth order. The laser bandwidth is narrowed from approximately 1 to 0.1 Å fwhm by inserting a 6X beam expander and a Fabry-Pérot etalon inside the laser cavity. The NO₂ cell is also placed inside the laser cavity.

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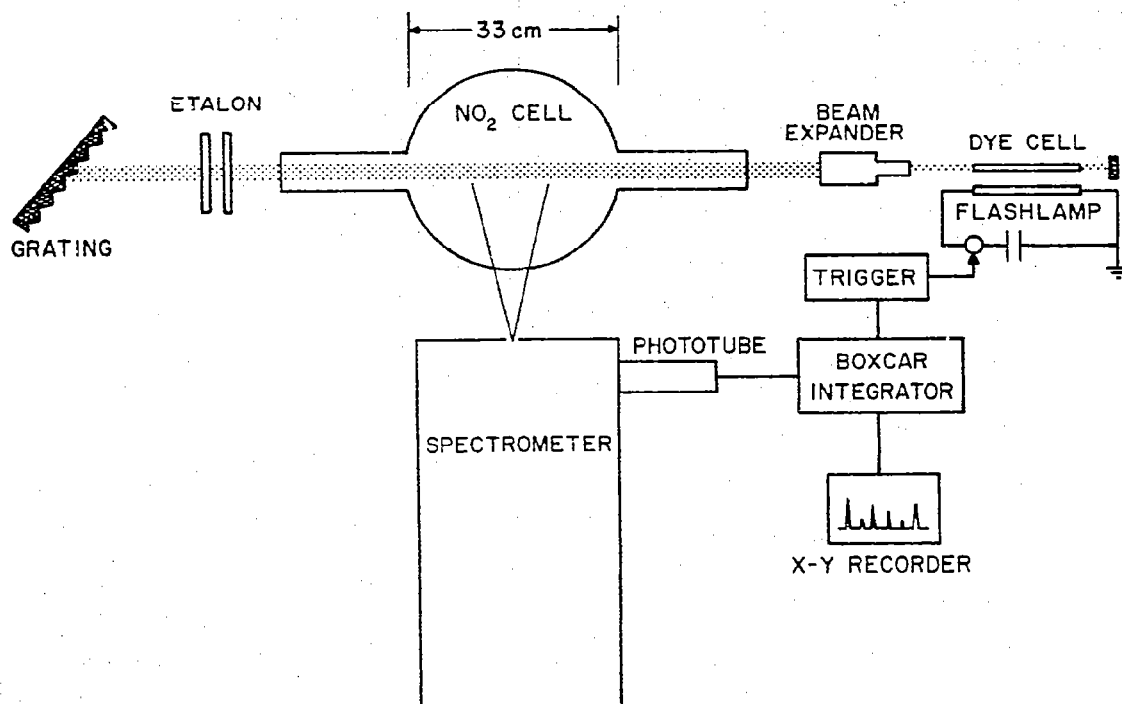


Fig. 1. Block diagram of experimental apparatus.

Matheson reagent grade NO_2 (99.5% purity) is condensed in a liquid-nitrogen-cooled coldfinger and the sample is then pumped on to remove more volatile impurities. Only NO_2 obtained from pure white condensate is admitted into the fluorescence cell. The vacuum system is entirely grease and Hg free and the background pressure is 10^{-6} torr or less. NO_2 pressures are measured with a capacitance manometer. A Spex 3/4 m spectrometer ($f/6.8$) is used for energy resolved fluorescence studies. The signal from an EMI 6256Q photomultiplier (S-20 response) drives a PAR CW-1 boxcar integrator the gate of which is activated by the flashlamp trigger. The output of the boxcar is then displayed on an X-Y recorder. For lifetime studies the fluorescence decay is observed both through the spectrometer as well as directly with the photomultiplier in conjunction with a Corning 2-60 filter.

3. Fluorescence spectra and lifetimes

Fig. 2 shows a low-resolution absorption spectrum of NO_2^* . The complex nature of the gross features

suggests why no vibrational analysis has been carried out for this system[†]. The region we have chosen to investigate is shown in the insert in fig. 2. Although absorption is low in this region we anticipate that analysis will be facilitated because of less band overlap.

Fig. 3 shows a low resolution fluorescence spectrum obtained for excitation at 5935.7 Å. The displacements of the strong fluorescence features correspond to the successive ground state vibrational quanta shown. The strong-feature intensity pattern is characteristic of emission resulting from excitation between 5934 and 5940 Å and shows that the strong absorption lines in this spectral region all have essentially the same upper state vibrational character. In addition to these strong emission features, weaker transitions appear whose displacements do not correspond to vibrational spacings of the ground state. Previously

* We wish to thank J.C.D. Brand and R. Pirkle for providing us with the absorption spectra of NO_2 .

† Douglas and Huber [3] succeeded in identifying a progression of unperturbed bands in the 3700–4600 Å region.

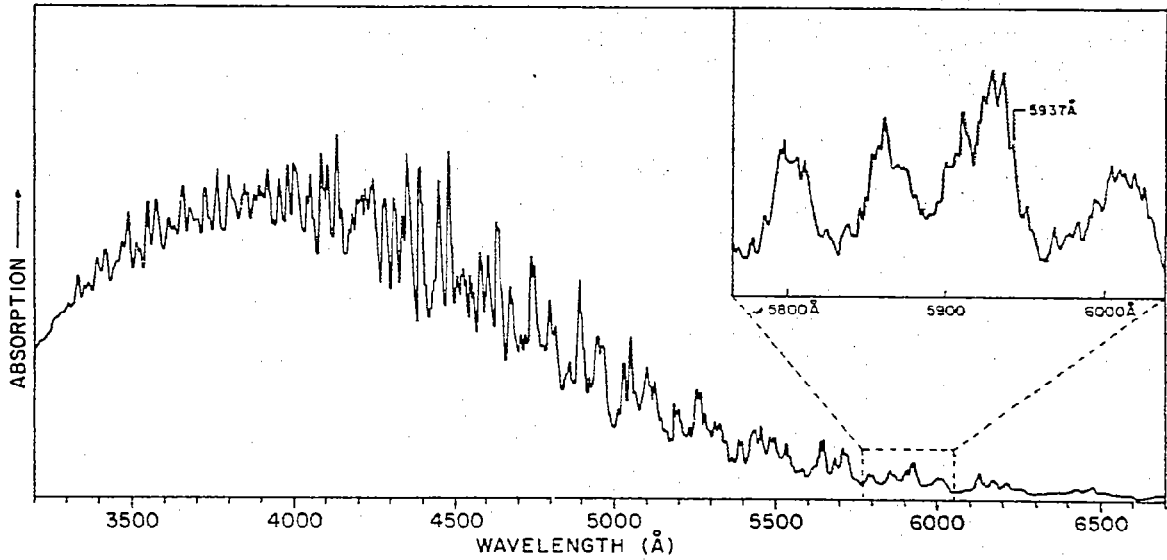


Fig. 2. Low resolution absorption spectrum of NO_2 . Insert shows medium resolution spectrum of 5800–6000 Å region.

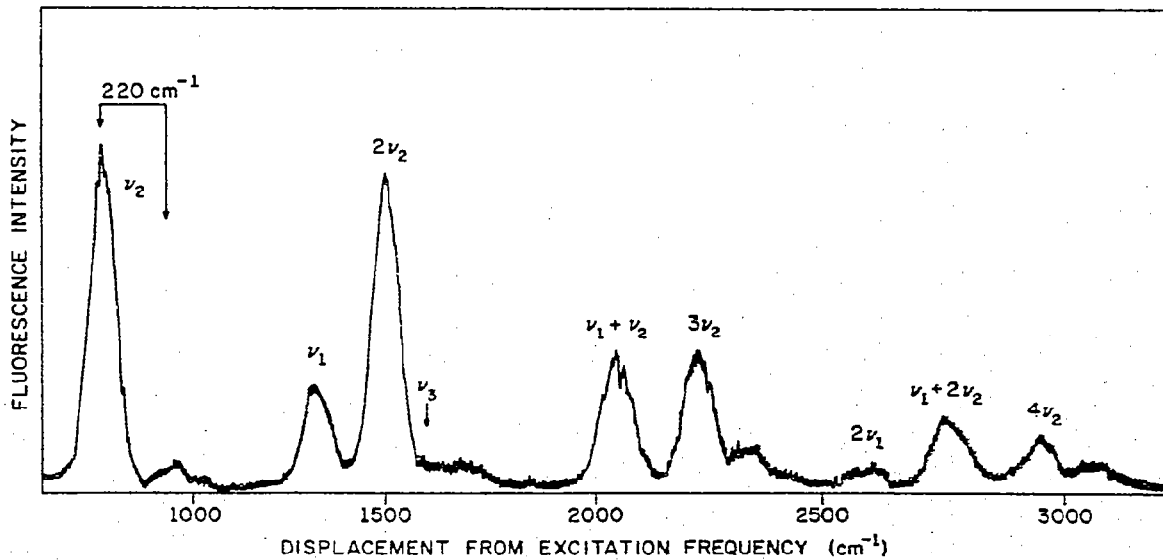
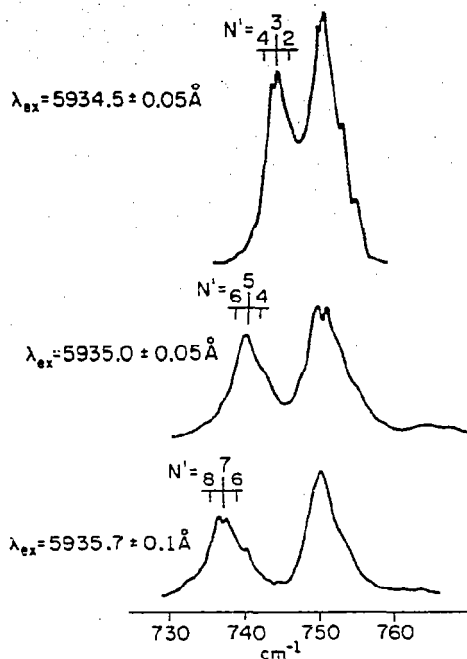


Fig. 3. Low resolution (30 Å) fluorescence spectrum for excitation at $5935.7 \pm 0.1 \text{ \AA}$ at 0.1 mtorr NO_2 pressure.

published narrow-band excitation fluorescence taken at higher pressures show sharp features superimposed on an apparent emission continuum [4,5]. Excitation in this wavelength region results in no discernible continuum and the observed features, both strong and weak, are established as originating from the initially populated state(s) since no change in relative intensity is observed as the NO_2 pressure is reduced to 0.01 mtorr. There have been several studies of the NO_2 lifetime using both narrow and broad band excitation but in all cases relatively broad band fluorescence monitoring techniques [2, 6–9]. While there is general agreement that the lifetime is much longer than that calculated from the integrated absorption coefficient, lifetimes have been reported to be both exponential [2,6] and non-exponential [9] as well as both independent [7] of and dependent [8,9] on excitation wavelength. We have monitored the decay (0.5 mtorr NO_2) of the unresolved fluorescence using our filtered photomultiplier as well as the decay of the strong ν_2 feature and the weak feature between ν_1 and ν_2 (see fig. 3) using our spectrometer (30 Å resolution). For excitation at 5934.5 Å the decay of the unresolved fluorescence is highly nonexponential with an "apparent lifetime" of roughly 60 μsec , whereas the decays of the resolved features are exponential. We find for the strong ν_2 feature $\tau = 30 \pm 5 \mu\text{sec}$ and for the weak feature between ν_1 and ν_2 $\tau = 115 \pm 10 \mu\text{sec}$ *. These strikingly different lifetimes show that the emission originates from two distinct upper states.

In fluorescence spectra the displacements of the emission lines from the excitation frequency correspond to the energy separation between the initial (double-primed) and the final (unprimed) vibration-rotation energy levels of the ground state. With the aid of ground state spectroscopic constants [5, 10] the fluorescence spectrum may then be used to assign quantum numbers to the observed transitions.

Fig. 4 shows the fluorescence spectrum in the frequency range of the ν_2 bending mode resulting from excitation of three adjacent, strong absorption lines in the region of 5935 Å. The top trace is obtained by tuning the laser to the 5934.47 Å Ne line that is near-coincident with a strong NO_2 absorption line. In this case we find an intense fluorescence doublet whose



DISPLACEMENT FROM EXCITATION FREQUENCY

Fig. 4. High resolution (1 Å) fluorescence spectra monitored at ν_2 frequency for excitation at wavelengths shown. The apparent fine structure on the doublet features is instrumental.

strongest line is displaced $749.8 \pm 0.2 \text{ cm}^{-1}$ from the excitation frequency. Similarly, the strongest line of the $2\nu_2$ doublet is displaced by $1498.6 \pm 0.2 \text{ cm}^{-1}$. Excitation at 5935.0 and 5935.7 Å also results in fluorescence doublets displaced by approximately the same frequencies from excitation.

4. Analysis

The only satisfactory explanation of the observed fluorescence spectra is made by assigning the absorption lines to P-branch members of a $K'' = 0$ sub-band of a Π -type transition ($\Delta K = 0$). The displacement frequency ν involving only excitation of the ν_2 bending mode may be calculated from the approximate expression [1]†

† Infrared work [10] has shown the vibration-rotation constant α_2^B to be negligibly small.

* The error estimates do not include collisional lifetime shortening caused by the finite (0.5 mtorr) pressures used.

$$\begin{aligned}
 \nu &= F_{0\nu_2 0}(N, K) - F_{000}(N'', K'') \\
 &= \nu_2[\omega_2 + \frac{1}{2}(x_{12} + x_{23})] + \nu_2(\nu_2 + 1)x_{22} \\
 &\quad + \bar{B}_0[N(N+1) - N''(N''+1)] \\
 &\quad - \alpha_2^A \nu_2 K^2 + (A_0 - \bar{B}_0)(K^2 - K''^2), \quad (1)
 \end{aligned}$$

where the above constants and quantum numbers have their traditional spectroscopic meanings. For $K'' = 0$ and $N'' = N$, the ground state constants yield displacements of the strongest line of ν_2 and $2\nu_2$ of 749.8 cm^{-1} [5, 10] and 1498.4 cm^{-1} [10] (1498.6 cm^{-1}) [5] respectively, thus establishing $K'' = 0$. The presence of only one apparent fluorescence doublet (fig. 4) implies that the transition is a \parallel -type since a \perp -type transition would give rise to two sets of P, Q, and R lines separated by $4[\alpha_2^A \nu_2 - (A_0 - \bar{B}_0)](K'' + 1)^*$. The location of the less intense line at lower displacement frequencies shows that the upper state is populated by a $\Delta N = -1$ (P branch) transition. The separation of the fluorescence doublets allows the determination of the upper state quantum number N' . Using the value $\bar{B}_0 = 0.422 \text{ cm}^{-1}$ we calculate $N' = 3.0 \pm 0.2$, $N' = 5.1 \pm 0.2$, and $N' = 7.3 \pm 0.4$ for the three doublets shown in fig. 4. The calculated displacements for adjacent N' values are shown in the figure for comparison. Similarly, excitation at 5936.5 \AA yields $N' = 9.3 \pm 0.4$. In addition to these N' values we have tentatively identified members of this P branch up through $N' = 21$ and by combination-differences the corresponding R branch members.

The \parallel -type band observed here is assigned to a ${}^2B_2 - {}^2A_1$ transition that has been predicted to occur in this region [11]. According to nuclear statistics [1], only odd N values occur in the $K' = 0$ stack of the $N^{16}O_2$ 2B_2 state whereas only even N values occur in the $K'' = 0$ stack of the 2A_1 ground state. This accounts for the observation of only odd N' values. Further support for these assignments is provided by a comparison of relative intensity measurements with calculated Hönl-London factors. With the established N' values we may calculate the upper state rotational constant $\bar{B}_{\nu'}$, using the separation between successive

* An exception to this will occur when $K'' = 1$ and $\Delta K = -1$ in which case only one set of P, Q, R, emission lines will result.

rotational levels. From high resolution plates of the NO_2 absorption spectrum[†] we find for the intervals $N'_{i+2} - N'_i$ of 5-3, 7-5, and 9-7 the $\bar{B}_{\nu'}$ values of 0.42_2 , 0.41_7 , and 0.40_0 cm^{-1} respectively. These non-constant $\bar{B}_{\nu'}$ values clearly show that the upper 2B_2 state is perturbed.

The weaker feature between ν_1 and ν_2 cannot be attributed to a \parallel -type transition from the 2B_2 state. Instead, we believe this feature to arise from a \perp -type transition from the 2B_1 state. The alternative possibility of a 2A_1 vibronic state built from the electronic 2B_2 state by the addition of odd quanta of the asymmetric stretching mode, ν_3 , seems unlikely since ν_3 is not prominent in the fluorescence spectrum.

Although this technique, which we have illustrated with NO_2 , is capable of analyzing perturbed polyatomic spectra, its use is not limited to such systems, for it should greatly facilitate the analysis of unperturbed systems as well.

[†] We wish to thank both A.E. Douglas and M.M. Hessel for providing us with high resolution plates of NO_2 in this region.

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