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Authors

Robrish, P.

Rosen, H.

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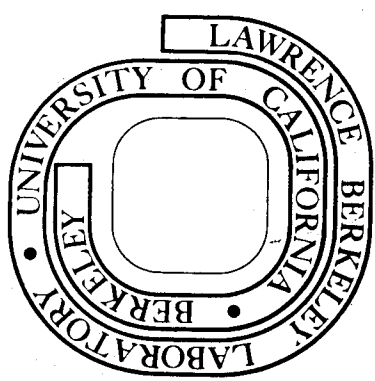
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OBSERVATION OF SHARP AND INTENSE STRUCTURES
IN THE EXCITATION SPECTRUM OF NO₂*

P. Robrish and H. Rosen

Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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ABSTRACT

We have measured the excitation spectrum for the ν_2 fluorescence mode of NO₂ throughout its visible absorption spectrum. The spectra show several narrow regions where the ν_2 fluorescence intensity is about two orders of magnitude larger than that found elsewhere.

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The visible absorption spectrum of NO_2 extends from about 4000-7000 \AA ¹ and seems to consist of numerous overlapping lines forming a quasi-continuum, with a few recognizable bands² superimposed upon it. Although several limited regions, usually near fixed frequency laser wavelengths, have been successfully analyzed using laser induced fluorescence³ and microwave-optical double resonance^{4,5} techniques, there is still considerable uncertainty in the interpretation of the overall absorption spectrum, including the sharp line structures found by Douglas and Huber.² There is also a continuing problem of reconciling the short excited state lifetimes deduced from the absorption spectrum⁶ with the long measured lifetimes,^{6,7} although several workers have reported evidence of short lived intermediate states.^{5,8} We are reporting on a technique which may further help to unravel the complex spectra of simple polyatomic molecules like NO_2 .

We have measured the excitation spectrum for the ν_2 mode of NO_2 using a narrow band ($.1\text{\AA}$) nitrogen-laser-pumped dye laser.⁹ This technique allows one not only to selectively excite the NO_2 molecule, but also to monitor a particular re-emission mode. We tuned the laser through most of the visible absorption spectrum of NO_2 (4200-6000 \AA) and observed the fluorescence through a spectrometer with a bandwidth of 25 \AA . As the laser was tuned, the spectrometer was advanced so as to keep its bandpass centered on the ν_2 mode located $\sim 750 \text{ cm}^{-1}$ from the laser frequency. Our excitation spectra show several narrow regions where there are large enhancements in the intensity of the ν_2

fluorescence mode. These narrow structures, which consist of sharp and intense lines, are shown in Figure 1. For a given dye, other structures were observed, but they were either of lower intensity or did not consist of resolved sharp lines. The positions of five of the structures in Figure 1, whose leading edges are located at 18215, 19523, 21099, 21996, and 22989 cm^{-1} , are given to within 10 cm^{-1} by the following formula:

$$\nu = 18215 + 576.22N + 36.38N^2 \quad (1)$$

with N respectively equal to 0, 2, 4, 5, 6. The frequencies corresponding to N=1 and N=3 occur at gaps between the dyes and we speculate that there are similar structures in these two regions with all seven forming a smooth progression. We are uncertain of the explanation for this progression, but if it is due to vibrational spacing in the upper state, then it has a peculiar anharmonicity since the spacing between members of the progression increases with frequency. It should be noted that, of the six observed structures, only the one near 4545 Å (21996 cm^{-1}) corresponds to any of the bands reported by Douglas and Huber.² For this band, however, there is a one to one correspondence between the lines in the excitation spectrum and those in the absorption spectrum. A more detailed analysis of this band will be presented elsewhere.¹⁰

When the laser is narrowed to a bandwidth of .01 Å the excitation spectrum is more clearly resolved into individual lines as shown in Figure 2. With the laser tuned to the peak of an intense line within this structure, the ν_2 fluorescence cross-section is found to be about two orders of magnitude larger than those typically obtained using fixed frequency lasers.¹¹ This large cross-section is particularly surprising given the

fact that the absorption cross-sections we have measured at lines near 4545 Å are comparable to that of the background absorption.

These sharp and intense structures may be due to transitions to intermediate states which are not perturbed by high lying vibrational levels of the ground state.^{2,12} Such an explanation is consistent with the large enhancement we have measured. One test of this hypothesis would be to measure the fluorescence lifetime within these structures to see if they are in better agreement with the short lifetimes deduced from the absorption spectrum.

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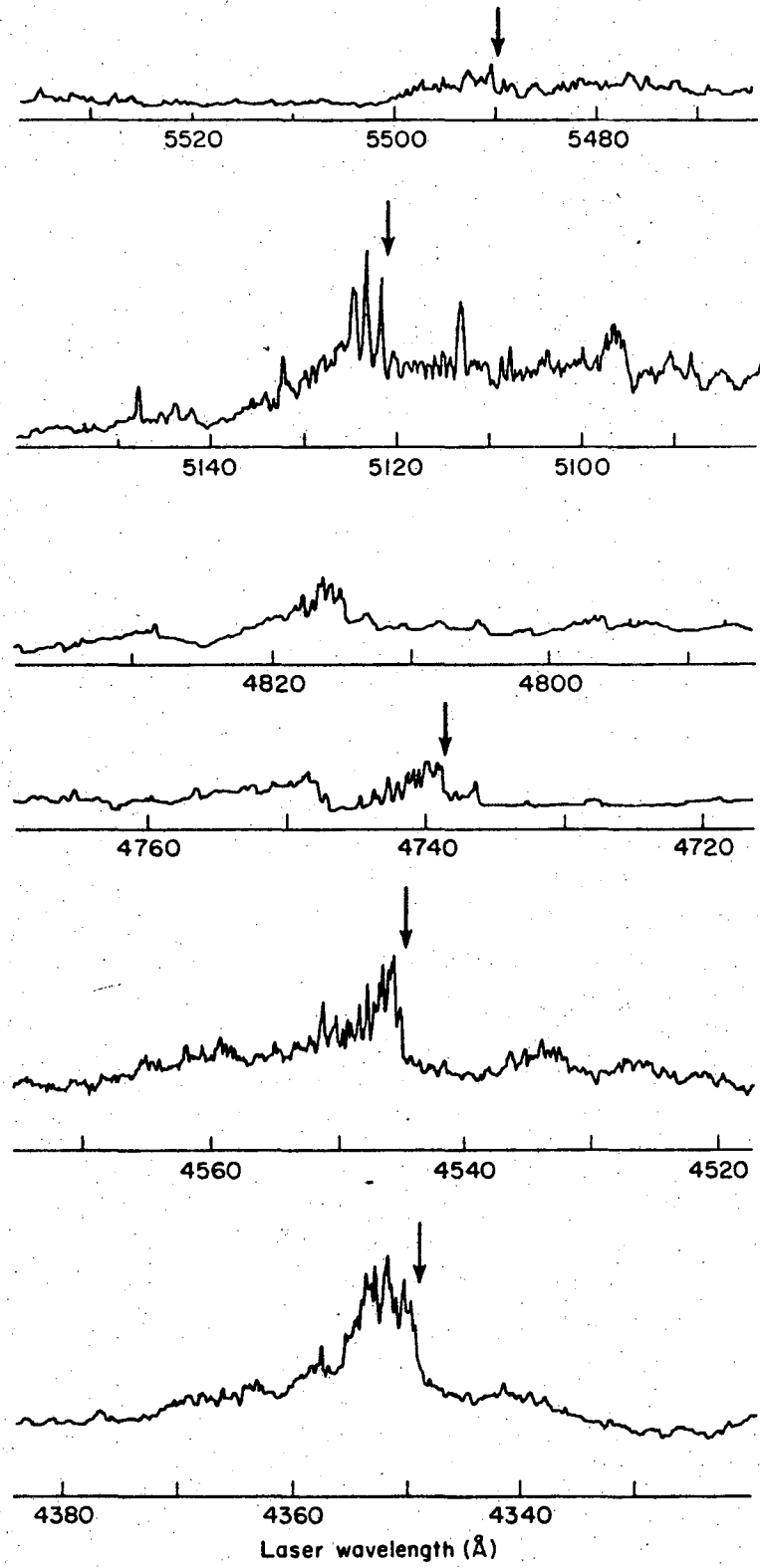
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FIGURE CAPTIONS

- 1) Intensity in the ν_2 mode as a function of laser wavelength near certain selected wavelength regions where sharp and intense structures were observed. The bandwidth of the laser was $\approx .1 \text{ \AA}$ and the spectrometer bandwidth was set to 25 \AA . The absolute intensities in the different scans can not be compared directly, due to different laser powers and scale factors. The spectra were taken from a cell containing 1 mm of NO_2 . Random fluctuations in the background were typically less than 1/5 of the maximum peak height above the background. The arrows in the figure mark the position of the leading edge of the structures used in the fit to Eq. (1).

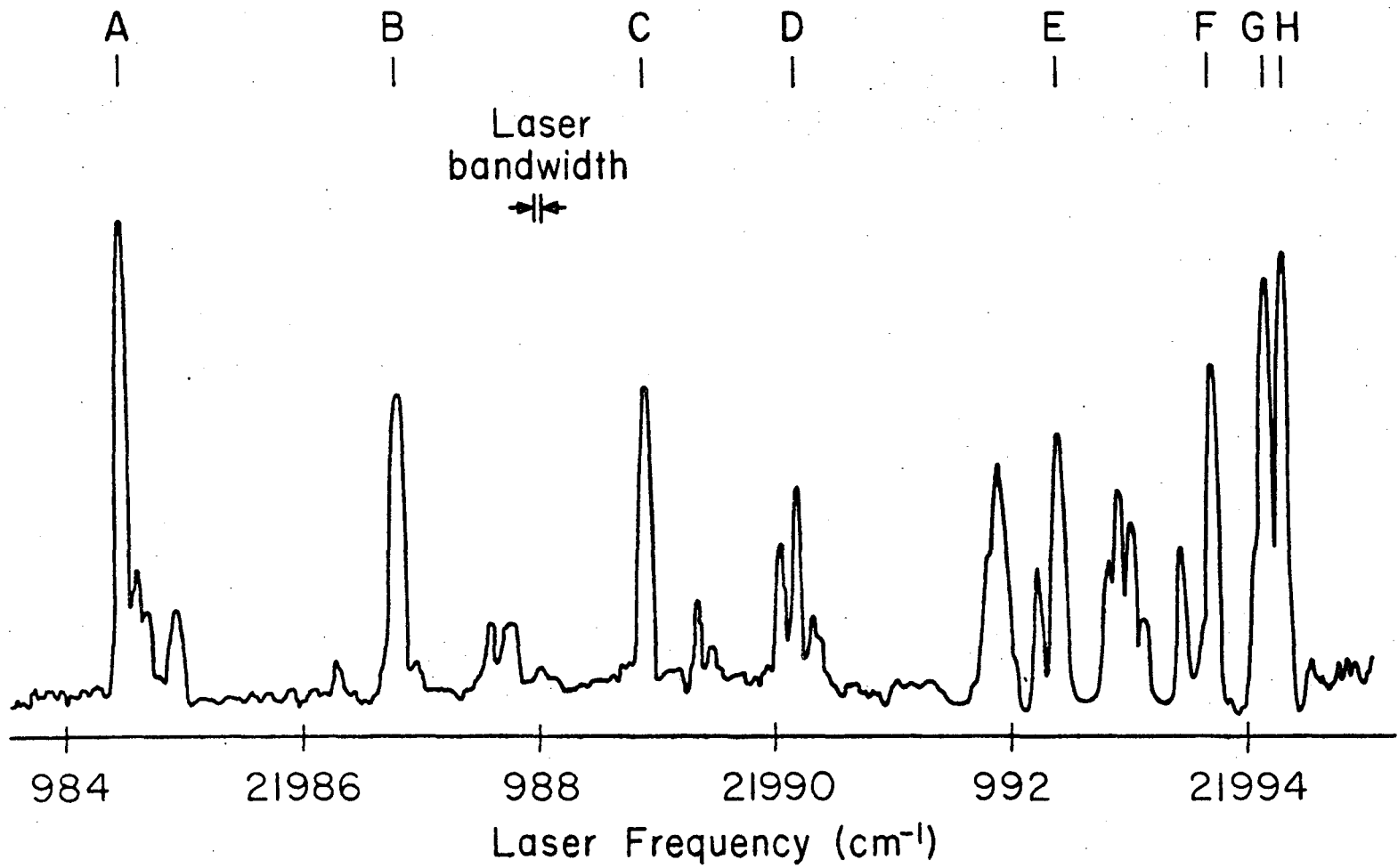
- 2) Intensity in the ν_2 mode as a function of laser frequency, near $21,996 \text{ cm}^{-1}$ (4545 \AA), with narrow band laser excitation. The linewidth of the laser was $.01 \text{ \AA}$ and the bandwidth of the spectrometer 25 \AA . The relative positions of the lines could be determined to $\pm 3\%$ and the absolute positions were set using the wavelength determination of Douglas and Huber² for the Q(13) line which corresponds to line B in our scan.

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FIGURE 1



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Figure 2

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