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STUDY OF THE SPECTROSCOPY OF $N0_2$ BY SELECTIVE EXCITATION WITH A TUNABLE LASER

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STUDY OF THE SPECTROSCOPY OF NO_2 BY SELECTIVE EXCITATION WITH A TUNABLE LASER*

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ABSTRACT

We have tuned a narrow band laser through the visible absorption spectrum of NO_2 and have observed the variation in the intensity of the ν_2 fluorescence mode located at $\sim 750 cm^{-1}$ from the incident laser frequency. Several narrow structures which consist of sharp and intense lines were found. We have investigated one of these structures, which corresponds to a set of absorption lines found by Douglas and Huber, in detail and have performed a partial rotational analysis of it by resolving the ν_2 fluorescence.

INTRODUCTION

There is an enormous body of literature on the spectroscopy of NO_2; however, there are still great uncertainties associated with the interpretation of its complex absorption spectrum, even though several limited regions have been analyzed successfully using absorption[1], laser induced fluorescence[2,3,4,5,6] and microwave-optical double resonance[7,8] techniques. There is also a continuing problem of reconciling the short excited state lifetimes deduced from the absorption spectrum with the long measured lifetimes[9], although several workers[7,10] have reported evidence of short lived intermediate states in NO_2. Recently, Stevens et. al.[5] have used high resolution fluorescence spectra excited by a tunable laser to attempt to make assignments of certain absorption features in the NO_2 spectrum near 5940 Å. Their work points out the value of tuning a laser to a particular absorption feature in order to facilitate spectroscopic analysis.

As part of a project designed to determine the feasibility of narrow-band fluorescence or resonance Raman scattering[11] as a remote pollutant monitor,[12] we have been searching for large fluorescence cross-sections from NO_2 using a narrow-band tunable dye laser. In the course of this investigation, we have looked at the intensity of the ν_2 fluorescence mode, which is located $\sim 750 cm^{-1}$ below the laser frequency, while scanning the laser from 4235 Å to 6025 Å with a bandwidth of $\sim$.1 Å. We have found several narrow regions which have greatly enhanced cross-sections.

One of these regions, which corresponds to a set of absorption lines found by Douglas and Huber[1] near 4545 Å ($22000 cm^{-1}$), has been investigated in considerable detail. For this region we have performed an analysis similar to that of Abe et. al.[2] and Stevens et. al.[5] and confirm the rotational assignments made by Douglas and Huber[1]. Our results show that these sharp structures are not due to accidental overlap of absorption lines but to well defined states in the NO_2 molecule.

EXPERIMENTAL DETAILS

The light source used in this experiment was a nitrogen-laser-pumped dye laser similar to that of Hänsch[13]. The six dye solutions used to cover the wavelength region from 4235-6025 Å are listed in Table I. The laser bandwidth was narrowed by using an intra-cavity beam expanding telescope in series with a grating which formed one end mirror of the cavity. The grating was blazed at 61° and operated in fifth or sixth order. In this configuration the laser had a bandwidth of $\sim .5 cm^{-1}$, and could be continuously tuned over the entire gain profile of a single dye by using a small clock motor to drive a micrometer which controlled the grating tilt angle. During such tuning, occasional slight adjustment of the vertical tilt of the grating was necessary to maintain maximum output power. In order to further decrease the linewidth for higher resolution scanning of a limited region, an air spaced etalon which had a free spectral range of $1 cm^{-1}$ and a finesse of about 20 was inserted between the telescope and the grating. In this configuration, the laser had a bandwidth of ∿.04cm^{-1}. The etalon and the grating were enclosed in a vacuum tight chamber so that fine tuning could be accomplished by varying the pressure within the chamber. Since pressure tuning requires no mechanical manipulation of either the grating or the etalon, the bandpass of the etalon automatically remains centered on that of the grating. Pressure tuning allows us to scan a frequency interval of 5cm^{-1} in steps of .01cm^{-1} in a stable and reproducible manner. The pressure was monitored by means of a mercury manometer.

A quantity of purified NO_2 was obtained from Dr. Harold Johnston's group in the Chemistry Department at the University of California, Berkeley. Purification[14] was carried out by first storing liquid N_2O_4 in one atmosphere of oxygen at 0°C for 24 hours. The material was then placed in a dry ice bath and uncondensed gas was removed by pumping. The condensate was then distilled from -20°C to -76°C several times, with the first portion of the distillate discarded in an attempt to remove HNO_3. A sample of the resulting gas, at 1mm pressure, was enclosed in a pyrex cell 4.5cm in diameter and 5cm long. Fluorescence from the sample was collected in a direction perpendicular to the incident beam with an f/3.4 lens and focused onto the entrance slit of a Jarrell Ash double monochromator. In order to avoid heating or dissociation of the NO_2, a cylindrical lens was placed before the sample. This lens defocused the incident laser along a line coincident with the axis of the spectrometer, forming a beam about 2mm X 3cm at the position of the sample. The incident light was polarized perpendicular to the entrance slit of the monochromator, and no attempt was made to analyze the scattered light. Light reaching the exit slit of the monochromator was detected by a photomultiplier (either RCA 8575 or RCA 7265) whose output passed through a gated integrator[15] which displayed the results on a chart recorder.

Four types of experiments were performed with the apparatus just described. First, a coarse scan was taken through the gain profiles of the six dyes listed in Table I. For this experiment, the laser did not contain the intra-cavity etalon, and its frequency was varied by using a clock motor to drive the grating mount. The spectrometer was set to the ν_2 mode of NO_2 at 750cm^{-1} from the laser frequency and was advanced by hand every time the laser scanned ∿ 7Å. The bandpass of the spectrometer was 25Å for these experiments. Any sharp, intense structure seen on this first scan was rescanned in the same manner to check reproducibility. In Fig. 1 we present the most interesting structures found with this experimental procedure. For a given dye, other structures were observed, but they were either of lower intensity or did not consist of resolved sharp lines. One of the structures shown in Fig. 1 occurs in a region described by Douglas and Huber[1] in their study of the NO_2 absorption spectrum, and we chose to investigate this region in more detail. For this purpose, we inserted the intra-cavity etalon into the laser and, with the spectrometer set 750cm^{-1} from the central frequency of the band, we used our pressure tuning to vary the laser frequency across the band. The result of this scan is shown in Fig. 2 where now one can see the individual lines resolved clearly. The spectrometer bandwidth was ∿ $120cm^{-1}$ for these experiments. The lines shown can be correlated directly with those seen in absorption by Douglas and Huber[1].

By scanning the spectrometer with the laser tuned to frequencies near line B in Fig. 2, we have taken low resolution spectra of the fluorescence from NO_2. Fig. 3 shows scans taken at laser frequency shifts of $\Delta\nu = 0, -0.04$, and $-0.2cm^{-1}$ from line B with a spectrometer bandwidth of $120cm^{-1}$. It is apparent that the intensities of the ν_2 mode and its first and second overtones are strongly frequency dependent. Finally, we have made high resolution spectrometer scans of the ν_2 mode with the laser set to the peak frequencies of the strong lines in Fig. 2 (designated by the letters A through H). The monochromator bandwidth for these experiments was set to $4cm^{-1}$. Each scan included not only the ν_2 mode, but also a Xenon calibration line located at 4697.0Å. Using this calibration line we could determine the absolute location of the ν_2 mode to about ± $.5cm^{-1}$. Some examples of these high resolution spectra are shown in Fig. 4. We have made use of the observed splittings of the ν_2 mode to identify the initial, intermediate and final rotational states for the transitions shown.

DISCUSSION

The visible absorption spectrum of NO_2 extends from about 4000Å to 7000Å[16] and has a complex structure which has been analyzed only to a limited extent. We have studied the intensity of the ν_2 fluorescence mode throughout most of the visible absorption spectrum and have observed the six intense and sharp structures shown in Fig. 1. The positions of five of these structures located at 18215, 19523, 21099, 21996 and 22990cm^{-1} are given to within 10cm^{-1} by the following formula $\nu = 18215 + 576.22N + 36.38N^2$ with N respectively equal to 0, 2, 4, 5, 6. The frequencies corresponding to N = 1 and N = 3 occur at gaps between wavelength regions covered by the dyes. We speculate that there may be similar structures corresponding to N = 1 and N = 3, with all seven strucutres forming a smooth progression. We are uncertain of the explanation for this progression; however, 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 4545Å corresponds to any of the bands reported by Douglas and Huber[1]. With the laser tuned to the peaks of the most intense lines within these structures, we observe fluorescence cross-sections into the ν_2 mode which are about 2 orders of magnitude larger than those typically observed using fixed frequency lasers[17]. For example, at the peak of line B in Fig. 2 we have measured a cross-section of 1.4×10^{-24}cm^2/sr at 1mm of NO_2 pressure. The large scattering cross sections are particularly surprising given the fact that the absorption cross-sections we have measured at lines near 4545Å are comparable to that of the background absorption. These sharp and intense structures might be due to transitions to intermediate states which are not perturbed by high lying vibrational levels of the ground state[1,18]. Such an explanation is consistent with the large enhancements we have measured.

We have investigated the band near 4545Å in much greater detail than the other bands. As shown in Fig. 2, this band has a sharp and complex structure. We have attempted to make a partial rotational analysis of this region by tuning the laser to several of the most intense lines, designated by the letters A through H in Fig. 2, and resolving the ν_2 fluorescence mode located[19] at 749.8 cm^{-1}. In Fig. 4 the resolved fluorescence for the laser tuned to lines A, B, C, E and G are presented. Since the narrow band laser selects a single initial to intermediate state transition, the observed triplet structures can be used in combination with the selection rules for a slightly asymmetric top ($\Delta N = \pm 1.0$; $\Delta K = \pm 1.0$) and the ground state spectroscopic constants, to assign the final state quantum numbers. This determination then allows one to make assignments for both the initial and intermediate states.

The rotational energy levels of a slightly asymmetric top can be written approximately as:[20]

$$E(N,K) = \frac{1}{2}(B_o+C_o)N(N+1)+[A_o-\frac{1}{2}(B_o+C_o)](1-3/8b^2-\ldots)K^2 + \Delta B^K_{eff}\, N(N+1) + \Delta D^K_{eff}\, N^2(N+1)^2+\ldots \tag{1}$$

where N and K are the quantum numbers appropriate in the symmetric top limit. The quantity b is an asymmetry parameter given by:

$$b = \frac{C_o - B_o}{2[A_o - \frac{1}{2}(C_o+B_o)]} \tag{2}$$

ΔB^K_{eff} and ΔD^K_{eff} are K dependent functions of b which vanish as b goes to zero. The formulae for ΔB^K_{eff} and ΔD^K_{eff} are given in full detail by Herzberg[20]. In equation (1) we have neglected the vibrational rotational interaction since this correction is small[21] for the first excited vibrational state. For NO_2 half of these levels are missing due to nuclear statistics. The oxygen atoms have spin 0 and therefore the total wavefunction (electronic - vibrational - rotational) must be symmetric under interchange of the oxygen nuclei. In the ground state of NO_2, both the electronic and ν_2 vibrational wavefunctions are symmetric under interchange of the oxygen atoms (they both have A_1 symmetry). Therefore, for states in which only the ν_2 vibrational mode is excited, no antisymmetric rotational levels will be found. Using equation (1) and the appropriate spectroscopic constants[19] (A_o = 8.0012cm^{-1}, B_o = 0.43364cm^{-1}, C_o = 0.41040cm^{-1}) along with Dennison's rules[22] for determining the symmetry of a rotational level, one can construct the energy level diagram of the ground state. By comparing the spacing of adjacent levels with the observed splittings in the triplet structures shown in Fig. 4,one can identify the final state of the transitions. These identifications are shown in Fig. 4 and a comparison of calculated and observed splittings is made in Table II. We can now identify the initial state quantum numbers by noting that the displacement of the emission lines from the laser frequency corresponds to the difference in energy between the initial and final vibrational-rotational states. Since the vibrational frequency of the ν_2 mode is 749.8cm^{-1} it is easy to see from Fig. 4 that the initial states for the transitions A, B, C, E and G are, respectively, $K''=1$ $N''=15$, $K''=1$ $N''=13$, $K''=1$ $N''=11$, $K''=1$ $N''=16$ and $K''=1$ $N''=14$. From the initial and final state N values and the selection rule $\Delta N = \pm 1, 0$ the corresponding intermediate state N values must be $N'=15$, $N'=13$, $N'=11$, $N'=17$ and $N'=15$. The observation of only odd N' values suggests that $K' = 0$ and the the intermediate state vibronic wave function is antisymmetric under interchange of the oxygen nuclei. For all other K' values, one would expect to observe both even and odd values of N'[22]. These assignments are consistent with those made by Douglas and Huber[1] from their high resolution absorption measurements. We have also tried to make further assignments by tuning the laser to lines D, F and H. However, the fluorescence did not show a triplet structure and could not be used for identification.

In conclusion, we would like to stress that the use of tunable lasers to excite molecules with complicated spectra seems to allow one to find regions in the spectrum which hold some promise of yielding to detailed analysis. Perhaps such analysis will help to clarify the present confusion concerning the complex spectra of simple polyatomic molecules such as NO_2.

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TABLE CAPTIONS

TABLE I: Laser dyes used in scans of NO_2 spectrum. Nitrogen laser powers were 20-25mW during these runs.

TABLE II: Comparison of calculated and measured splittings between members of triplet structures shown in Fig. 4.

TABLE I

DYE	TUNING RANGE(Å)	MAXIMUM POWER DURING SCAN (mW)
Coumarin 120	4235 - 4454	0.5
7 Diethylamino-4 Methyl-Coumarin (7D4MC)	4413 - 4714	1.5
Coumarin 102	4651 - 4935	1.8
50% (7D4MC) + 50% Coumarin 6	5014 - 5307	0.4
Fluorescein Disodium Salt	5357 - 5580	0.4
Rhodamine 6G	5712 - 6025	0.7

TABLE II

TRANSITION	FINAL STATE N VALUE	FREQUENCY SHIFT FROM CENTRAL N VALUE (cm^{-1})	
		CALCULATED	MEASURED
A	16	16.5	17.5
	15	-	-
	14	-10.0	- 9.3
B	14	14.1	13.8
	13	-	-
	12	- 9.0	- 8.8
C	12	11.8	11.7
	11	-	-
	10	- 7.9	- 7.2
E	18	20.2	19.0
	17	-	-
	16	-11.3	-11.0
G	16	16.5	16.7
	15	-	-
	14	-10.0	-10.1

FIGURE CAPTIONS

1) Intensity in the ν_2 mode as a function of laser wavelength over wavelength regions where sharp and intense structures were observed. The bandwidth of the laser was ≃ .1Å and the spectrometer bandwidth was set to 25Å. The intensities in different scans can not be compared directly due to variations in laser power and detector sensitivity.

2) Intensity in the ν_2 mode as a function of laser frequency, near 22,000cm^{-1} (4545Å), with narrow band laser excitation. The linewidth of the laser was ∿.04cm^{-1} and the bandwidth of the spectrometer 120cm^{-1}. The relative positions of the lines could be determined to ± 3% and the absolute positions were set using the wavelength determination of Douglas and Huber[1] for the Q(13) line which corresponds to line B in our scan.

3) Low resolution scans of the fluorescence taken with laser frequency shifts of 0, -0.04 and -0.2cm^{-1} from line B of Fig. 2. The bandwidth of the spectrometer was 120cm^{-1} and the laser bandwidth was .04cm^{-1}.

4) High resolution spectrometer scans of the ν_2 mode located ∿ 750cm^{-1} lower in frequency than the laser. The laser was tuned to the peaks of lines A, B, C, E and G of Fig. 2. The

K and N values refer to the final state of the various transitions. The spectrometer bandwidth was 4cm^{-1} and the laser bandwidth 0.04cm^{-1}.

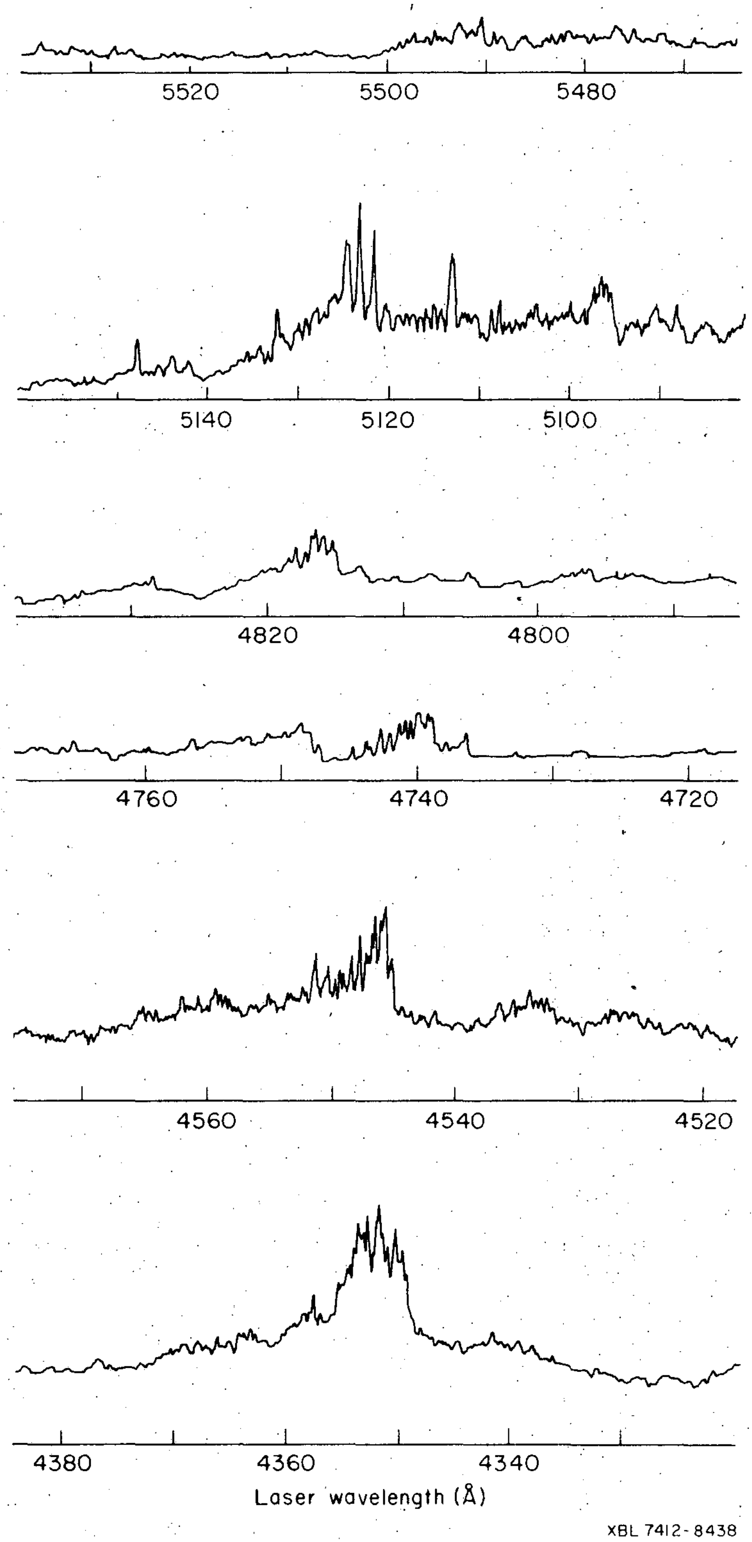
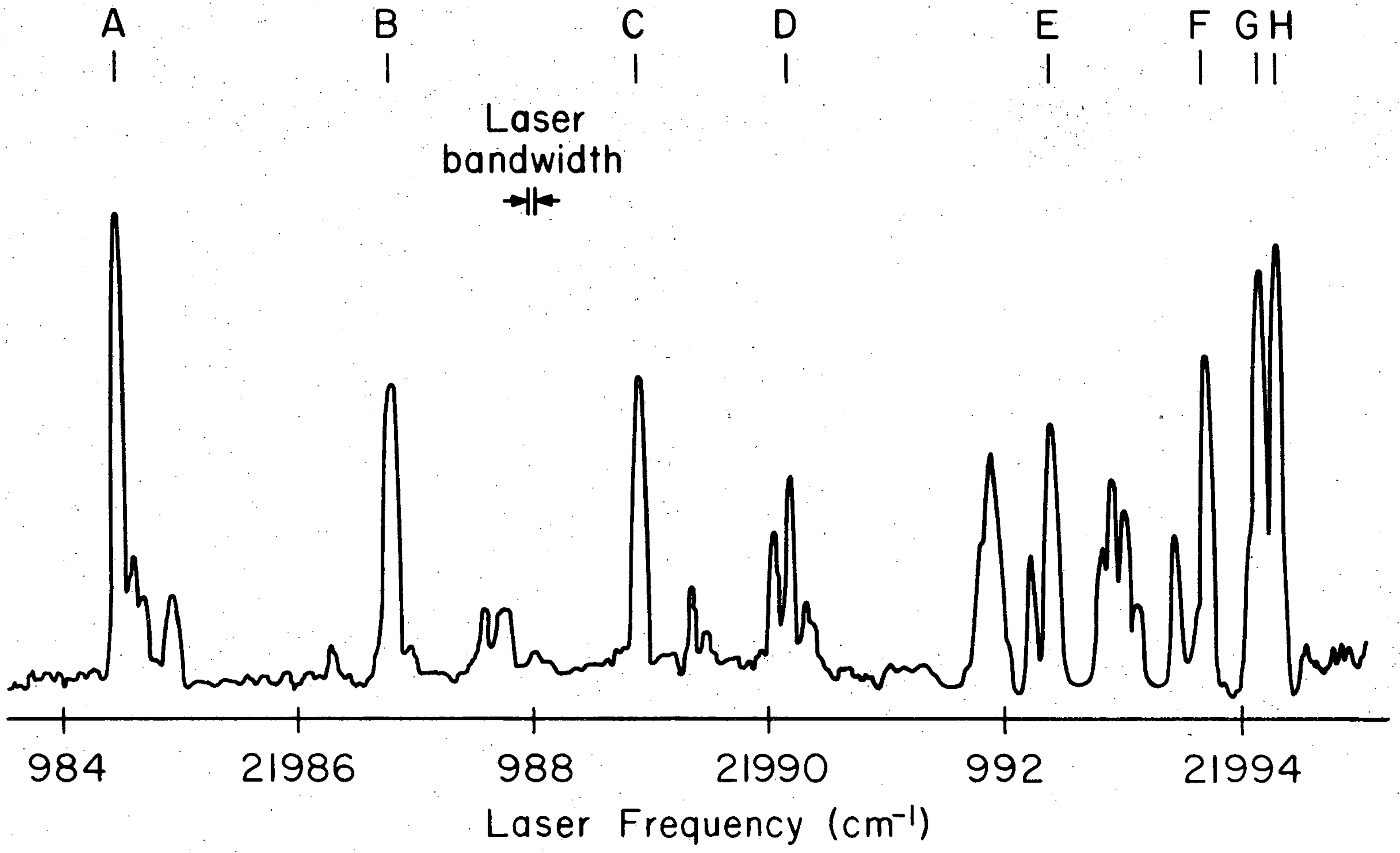

5520
5500
5480
5140
5120
5100
4820
4800
4760
4740
4720
4560
4540
4520
4380
4360
4340
Laser wavelength (Å)
XBL 7412-8438

FIGURE 1



XBL 7412-8437

FIGURE 2

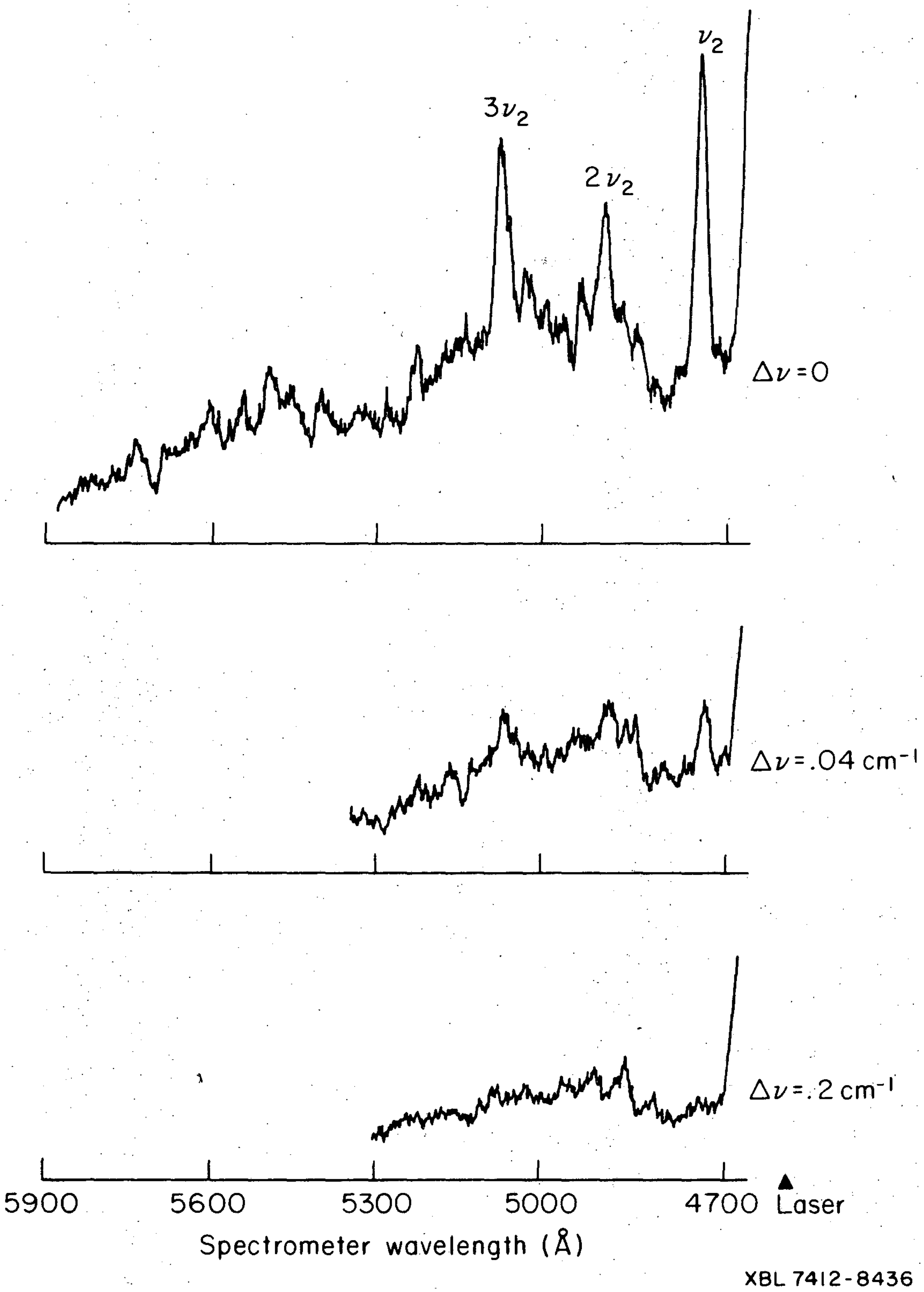
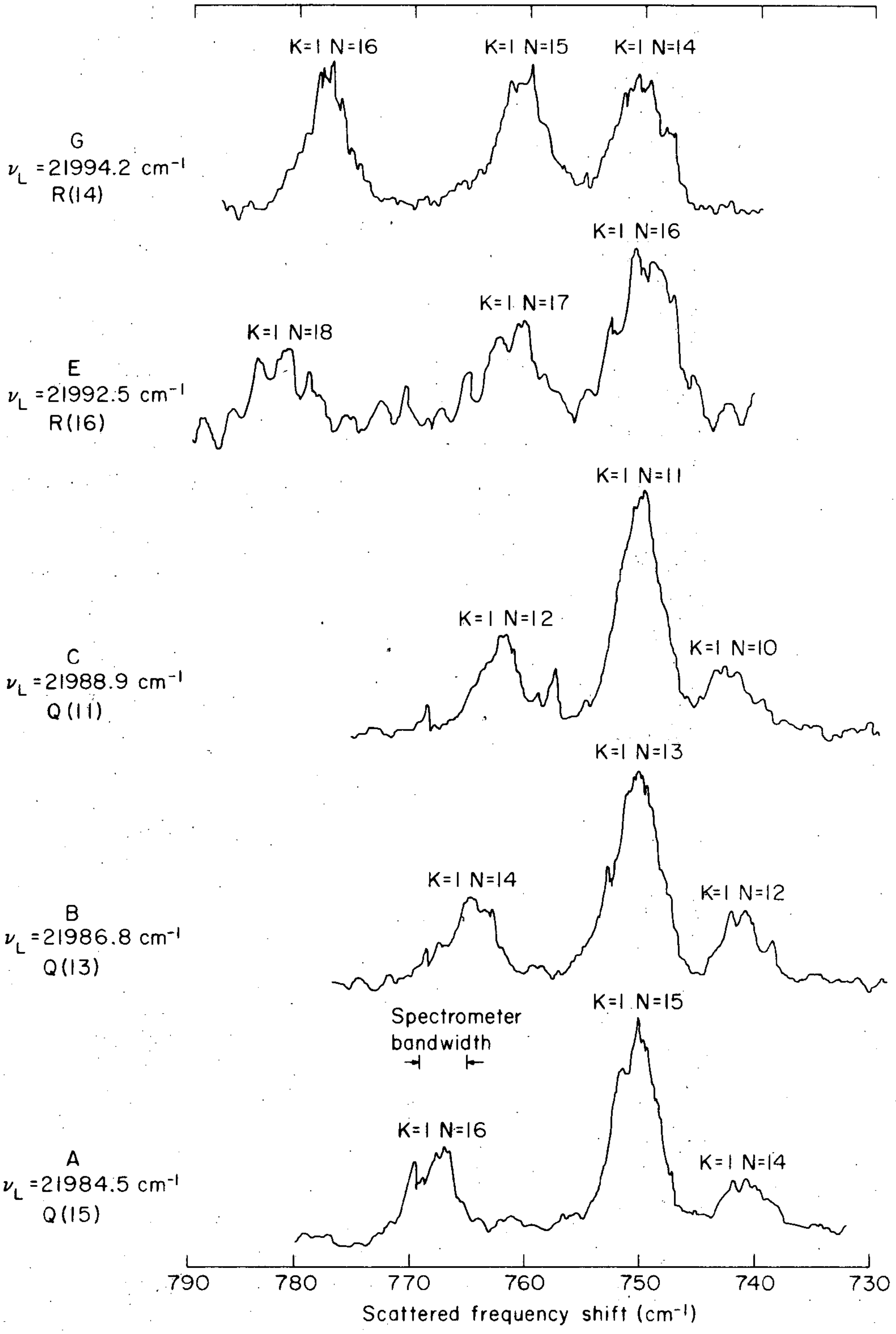

ν_2
$3\nu_2$
$2\nu_2$
$\Delta\nu=0$
$\Delta\nu=.04\ \mathrm{cm}^{-1}$
$\Delta\nu=.2\ \mathrm{cm}^{-1}$
5900
5600
5300
5000
4700
▲ Laser
Spectrometer wavelength (Å)
XBL 7412-8436

FIGURE 3



XBL 7412-8439

FIGURE 4

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