

Microwave optical double resonance of NO<sub>2</sub> with a tunable cw dye laser\*Takehiko Tanaka<sup>†</sup>, Alan D. English, Robert W. Field, Donald A. Jennings<sup>‡</sup>, and David O. Harris

Quantum Institute, University of California, Santa Barbara, California 93106

(Received 11 June 1973)

Nitrogen dioxide is known to have a complicated spectrum in the visible region. Recent investigations of the NO<sub>2</sub> spectrum have employed photoluminescence excited by ion lasers<sup>1,2</sup> or by a pulsed dye laser<sup>3</sup> and microwave optical double resonance (MODR) with an Ar<sup>+</sup> laser.<sup>4</sup>

We report a complete rotational assignment of four NO<sub>2</sub> absorption lines at 593.6 nm by MODR using a tunable cw dye laser. A similar technique has been used in an investigation of the microwave spectrum in the A<sup>1</sup>Σ excited state of BaO.<sup>5</sup> The present experiment shows the power of dye laser MODR for investigating complex optical spectra.

NO<sub>2</sub> was flowed through a stainless steel photoluminescence cell at a pressure of <10 mtorr. A single frequency, 50 mW, cw, rhodamine 6 G dye laser was used to excite NO<sub>2</sub>. Photoluminescence from NO<sub>2</sub> was photoelectrically monitored through a short wavelength cutoff filter. Microwave radiation generated by a 700 mW klystron was introduced into the photoluminescence region via a horn radiator. The phase-locked klystron was swept repetitively at a rate of 0.05 MHz/channel in synchronism with a 100 channel signal analyzer which averaged the output of a photomultiplier. Various fine and hyperfine components of the 9<sub>1,9</sub> - 10<sub>0,10</sub> rotational transition of the ground vibronic state of NO<sub>2</sub> are near 40 GHz.<sup>6</sup> Strong components at 40.661, 40.671, 40.703, 40.931, 40.964, and 40.993 GHz were used for the MODR experiment. The first three and the last three frequencies correspond to  $J=19/2-21/2$  and  $J=17/2-19/2$  spin components, respectively.

The upper part of Fig. 1 shows the "absorption" spectrum of NO<sub>2</sub> near 593.6 nm obtained by scanning the dye laser while photoluminescence was observed. Separations between adjacent lines were measured ( $\pm 10\%$ ) by monitoring the frequency of the laser with a spectrum analyzer. Wavelengths of the lines a, b, and d were measured ( $\pm 0.01$  nm) as 593.65, 593.63, and 593.61 nm by scanning a spectrometer which simultaneously viewed the laser and a mercury lamp, using the Hg 296.73 nm line in second order as a wavelength standard.

The four lines designated as a, b, c, and d were

observed to give a MODR effect. For a and c, MODR was observed at microwave frequencies 40.661, 40.671, and 40.703 GHz, but no signal was detected at 40.931, 40.964, and 40.993 GHz. Conversely, for b and d MODR was observed only at the latter three frequencies. In all cases the MODR signal appeared as an increase (typically 1%) of photoluminescence at microwave resonance with a linewidth of 1 MHz FWHM. S/N was 3-10 after averaging for two minutes.

The a line was assigned as follows. The photoluminescence transition to  $v_2''=1$  near 620 nm was

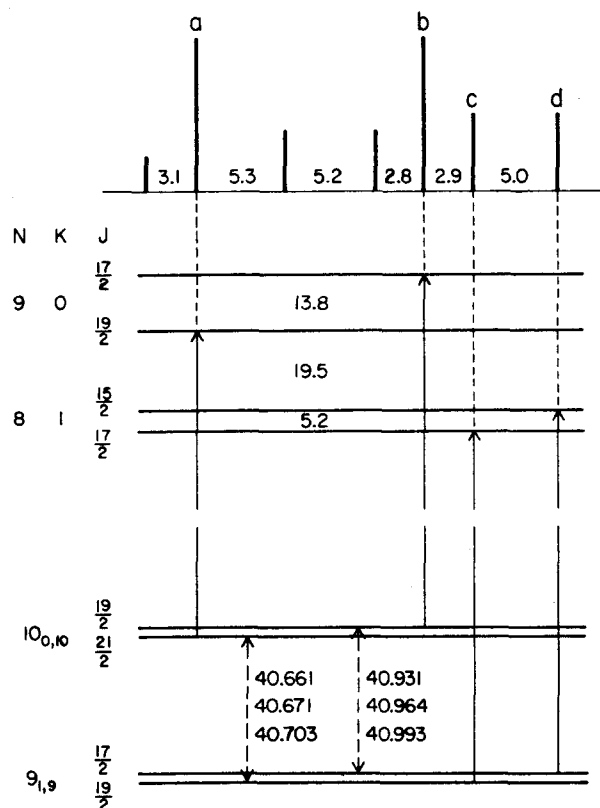


FIG. 1. Assignment of "absorption spectrum" of NO<sub>2</sub> near 593.6 nm as determined by photoluminescence. Frequency separations are marked in GHz. Spin splittings in the ground state have been exaggerated. Optical and microwave transitions are shown by solid and broken arrows, respectively.

observed as a pair of lines separated by 0.62 nm with almost equal intensity, assignable as *P* and *R* branch lines of a parallel type band ( $\Delta K=0$ ). The observed separation between *P* and *R* photoluminescence lines gave the upper state rotational quantum number  $N'=9$ . From the measured wavenumber difference between the laser and the *P* branch photoluminescence line we concluded that the laser coincided with a *P* branch line. The same method was applied to assign *b*. Thus both *a* and *b* were identified as transitions from  $10_{0,10}$  of the ground state to  $N'=9, K'=0$  of the excited state. Since these two lines were observed by MODR to be connected with different spin components of the microwave transition, these lines were assigned as different spin components of an optical transition. The  $J'$  assignment was made assuming the laser pumped optical transitions with  $\Delta J=\Delta N$ . *c* and *d* were assigned similarly. Assignments for the three unlettered lines have not been made. Figure 1 summarizes the assignment and the pertinent energy levels. Either *a* or *b* is the line identified as a *P*(10) transition by Stevens *et al.*<sup>3</sup>

Spin splittings found in the excited state are very large compared with those in the ground state. The molecule is likely to be bent in the excited state,

since we have observed both  $K'=0$  and  $K'=1$  levels. However, there is a remote possibility that these two levels belong to different vibronic states. MODR detection of the excited state microwave transition  $N'=9, K'=0 \rightarrow N'=8, K'=1$  might prove these levels belong to a single nonlinear vibronic state.

\*This research was supported by Army Grant No. DA-ARO-D-31-124-72-G181, NSF Grant No. GP-35672X, and AFOSR Grant No. AFOSR-70-1851.

†Visiting Scientist from the Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka, Japan.

‡On leave from the National Bureau of Standards, Boulder, Colorado 80302.

<sup>1</sup>K. Sakurai and H. P. Broida, *J. Chem. Phys.* **50**, 2404 (1969).

<sup>2</sup>K. Abé, F. Myers, T. K. McCubbin, and S. R. Polo, *J. Mol. Spectrosc.* **38**, 552 (1971).

<sup>3</sup>C. G. Stevens, M. W. Swagel, R. Wallace, and R. N. Zare, *Chem. Phys. Lett.* **18**, 465 (1973).

<sup>4</sup>R. Solarz and D. H. Levy, *J. Chem. Phys.* **58**, 4026 (1973).

<sup>5</sup>R. W. Field, A. D. English, T. Tanaka, D. O. Harris, and D. A. Jennings, *J. Chem. Phys.* **59**, 2191 (1973).

<sup>6</sup>(a) G. R. Bird, J. C. Baird, A. W. Jache, J. A. Hodgeson, R. F. Curl, Jr., A. C. Kunkle, J. W. Bransford, J. Rastrup-Andersen, and J. Rosenthal, *J. Chem. Phys.* **40**, 3378 (1964). (b) R. M. Lees, R. F. Curl, Jr., and J. G. Baker, *J. Chem. Phys.* **45**, 2037 (1966).