

Laser induced fluorescence of the 0-6, 1-6, and 0-5 bands of the transition $AO_u^+ - XO_g^+$ of Bi_2

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Analysis of the 0-6, 1-6, and 0-5 bands of the $A-X$ transition of Bi_2 with a single-mode, tunable cw dye laser gave the following rotational constant values: A state: $B'_0 = 0.0196426(15)$, $10^9 D'_0 = 1.742(25)$, $B'_1 = 0.0195911(15)$, $10^9 D'_1 = 1.719(30)$; X state: $B''_0 = 0.0225136(15)$, $10^9 D''_0 = 1.622(25)$, $B''_1 = 0.0224593(15)$, $10^9 D''_1 = 1.598(30)$.

The electronic symmetries of the A and X states are confirmed to be O_u^+ and O_g^+ , respectively, supporting the assignment of the X state as the ground state.

En utilisant un laser à colorant continu, accordable, mono-mode, on a analysé les bandes 0-6, 1-6 et 0-5 de la transition $A-X$ de Bi_2 . On a obtenu les valeurs suivantes des constantes de rotation: état A : $B'_0 = 0.0196426(15)$, $10^9 D'_0 = 1.742(25)$, $B'_1 = 0.0195911(15)$, $10^9 D'_1 = 1.719(30)$; état X : $B''_0 = 0.0225136(15)$, $10^9 D''_0 = 1.622(25)$, $B''_1 = 0.0224593(15)$, $10^9 D''_1 = 1.598(30)$. On a confirmé que les symétries électroniques des états A et X sont respectivement O_u^+ et O_g^+ en se basant sur l'attribution de l'état X en tant qu'état fondamental.

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Introduction

The Bi_2 molecule is the least known dimer in the 5th column of the periodic table because its spectrum is rendered very complex by its large reduced mass and many electronic states. There is now a considerable body of experimental evidence showing the great usefulness of fluorescence techniques employing a tunable single-mode laser in the study of such dense spectra (for example, refs. 1-4).

Moreover, the richness of its spectrum and the width of its lines (~ 0.020 cm⁻¹ fwhm, less than that of I_2) make the Bi_2 molecule an interesting candidate for the establishment of a secondary standard atlas. The large number of lines facilitates the construction of an optically pumped laser. Laser emission in the $A-X$ transition was obtained by West and Broida (5) pumping with a pulsed dye laser and by Wellegehausen *et al.* (6) with the 5145 Å line of the Ar^+ laser. The cw laser had excellent conversion efficiency (about 10%) and an output power of 350 mW.

The first laser fluorescence studies of Bi_2 were performed by Gerber *et al.* (7) (and extended by Gerber and Broida (8)). They used several Ar^+ lines and a broad-band Rhodamine 590 cw dye laser. Many results were obtained with the fixed-frequency laser (in acci-

dental coincidence with some molecular transitions) and led, in particular, to the detection of new electronic states. However, their lack of a tunable single-mode laser meant that they were unable to fully control their experiment.

Exploration of part of the domain covered by Rh590 with a tunable single-mode continuous dye laser was performed by using the technique of excitation spectroscopy. The total intensity of the fluorescent emission was recorded as a function of the frequency of the dye laser. Since the bandwidth of the laser (~ 1 MHz) was much narrower than the Doppler broadened absorption lines, the resolution was Doppler-limited. The spectrum obtained by the excitation technique is similar to an absorption spectrum, but the sensitivity is much greater. Some fixed-frequency laser fluorescence patterns were spectrally resolved to facilitate determination of the absolute rotational numbering.

The only rotational analysis carried out so far on the Bi_2 molecule was that of Åslund *et al.* (9), who studied the 8-0, 9-0, and 11-0 bands of the $A-X$ system obtained in absorption.

This paper reports the application of laser excitation spectroscopy to the 16 676 to 16 866 cm⁻¹ spectral region covering 0-6, 1-6, and 0-5 bands of the $A-X$ transition. The frequency domain covered by Rh590 is much larger, and we also observed intense fluorescence with Rh640 and 560. Nevertheless, we confined our

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attention to a small part of the spectrum because the dye laser provides continuous scans of only 1 cm^{-1} spectral intervals, making complete coverage of the $12\,500\text{--}22\,000 \text{ cm}^{-1}$ extent of the $A\text{--}X$ transition very tedious.

Experimental

The Bi_2 spectrum was obtained with a Broida-type oven (10) using an argon flow to carry the bismuth vapour into the laser excitation region and with a King furnace. Most spectra were recorded with the King furnace at temperatures of about 1000 K. The carbon heating element was pierced vertically to allow the laser beam to pass and fluorescence was observed horizontally. Bismuth was loaded into two molybdenum crucibles placed symmetrically on either side of the laser beam. A charge of a few grams was enough for several hours of work.

Fluorescence of the $A\text{--}X$ system was excited by a Coherent Model CR599-21 dye laser (1 MHz jitter) employing Rh590 and pumped by a Coherent CR12 Ar^+ laser. The single-mode operation of the dye laser was monitored during each scan by a Model 240 Tropel spectrum analyser (30 GHz free spectral range).

A series of 30 GHz (1 cm^{-1}) scans was made. By adjusting the angle of the thin etalon, one can hop two thick etalon modes (20 GHz) to provide overlapping scans.

The total fluorescence was detected by a Hamamatsu R928 photomultiplier. The fluorescence could also be analysed by a Jobin-Yvon THR monochromator equipped with a thermoelectrically cooled Hamamatsu R928 photomultiplier. The laser beam was mechanically chopped at 1 KHz to eliminate detection of the thermal radiation from the oven and the signal was detected by a Tekelec 9602 lock-in amplifier.

Part of the laser beam was used for simultaneous recording of the iodine excitation spectrum. The Bi_2 lines were calibrated using the Gerstenkorn and Luc I_2 atlas (11). Relative frequency calibration was supplied by the fringes of a temperature-stabilized Fabry-Perot etalon with a 200 MHz free spectral range. The 0.0056 cm^{-1} correction suggested by Gerstenkorn and Luc (12) was applied in calculating the wavenumbers of the Bi_2 lines. The I_2 and Bi_2 lines were about 0.03 and 0.020 cm^{-1} wide, respectively, due to the Doppler effect and unresolved hyperfine structure. The absolute accuracy of the Bi_2 lines was of the order of $0.002\text{--}0.003 \text{ cm}^{-1}$. This uncertainty is primarily attributable to the reference lines, and could be reduced by using an interferometric device, such as a lambda-meter (13, 14).

Rotational numbering

In their rotational analysis of bands 8-0, 9-0, and 11-0, Åslund *et al.* (9) discussed the question of num-

bering at some length. Briefly, their procedure provided a relative numbering of the branches of two bands with a common vibrational level by using the fit between the common combination differences and comparing trial values of α with those calculated from the Pekeris relation. Absolute numbering was determined from least squares fits of the term values for different given values of J . The selection of the corrected numbering was based on: (i) the quality of the fit between the calculated and the observed term values and (ii) the agreement between the ω value given by the Kratzer relation and the value deduced from the vibrational analysis.

It should be pointed out that (i) was an inadequate criterion for their data. The choice made by Åslund *et al.* (9) was determined by the ω value. In our case, however, accuracy and resolution were greatly enhanced by the use of laser excitation techniques. Unambiguous numbering, therefore, was readily accomplished using criterion (i).

A. Relative numbering

Near their head, the bands studied display wide regions where R and P lines are overlapped. When the laser was tuned to one of these lines, the fluorescence pattern from the selected levels and the rotational levels populated by collisional relaxation clearly established the relative numbering of the R and P series. In addition, measurement of the interval $R(J-1) - P(J+1)$ from the fluorescence spectrum gave the value of J (i.e., the absolute numbering) with an uncertainty of one or two units, using the previously published spectroscopic constants (9).

B. Absolute numbering

Direct comparison was made between the observed and the calculated R and P wavenumbers for each line. The rotational energies involved in the transition were described by the usual expression:

$$F(J) = T + BJ(J+1) - DJ^2(J+1)^2$$

The parameters were iteratively improved by applying the least squares program described by Athenour (15). Different rotational numberings were tested and the RMS error was used to choose the correct one.

Results and discussion

A set of 774 lines belonging to the three bands were identified, of which 718 were retained for their good quality.²

Table I summarizes the evolution of the RMS error as a function of ΔJ , the shift from the best numbering.

²The list of vacuum wavenumbers (Table A.1) is available, at nominal charge, from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Canada K1A 0S2.

TABLE 1. Evolution of the RMS error (10^{-3} cm^{-1}) with the numbering, each band treated separately

ΔJ	-3	-2	-1	0	+1	+2	+3
0-5 band (325 lines)	146.0	95.7	46.7	2.4	47.0	91.6	134.9
0-6 band (159 lines)	47.5	34.6	18.7	2.3	18.2	35.2	50.8
1-6 band (234 lines)	106.3	69.4	33.9	2.0	33.4	65.2	95.8

TABLE 2. Constants deduced from the analysis of the 0-5, 0-6, and 1-6 bands of the A-X transition (in cm^{-1})

	$v' = 0$	$v' = 1$	$v'' = 5$	$v'' = 6$
T_v''	16 866.5703(4)	16 998.3394(9)	0	168.4700(8)
B_v''	0.0196429(15)	0.0195904(15)	0.0225139(15)	0.0224586(15)
$10^6 D_v''$	1.756(25)	1.692(30)	1.636(25)	1.571(30)

NOTE: Numbers in parentheses are twice the standard error.

"Taking $T_v'' = 0$.

It can be seen that the results allow the absolute numbering to be determined without ambiguity. The global treatment of the three bands gives the constants presented in Table 2.

Quite apart from its importance in the determination of molecular constants, the establishment of the absolute numbering enables the symmetry of the states involved in the transition to be discussed.

Åslund *et al.* (9) assigned the symmetries O_u^+ and O_g^- to the A and X states, respectively. These assignments were based on the fact that the spectrum displayed only two branches and on the assumption that the X state, having the lowest observed energy, was the ground state. The electronic configuration of the X state can be given by analogy with the ground state of N_2 and can only give rise to a O_g^+ state. Note that a description based on Hund's case (c) notation is appropriate for the heavier Group V elements. Gerber and Broida's (8) observation of an X' state, which they assigned to Bi_2 and placed 1500 cm^{-1} below the X state, led them to reconsider the nature of A and X states and to suggest that they have O_u^- and O_g^- symmetry respectively. The intensity alternation of successive rotational lines permits a choice between the O^+ and O^- alternatives.

The spectrum displays the intensity alternation typical of homonuclear molecules. The odd J lines, where J is the quantum number of the lower state, are the most intense. For a half integer nuclear spin (here 9/2) the nuclei follow Fermi statistics and the antisymmetric levels have the greater weight. Thus our results indicate that for the state X the odd J levels are antisymmetric. This is the case for a O_g^+ state (negative odd J levels for

an O^+ state, and antisymmetric negative levels for a g state), but not a O_g^- state (see Herzberg, ref. 16, p. 246).

Our conclusions are in agreement with the interpretation of recent rare gas matrix isolation experiments on Bi_2 (17-20) by Bondybey and English (18). These workers have shown that the X state is indeed the ground state of Bi_2 and that the X' state probably belongs to Bi_4 .

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