

Matrixisolated bismuth. I. The AX band system of Bi₂ in solid argon

Fakhruddin Ahmed and Eugene R. Nixon

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Matrix-isolated bismuth. I. The $A \rightarrow X$ band system of Bi_2 in solid argon

Fakhruddin Ahmed and Eugene R. Nixon

Department of Chemistry, and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

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The $A \rightarrow X$ fluorescence system of the Bi_2 molecule in solid argon has been explored by means of tunable dye laser radiation. About 135 bands involving A state levels from $v' = 0$ to $v' = 6$ and X state levels up to $v'' = 26$ are observed. Analysis yields ω_e values of 133.4 and 174.3 cm^{-1} for the A and X states, respectively, and a band system origin at 17 719 cm^{-1} . The Raman spectrum of the fundamental vibration and two overtones of Bi₂ appear along with the fluorescence.

I. INTRODUCTION

In a recent paper on the absorption and fluorescence of bismuth in solid argon and krypton matrices,¹ we reported among other features the $A-X$ absorption system previously observed for the gaseous Bi_2 molecule.² In the argon matrix case our derived values of ω_e and $\omega_e x_e$ for the A state were very close to those given for the

vapor. Our estimate of 17859 cm^{-1} for the ν_{00} of the $A-X$ system was just slightly higher than the 17719 cm^{-1} gas value.³ The only emission we reported at that time, aside from some obviously due to the atomic species, was a reasonably intense system with $\nu_{00} = 12395$, $\omega_e'' = 151$, and $\omega_e x_e'' = 0.1\text{ cm}^{-1}$. That fluorescence, along with the corresponding absorption system ($\nu_{00} = 12395$ and $\omega_e' = 123\text{ cm}^{-1}$) were attributed to Bi, even

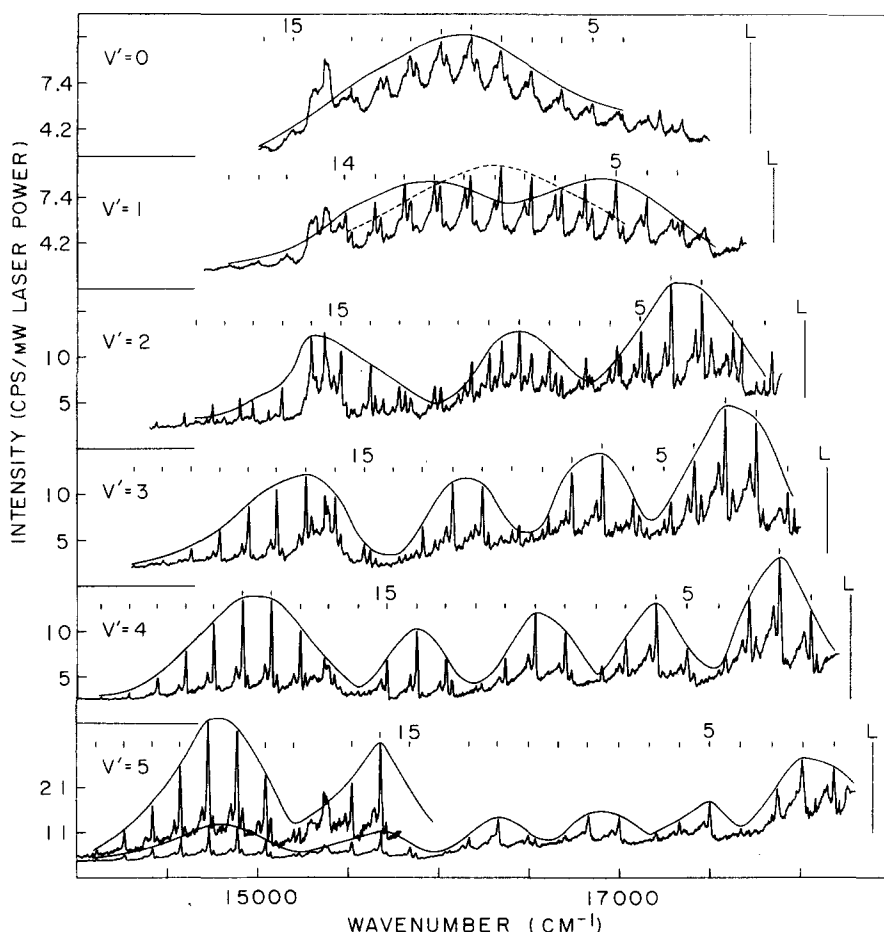


FIG. 1. The $A \rightarrow X$ fluorescence system of Bi_2 in solid (unannealed) argon matrix at 10 K. The largely unrelaxed emission shown for the $V' = 0, 1, 2, 3, 4$, and 5 levels of the A state was obtained by irradiation with the dye laser lines indicated by L. From top to bottom of the figure, dye laser frequencies (cm^{-1}) and power (mW) were 17 725 (200), 17 854 (200), 18 024 (130); 18 149 (130); 18 279 (140); and 18 399 (120). Band positions for the transitions from each V' level are marked above each spectrum and labeled with the V'' number. Curves are added to outline the intensity profiles. The lower frequency portion of the $V' = 5$ spectrum is also shown on an expanded intensity scale. Features not identified in the figure are discussed in the text.

TABLE I. Deslandres table for $A-X$ system of Bi_2 .

V''	0	1	2	3	4	5	6
0							
1			17 811	17 941	18 070	18 202	
			172	172	170	170	
2			17 639	17 769	17 900	18 032	
			172	172	170	171	
3	17 200	17 334	17 467	17 597	17 730	17 861	
	171	170	171	171	170	172	
4	17 029	17 164	17 296	17 426	17 560	17 689	
	171	172	170	170	171	172	
5	16 858	16 992	17 126	17 256	17 389	17 517	
	169	168	169	168	172	169	
6	16 689	16 824	16 957	17 088	17 217	17 348	
	168	169	169	170	170	169	
7	16 521	16 655	16 788	16 918	17 047	17 179	
	168	168	169	169	168	170	
8	16 353	16 487	16 619	16 749	16 879	17 009	
	168	169	167	167	166	168	
9	16 185	16 318	16 452	16 582	16 713	16 841	
	167	167	167	166	168	166	
10	16 018	16 151	16 285	16 416	16 545	16 675	
	168	166		166	166	168	
11	15 850	15 985		16 250	16 379	16 507	16 641
	168	165		165	164	164	168
12	15 692	15 820		16 085	16 215	16 343	16 473
	166	163		165	165	165	163
13	15 526	15 657	15 790	15 920	16 050	16 178	16 310
	165	164	165	164	165	163	165
14	15 361	15 493	15 625	15 756	15 885	16 015	16 145
	162	163	162	162	162	162	161
15	15 199	15 330	15 463	15 594	15 723	15 853	15 984
		164	162	162	162	163	165
16		15 166	15 301	15 432	15 561	15 690	15 819
		158	161	160	162	161	161
17		15 008	15 140	15 272	15 399	15 529	15 658
		157	158	159	159	158	158
18		14 851	14 981	15 111	15 240	15 371	15 500
			159	159	158	158	159
19			14 822	14 952	15 082	15 213	15 341
				158	160	159	
20				14 794	14 922	15 054	
				156	157	159	

TABLE I (Continued)

v''	v'	0	1	2	3	4	5	6
21					14 738	14 765	14 895	15 023
					156	127	130	128
						157	157	156
22					14 482	14 608	14 738	14 867
						126	130	129
						157	157	155
23						14 451	14 581	14 712
						155	130	131
							156	155
24						14 296	14 425	14 557
						155	129	132
							156	157
25						14 141	14 269	14 400
							128	131
							154	154
26							14 115	14 246
								131

though the ω_e'' of 151 cm^{-1} was drastically smaller than the 172.7 cm^{-1} value given for the ground state X of the gaseous molecule.² Interpretation of the bismuth spectrum was made more puzzling by the conclusion of Gerber *et al.*³⁻⁴ on the basis of their gas spectra that the electronic ground state of Bi_2 was not the previously accepted X state but rather their X' state lying about 1500 cm^{-1} below X and having an ω_e of 154 cm^{-1} .

Most recently Bondybey and English⁵ have reinvestigated bismuth in neon and argon matrices. They report that their argon absorption spectra agree with ours but they demonstrate that the two lower frequency absorption systems with origins at 15250 and 12396 cm^{-1} and respective vibrational spacings of 131 and 123 cm^{-1} are due to the same species responsible for the 12395 cm^{-1} emission system and further that this species is not Bi_2 . They provide evidence for proposing the tetrahedral Bi_4 molecule as the most likely candidate.

While Bondybey and English report that they observed no emission resulting from excitation of the $A \rightarrow X$ absorption bands of Bi_2 , our experimental conditions did permit us to record about 135 bands of the weak $A \rightarrow X$ fluorescence system. These observations establish 174 cm^{-1} as the value of ω_e for the ground state of the molecule in an argon matrix.

II. EXPERIMENTAL METHODS AND RESULTS

As in our previous work,¹ the matrices were formed by condensing onto a polished copper finger (at 10 K) argon gas and the effluent from a Knudsen-type cell containing bismuth metal (Baker Analyzed Reagent, 99.98% assay) heated to about 600°C . The rates of deposition of the argon and the bismuth vapor over the 1 h deposition period resulted in a very pale pink matrix whose concentration we estimate was about $1500:1$ in g atom ratio.

The fluorescence spectra reported here were excited

by means of a dye laser containing rhodamine (Exciton 560) pumped by about 3.5 watts of the green line (19436 cm^{-1}) of an argon ion laser. The dye laser was tuned into the phonon sideband regions lying just to the high frequency sides of the zero phonon lines (ZPL) of successively higher frequency vibronic bands in our $A \rightarrow X$ absorption system.¹ The results are shown in Fig. 1.

III. DISCUSSION

We point out first that we did not anneal our matrices to avoid the loss in emission intensity that attends that process. As a consequence we observe, particularly in the $v'=0$ fluorescence and to a lesser extent with each of the other v' level excitations (Fig. 1), emission features centered about 15375 cm^{-1} , which we are convinced corresponds to the $^3D_{5/2}^0 \rightarrow ^4S_{3/2}^0$ transition occurring at 15438 cm^{-1} in the gaseous bismuth atom.⁶ The emission bands arising from the $v'=0$ level of the A state of Bi_2 (top panel of Fig. 1) are not as sharp as the others; the set of weaker peaks to the high frequency side of the labeled ones are probably due to Bi_2 molecules in a second matrix site. A similar second side effect in unannealed matrices was observed with the 12395 cm^{-1} emission system.¹

Excitation of the matrix with 17854 cm^{-1} radiation results in roughly equally intense emission from the $v'=1$ and $v'=0$ levels. When Bi_2 is pumped into the $V'=2$ state, the fluorescence bands originating in that level are dominant but emission from $V'=1$ and $V'=0$ is significant. With $v'=3$ excitation, successively weaker emission bands originating from $V'=2$, 1, and 0 also appear. Only weak $v'=3$ transitions accompany the $v'=4$ bands when 18279 cm^{-1} pump radiation is used and similarly weak $V'=4$ transitions are observed along with the more intense $V'=5$ bands when the matrix is irradiated with the 18399 cm^{-1} laser line. The conclusion is that especially for levels above $v'=1$, most of

TABLE II. Molecular constants for Bi_2 .

State	ν_{00}	Gas ^a		ν_{00}	Ar matrix	
		ω_e	$\omega_e x_e$		ω_e	$\omega_e x_e$
X	0	172.98 (173.03) ^b	0.385 (0.384)	0	174.3 ₄	0.39 ₃
A	17719.1	132.49	0.302	17719	133.4	0.4

^aReference 3.^bReference 7.

the emission intensity comes from the vibrationally unrelaxed molecule.

We turn our attention now to those few features in the spectra which are clearly not ZPL's or accompanying phonon sidebands of the $A \rightarrow X$ system of Bi_2 . In the $v' = 5$ spectrum there is a sharp weak band at 18227 cm^{-1} , 172 cm^{-1} to the red of the exciting line. Correspondingly, a weak peak appears at 18105 cm^{-1} in the $V' = 4$ spectrum, shifted by 174 cm^{-1} from the laser frequency. These clearly are the Raman fundamentals of Bi_2 . In the $v' = 3$ emission, the Raman fundamental and first overtone appear with shifts of 172 and 344 cm^{-1} at 17977 and 17805 cm^{-1} . The 18024 cm^{-1} laser line which pumps the $V' = 2$ level of the A state also produces Raman bands at 17854 , 17685 , and 17517 cm^{-1} with shifts of 170 , 339 , and 507 cm^{-1} .

On the low frequency end of the $v' = 2$ fluorescence is a series of weak sharp peaks at 15067 , 14911 , 14754 , 14600 , and 14446 cm^{-1} , even spaced at about 155 cm^{-1} . In the $V' = 0$ and $V' = 1$ emission spectra three peaks with spacing of about 123 cm^{-1} appear at 17481 , 17358 , and 17235 cm^{-1} . Further discussion of these two sets of weak bands will be given elsewhere.

The frequencies of the observed ZPL's of the $A \rightarrow X$ system of Bi_2 are collected in Table I. A least squares fit of the data gives the vibrational constants for the A and X states shown in Table II. These constants reproduce almost all of the frequencies to within $\pm 1 \text{ cm}^{-1}$. Table II compares the matrix constants with those given for the gaseous molecule and it is clear that the matrix perturbation of the molecule is a very slight effect.

The intensity contours of the fluorescence spectra in Fig. 1 show that the most intense $V' = 0$ transition is to $V'' = 9$. For $V' = 1$, the intensity maxima occur at $V'' = 5$ and $V'' = 11$. Similarly the transitions from $V' = 2$ to $V'' = 4$, 9 , and 16 give emission maxima; the four maxima for $V' = 3$ fall at $V'' = 3, 7, 11$, and 17 , etc.

We have not attempted any Franck-Condon factor calculations but we have examined our results in light of the potential energy functions tabulated by Gerber and Broida⁴ for the A and X states. Their RKR curves, derived from spectroscopic constants for gaseous Bi_2 , have equilibrium bond lengths of about 2.66 and 2.86 \AA for the X and A states. Constructing their curves and overlaying them with harmonic oscillator wave functions shows that the maxima in each v' vibrational wave function occur at internuclear distances which fall slightly inside the outer turning points of the X state curve at just the predicted v'' levels. Thus our fluorescence intensities are qualitatively consistent with the gas molecule data.

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- ¹R. A. Teichman III and E. R. Nixon, J. Chem. Phys. **67**, 2470 (1977).
- ²G. M. Almy and F. M. Sparks, Phys. Rev. **44**, 365 (1933); G. Nakamura and T. Shidei, Jpn. J. Phys. **10**, 11 (1934); N. Aslund, R. F. Barrow, W. G. Richards, and D. N. Travis, Ark. Fys. **30**, 171 (1965).
- ³G. Gerber, K. Sakurai, and H. P. Broida, J. Chem. Phys. **64**, 3410 (1976).
- ⁴G. Gerber and H. P. Broida, J. Chem. Phys. **64**, 3423 (1976).
- ⁵V. E. Bondybey and J. H. English, J. Chem. Phys. **73**, 42 (1980).
- ⁶Atomic Energy Levels, Natl. Bur. Stand. Circ. 467, Vol. III (1958).
- ⁷J. M. Blondeau, G. Gandara, P. Carette and J. Messelyn, Chem. Phys. Lett. **71**, 246 (1980).