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Fakhruddin Ahmed

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# Fluorescence spectra of matrix-isolated BiS, BiSe, and BiTe

Fakhruddin Ahmed<sup>a)</sup>

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

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Laser-induced fluorescence spectra are reported for BiS, BiSe, and BiTe for the first time in argon matrices. A total of nine band systems have been observed, out of which eight are believed to be new low energy electronic states of these molecules. Two of these belong to BiSe, and three each to BiS and BiTe.

## I. INTRODUCTION

The absorption spectra of BiS<sup>1</sup>, BiSe,<sup>1-3</sup> and BiTe<sup>2</sup> have been reported in the gas phase. For BiS, the lowest-lying transition has been attributed to  $A^2\Pi_{1/2}-X^2\Pi_{1/2}$ . For the heavier BiSe and BiTe molecules, with a very large spin-orbit coupling, this transition is better described by Hund's case (c) approximation as  $A\Omega = 1/2-X\Omega = 1/2$ .<sup>1</sup> Rotational analysis was carried out for four red-degraded BiS bands of this system. It was found that, as in the corresponding system of BiO,<sup>4</sup> both BiS and BiSe rotational lines were broadened due to unresolved nuclear magnetic hyperfine structure<sup>1</sup> between the <sup>209</sup>Bi nucleus and a  $\pi$  electron. The two BiSe and five BiTe high energy upper states reported in the ultraviolet<sup>2</sup> must be Rydberg states. The  $A-X$  system of gaseous BiS has been examined in laser resonance fluorescence.<sup>1</sup>

Recently, in two papers,<sup>5,6</sup> we established the ground state vibrational frequency for diatomic bismuth and reported a new emission system for the molecule in solid argon matrices. At the same time, in our work on the group VIB-VIB molecules, we reported at least one new electronic state each for the Se<sub>2</sub>,<sup>7</sup> Te<sub>2</sub>, TeS, and TeSe<sup>8</sup> molecules in inert matrices. An inspection of the published work in the literature suggested that more work needed to be done on the spectra of BiS, BiSe, and BiTe. With the expectation that cryogenic temperatures in an inert rare gas matrix environment would reveal unknown electronic transitions, we decided to investigate the spectra of these bismuth-group VIB diatomic molecules.

We report the emission spectra of these molecules, for the first time, in argon matrices. In all, we observe three systems each for BiS, BiSe, and BiTe molecules. Except for the  $D-X$  system of BiSe, all are hitherto unknown transitions. The 32 400 cm<sup>-1</sup> system that appears in the absorption spectra of BiS matrices, is probably the  $B^3\Sigma_u^- - X^3\Sigma_g^-$  system of S<sub>2</sub> molecule, well known in the gas phase.

In no case do we observe the  $A^2\Pi_{1/2}-X^2\Pi_{1/2}$  system reported for BiS ( $T_e \leq 13\,344$  cm<sup>-1</sup>) and BiSe ( $T_e \leq 13\,235$  cm<sup>-1</sup>) in the gas phase. These band systems are probably red shifted to beyond the sensitivity of our PM tube (11 500 cm<sup>-1</sup>).

## II. EXPERIMENTAL DETAILS

The samples of BiS, BiSe, and BiTe were prepared from naturally occurring elements. Stoichiometric amounts were sealed under vacuum in quartz tubes and heated for 1 h at 800 °C.

Vapors of the materials were produced by heating BiS (520 °C), BiSe (520 °C), and BiTe (440 °C) in a Knudsen-type cell. In each case the matrix was formed by condensing the particular vapor and argon gas at rates of about 1  $\mu$ mol and 15 mmol/h, respectively onto a polished copper finger maintained at approximately 10 K in the Air Products Displex Refrigerator.

Fluorescence spectra of the molecules in argon matrices were excited by Coherent Radiation Ar<sup>+</sup> and Ar<sup>+</sup>/Kr<sup>+</sup> laser lines and recorded on a Spex Ramacomp system. The absorption spectrum was recorded with the help of a Cary 14 spectrometer.

## III. RESULTS AND DISCUSSION

### A. BiS

The  $A^2\Pi_{1/2}-X^2\Pi_{1/2}$  system with  $T_e \leq 13\,343.9$  cm<sup>-1</sup> is the only BiS transition known in the gas phase. Unfortunately, we do not see the corresponding transition in the matrices, presumably for PM sensitivity reasons stated earlier. Instead we observe three new, vibrationally relaxed, fluorescence systems for BiS within the spectral range 14 000–21 000 cm<sup>-1</sup> in argon matrices. The lowest energy system, which we label  $B-X$ , is the weakest in intensity and reveals 11 bands with a peak to peak separation of about 400 cm<sup>-1</sup>. The bands are rather broad and difficult to measure [Fig. 1(a)]. Annealing did not sharpen the bands or bring out the ZPLs. We put the system origin  $\nu_{00}$  for this system at 18 400 cm<sup>-1</sup>. The nine bands of our  $C-X$  system give the best ZPLs [Fig. 1(b)]. This system appears with the 4765 Å laser line excitation but not with the 4880 Å line; our  $\nu_{00}$  at 20 652 cm<sup>-1</sup> lies between these two laser frequencies as expected. The ZPLs give 407.98 and 1.57 cm<sup>-1</sup> as the lower state vibrational constants  $\omega_e''$  and  $\omega_e''x_e''$ , respectively, for BiS. Comparison of these constants with those of the gas phase (Table I) indicates that they belong to the ground state  $X^2\Pi_{1/2}$  of BiS. The  $C-X$  system overlaps with the  $D-X$  system on the high frequency side [Fig. 1(c)]. The latter system with five measured bands has an origin  $\nu_{00}$  around 21 200 cm<sup>-1</sup>. For all these band

<sup>a)</sup> Present address: Department of Chemistry, Princeton University, Princeton, NJ 08544.

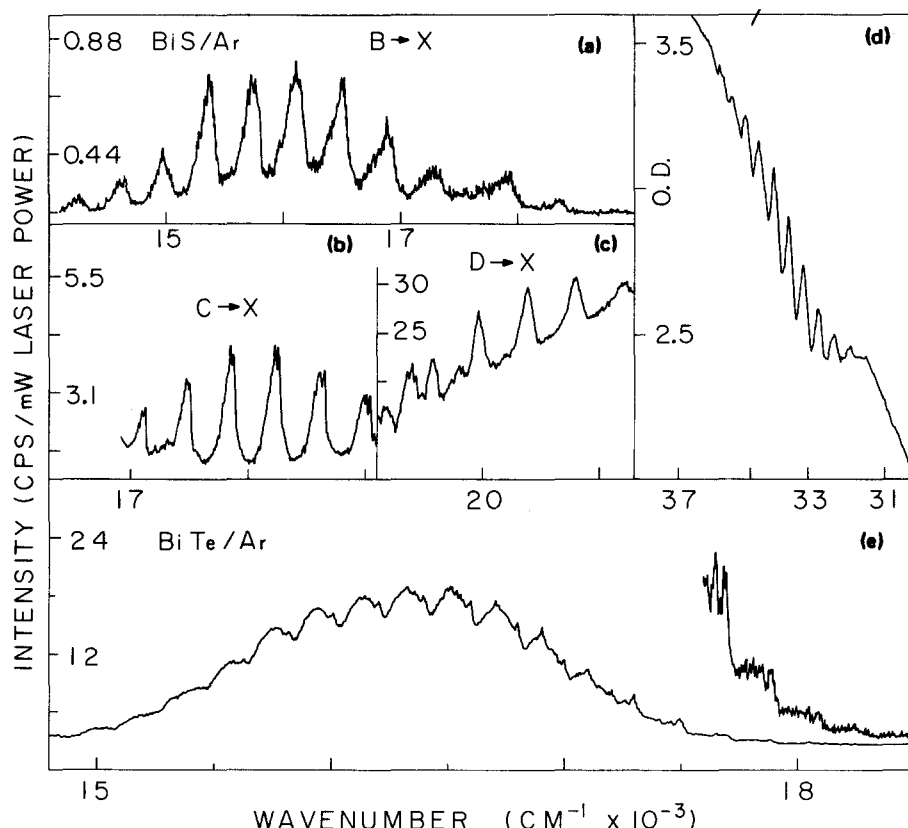


FIG. 1. Spectra of BiS and BiTe in argon matrices. Panels (a)–(c) show three new electronic transitions for BiS in emission. (b) and (c) were excited by the unresolved UV lines of Ar<sup>+</sup> laser (300 mW). (a) was excited by 3 W in the 5145 Å Ar<sup>+</sup> line. The absorption spectrum (d) is due to the  $B^3\Sigma_u^- - X^3\Sigma_g^-$  transition of S<sub>2</sub> molecule. Panel (e) shows the two new, overlapping states of BiTe emitting into the ground state. The first few bands on the high frequency side are shown on a more sensitive scale. Excitation is provided by the 5145 Å line of the Ar<sup>+</sup> laser (500 mW).

systems, annealing (30 min at 30 K) reduced the emission intensity without sharpening the bands.

Figure 1(d) shows an absorption band system observed

TABLE I. Molecular constants for BiS, BiSe, and BiTe.

BiS						
State	Vapor			Ar Matrix		
	$\nu_{00}$	$\omega_e$	$\omega_e x_e$	$\nu_{00}$	$\omega_e$	$\omega_e x_e$
X	0	408.71	1.46	0	407.98	1.57
A	13 323.9	303.74	1.159			
B				18 400		
C				20 652		
D				21 206		
Bi <sup>Nat</sup> Te						
X	0	208.5	0.52	0	207.92	0.67
A						
B				15 500		
C				18 025		
D				18 723		
E	(42 870)	(164.4)	(0.4)			
F	43 116	263	0.96			
Bi <sup>78</sup> Se <sup>a</sup>						
X	0	(264.8) <sup>b</sup>	0.4	0	264.0	0.61
A	13 235.7	190.9	0.59			
B				17 000		
C				19 950		
D	20 411	169.4	0.8	20 341		
E	35 618	304.0	2.0			
F	44 425	316.0	2.0			

<sup>a</sup> Gas phase values for Bi<sup>80</sup>Se.

<sup>b</sup>  $\Delta G_{1/2}$  value.

in concentrated BiS matrices which we originally thought was another new BiS system. It now appears that this is the  $B^3\Sigma_u^- - X^3\Sigma_g^-$  system of S<sub>2</sub>, well known in the gas phase ( $T_e = 31\,835\text{ cm}^{-1}$ ,  $\omega'_e = 434\text{ cm}^{-1}$ ,  $\omega'_e x'_e = 2.7\text{ cm}^{-1}$ ). The upper state vibrational frequencies are similar ( $\omega'_e \simeq 420\text{ cm}^{-1}$  in our case), and the band system seems to have a gas to matrix red shift of about  $365\text{ cm}^{-1}$ .

## B. BiSe

Three relaxed emission system are observed for matrix-isolated BiSe. For reasons explained earlier, again the gas phase  $A-X$  system is not observed. These three systems span the range  $12\,000\text{--}20\,000\text{ cm}^{-1}$ . As in the case of BiS, the lowest frequency  $B-X$  system, comprising of 17 bands, separated by  $250\text{ cm}^{-1}$ , between  $17\,000$  and  $12\,000\text{ cm}^{-1}$  are too broad for any meaningful peak frequency measurements (Fig. 2). The matrix annealing process did not sharpen these bands enough for isotopic correlation. We put the origin of this system around  $17\,000\text{ cm}^{-1}$ . It was easier to pin down the band origin of the  $C-X$  system, which exhibits 13 bands between  $17\,000$  and  $20\,000\text{ cm}^{-1}$ . The transition is excited by  $4965\text{ Å}$  ( $20\,141\text{ cm}^{-1}$ ) line, but not by  $5017\text{ Å}$  ( $19\,932\text{ cm}^{-1}$ ). The two isotopic bands,  $^{209}\text{Bi}^{80}\text{Se}$  and  $^{209}\text{Bi}^{78}\text{Se}$ , come to a common origin at  $19\,950\text{ cm}^{-1}$  yielding ground state vibrational frequencies  $\omega'_e = 264.00\text{ cm}^{-1}$ ,  $\omega'_e x'_e = 0.6\text{ cm}^{-1}$  for  $^{209}\text{Bi}^{78}\text{Se}$ . These compare well with the reported gas phase values of  $\Delta G_{1/2} = 264.8\text{ cm}^{-1}$  and  $\omega'_e x'_e = 0.4\text{ cm}^{-1}$  for  $^{209}\text{Bi}^{80}\text{Se}$  (Table I). As Fig. 2 bottom panel shows, annealing the matrix (20 min at 35 K), sharpens the selenium ZPL isotopic bands (lines mark the  $^{209}\text{Bi}^{79}\text{Se}$  peaks in the figure), and yields a broad, somewhat structured side band. The annealing process presumably increases the homogene-

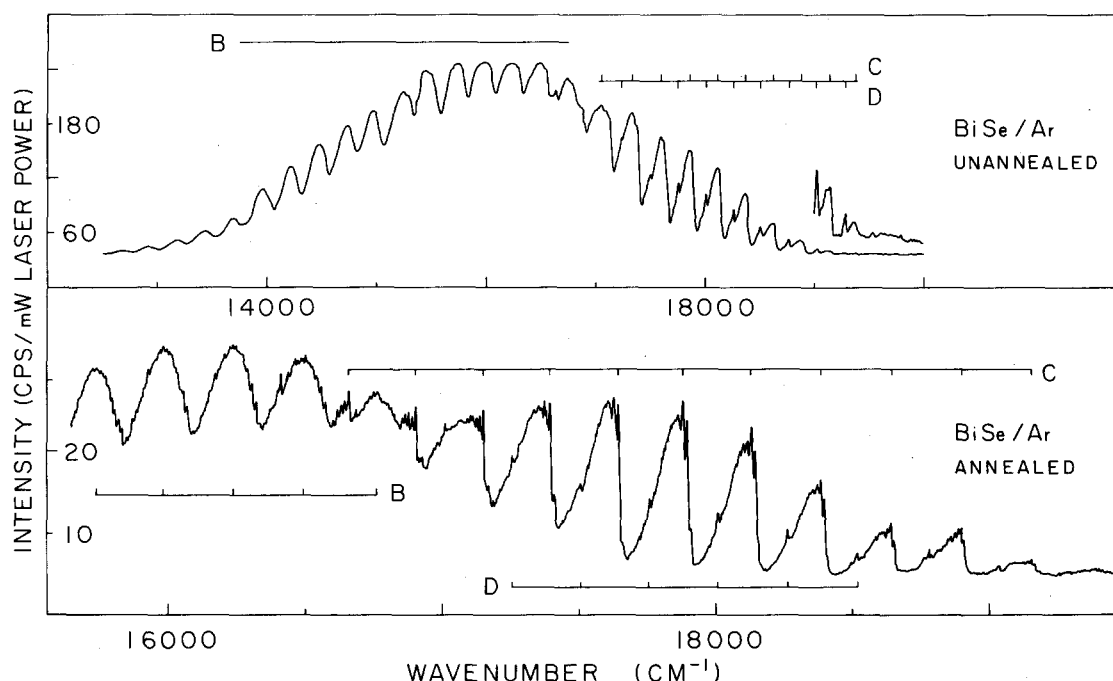


FIG. 2. Effects of annealing on the spectra of BiSe in solid argon. The top panel shows the new band systems of BiSe,  $B, C, D \rightarrow X$ , excited by the 4545 Å line of  $\text{Ar}^+$  laser (300 mW). The lower panel shows the same three systems on an expanded scale after the matrix had been annealed for 20 min at 35 K. Bands due to the selenium isotopes can clearly be seen for the  $C \rightarrow X$  transition. Lines mark  $^{78}\text{Se}$  peaks.

ity of the matrix so as to sharpen the bands. The 12 bands of the  $D-X$  system consist of only  $^{209}\text{Bi}^{78}\text{Se}$  molecule. The lowest frequency laser line that excites this transition is 4880 Å (20 436  $\text{cm}^{-1}$ ), and the system origin at 20 341  $\text{cm}^{-1}$  gives  $\omega_e'' = 264.13 \text{ cm}^{-1}$ ,  $\omega_e''x_e'' = 0.56 \text{ cm}^{-1}$  for the  $^{209}\text{Bi}^{78}\text{Se}$  molecule, in good agreement with the  $C-X$  transition.

### C. BiTe

Although the  $A\Omega = 1/2 - X\Omega = 1/2$  system has not been reported for BiTe in the gas phase, by comparison with BiO, BiS, and BiSe, one would assume that it would lie around 13 000  $\text{cm}^{-1}$  for BiTe. Once again the low frequency insensitivity of our PM tube made it unrealistic for us to expect to observe the transition. No low frequency transition has been reported for BiTe even in the gas phase. The lowest reported gaseous transition is around 34 000  $\text{cm}^{-1}$ .<sup>2</sup> For BiTe in argon matrices, we observe three new vibrationally relaxed fluorescence systems, heavily overlapping with each other [Fig. 1(e)]. Two systems, comprised of about nine bands each, lie between 19 000 and 15 000  $\text{cm}^{-1}$ . Both are excited by the 5145 Å  $\text{Ar}^+$  line (500 mW). Since isotopically mixed natural tellurium has been used in this study, the bands are rather broad. The  $B-X$  system appears at 18 400  $\text{cm}^{-1}$  in BiS and at 17 000  $\text{cm}^{-1}$  in BiSe. If the analogy holds, for BiTe it should appear around 15 500  $\text{cm}^{-1}$ . Indeed it does. We observe ten very weak, broadbands between 15 500 and 13 500  $\text{cm}^{-1}$ , with peak separations of 200  $\text{cm}^{-1}$ . We label it  $B-X$ . We label the next two systems as  $C-X$  and  $D-X$ . Close examination of the spectra suggest that the origin, for the  $C-X$  and  $D-X$  systems are 18 025 and 18 723  $\text{cm}^{-1}$ , respectively. The above assignments give for  $D-X$

ground state vibrational constants,  $\omega_e'' = 207.92 \text{ cm}^{-1}$ ,  $\omega_e''x_e'' = 0.67 \text{ cm}^{-1}$ , and for  $C-X$   $\omega_e'' = 207.67 \text{ cm}^{-1}$ ,  $\omega_e''x_e'' = 0.71 \text{ cm}^{-1}$ . These frequencies are quite close to the gas phase constants  $\omega_e'' = 208.5 \text{ cm}^{-1}$ ,  $\omega_e''x_e'' = 0.52 \text{ cm}^{-1}$ , for  $\text{Bi}^{\text{Nat}}\text{Te}$  (Table I). Matrix annealing does not sharpen the bands, only reduces the band intensity.

The frequencies of the zero phonon lines are given for all the measured bands in Table II. These frequencies are reproduced within  $\pm 1 \text{ cm}^{-1}$  by the molecular constants given in Table I.

### IV. DISCUSSION

In all of the band systems for which vibronic bands were well resolved, the spacings correspond very closely to the  $\omega_e$ 's for the ground states of the gaseous molecules. In the systems for which the bands were broad, the approximate  $\omega_e$ 's also correspond to the gaseous ground states. Therefore, it seems very reasonable that all the systems have the ground states of the molecules concerned as their terminal states.

Our excitations spanned the range 19 436–22 202  $\text{cm}^{-1}$ . In some cases we were able to define the range within which emission could be excited. Therefore, there is no reason to believe that two-photon processes were occurring.

Since the gas phase data for these molecules are rather sketchy, we have not tried to rigorously correlate our matrix results with vapor phase data. We have labeled our systems sequentially, from low to high energy. If one assumes moderate gas to matrix shifts, then the only obvious correlation would be between the 20 341  $\text{cm}^{-1}$  system of the matrix-isolated BiSe and the so-called  $B$  state of the gas phase at 20 411  $\text{cm}^{-1}$ , for which only vibrational analysis has been

TABLE II. Peak frequencies ( $\text{cm}^{-1}$ ) of  $v' = 0 \rightarrow v''$  bands of the fluorescence systems of BiS, BiSe, and BiTe in argon matrices.

C-X system			
$v''$	BiS	$^{209}\text{Bi}^{78}\text{Se}$	$\text{Bi}^{\text{Nat}}\text{Te}$
0			
1			
2	19 845		
3	19 446	19 165	
4	19 049	18 905	17 209
5	18 659	18 647	17 005
6	18 271	18 390	16 805
7	17 884	18 137	16 611
8	17 501	17 883	16 407
9	17 120	17 629	16 213
10	16 744	17 377	16 019
11		17 127	15 826
12		16 877	15 634
13		16 629	
D-X system			
0	21 206		
1	20 801		
2	20 400	19 816	18 311
3	20 001	19 555	18 107
4	19 605	19 296	17 904
5		19 039	17 703
6		18 783	17 503
7		18 524	17 305
8		18 268	17 108
9		18 014	16 912
10		17 759	16 717
11		17 508	
12		17 256	
13		17 009	

reported.<sup>3</sup> We believe that the unambiguous identification of the upper electronic states would have to await rotational analysis in the gas phase. Poor Franck-Condon factors involving low vibrational quantum numbers of the ground state, plus a modest red shift on the band system origin, might well move the observable transitions of the gaseous  $A-X$  system from  $13\,236\text{ cm}^{-1}$  in BiSe, for example, out of our experimental detection range.

For these molecules, the ground state electronic configuration is known to be  $\pi^4\sigma^2\pi^*$ ,  $^2\Pi_r$ , with  $X$  clearly the  $\Omega = 1/2$  of this state. Based on matrix work alone, it is not possible to ascertain what the upper electronic states might be. The  $A\ ^2\Pi_{1/2}$  state is regarded as one of the states of the configuration  $\pi^3\sigma^2\pi^{*2}$ . This configuration also yields  $^2\Pi_i$ ,  $^2\Pi$ , and  $^4\Pi_i$ . The  $B$  state of  $\text{BiO}^4$  is identified with the  $\Omega = 1/2$  component of the  $^4\Sigma^-$  state arising from the configuration  $\pi^4\sigma\pi^{*2}$ , and the  $C$  state is best described as the  $\Omega = 3/2$  component of the  $^2\Delta_{3/2}$  state from the same configuration. This configuration also corresponds to  $^2\Sigma^+$ ,  $^2\Sigma^-$  states. Our low lying, upper electronic states for BiS, BiSe, and BiTe could be the appropriate case (c)  $\Omega$  components of any of these states.

Our data are consistent for all the three molecules. The corresponding electronic states lie progressively lower in energy as one goes from lighter to heavier molecules. For example, we observe the  $B-X$  transition at  $18\,400\text{ cm}^{-1}$  in BiS, at  $17\,000\text{ cm}^{-1}$  in BiSe, and at  $15\,500\text{ cm}^{-1}$  in BiTe. The  $C-X$  system shows up at  $20\,652\text{ cm}^{-1}$  (BiS),  $19\,950\text{ cm}^{-1}$  (BiSe), and  $18\,025\text{ cm}^{-1}$  (BiTe). And finally, the origin of the  $D-X$  system is at  $21\,206\text{ cm}^{-1}$  in BiS, at  $20\,300\text{ cm}^{-1}$  in BiSe, and at  $18\,723\text{ cm}^{-1}$  in BiTe.

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