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V. E. Bondybey and J. H. English

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Laser fluorescence studies of metal clusters: Spectroscopy of molecular bismuth

V. E. Bondybey and J. H. English

Bell Laboratories, Murray Hill, New Jersey 07974 (Received 17 January 1980; accepted 12 March 1980)

The electronic spectra of Bi_n clusters in solid Ne and Ar matrices are studied by absorption and laser induced fluorescence techniques. The $Bi_2 \ \bar{X} \rightarrow \bar{A}$ spectrum appears to be unperturbed by the solid medium. A second, slightly lower lying excited electronic state may also be due to Bi_2 . Spectra belonging to another bismuth cluster, most likely to Bi_4 are also observed and analyzed. The vibrational frequencies of the emitting species are determined. The spectrum is consistent with a T_d structure for the tetramer, but shows no evidence of Jahn-Teller distortions.

I. INTRODUCTION

In the last several years there has been considerable interest in the chemistry and spectroscopy of small metal clusters.¹⁻³ Part of this interest has its origin in the importance of metals in catalytic processes. Organometallic cluster compounds have been shown to be highly specific catalysts in a wide variety of reactions. $^{4\mbox{--}5}$ Small metal clusters also provide a bridge between the properties of a free atom and those of the bulk metal. The understanding of the metal-metal bonds is therefore of fundamental importance. Low temperature matrix spectroscopy has proved to be a rather useful technique in studies of small metal clusters.⁶⁻⁸ A large number of diatomic metal molecules have been examined using laser induced fluorescence, both in our laboratory and by numerous other investigators.⁹⁻¹¹ In the present work we apply the matrix spectroscopy techniques to the study of molecular clusters of bismuth.

While the spectroscopy of Bi₂ has been previously studied rather extensively, a number of gaps still remain in our understanding of its electronic structure. The absorption spectra of bismuth vapor were examined by several investigators.^{12,13} Owing to the high molecular weight and low vibrational frequencies of Bi2, a large number of vibrational levels are thermally populated at temperatures needed to vaporize the metal, and the resulting spectra are extremely complex. Thus a prominent $\vec{X} - \vec{A}$ system in the visible region which was photographed by Almy and Sparks¹² consisted of more than 300 bands. Several other absorption systems occur in the ultraviolet. Three additional transitions with a common lower state were observed in emission by Reddy and Ali.¹⁴ This common lower state with $\omega_e = 132.49$ cm⁻¹ is apparently identical with the upper state of the $\tilde{A} \rightarrow \tilde{X}$ transition.

The Bi₂ spectra were recently reexamined by Gerber et al.^{15,16} using excitation of the bismuth vapor in a heatpipe oven by a cw Ar ion laser. These investigators report several new electronic states, and in particular, reassign the Bi₂ ground electronic state. Based on a study of intensities of the individual transitions as a function of temperature, they argue that a new state which they denote \tilde{X}' with $\omega_e \approx 154$ cm⁻¹, lies some 1 500 cm⁻¹ below the \tilde{X} state. Matrix spectra of Bi₂ were studied by Teichman and Nixon.¹⁷ In absorption, they observed four distinct electronic transitions in the visible and near infrared. Their shortest wavelength system with $T_e = 17\,859~{\rm cm}^{-1}$ and $\omega_e = 132~{\rm cm}^{-1}$ clearly appears to be the $\tilde{X} - \tilde{A}$ Bi₂ transition and suggests negligible perturbation of the absorber by the solid medium. They also excite their samples using various Ar⁺ and Kr⁺ laser lines and observe a fluorescent progression with $\omega_e = 152~{\rm cm}^{-1}$. This they assign to emission originating from a new low lying state of Bi₂, which they denote "a", into the \tilde{X} state.

Several serious questions arise from these last two studies. While Teichman and Nixon make no reference to the previous work of Gerber et al., the vibrational frequency derived from their fluorescence spectrum for the lower state suggests that this may be identical with the \bar{X}' state of the latter investigators. With the existing assignments, it is difficult to understand how the $\vec{X} - \vec{A}$ transition can appear in the absorption spectrum. The \bar{X} state is, according to Gerber *et al.*¹⁵ located 1500 cm⁻¹ above the ground state and should therefore not be populated in the 4 K matrix. Teichman and Nixon argue that the lower state of their fluorescent progression is the \tilde{X} state, which is perturbed by the rare gas matrices. This interpretation, however, appears rather unlikely, since no significant perturbation is observed for vibrational frequencies of the upper electronic state. The medium shifts in vibrational frequencies of covalently bound molecules are generally minor and a perturbation of this magnitude appears to be without precedent.

The interest in the spectroscopy of Bi₂ was enhanced by recent observations of efficient lasing over a wide wavelength range in optically excited bismuth vapor.^{18,19} In the present paper we use laser induced fluorescence techniques to demonstrate that Bi₂ exhibits negligible fluorescent quantum yields in the solid environment. We will further show that the \tilde{X}' state of Gerber *et al.* as well as the "b" and "a" states of Ref. 17 are not due to Bi₂, but should be assigned to a larger Bi_n cluster, quite possibly the tetrahedral tetramer Bi₄. We also derive from our emission and excitation spectra all three vibrational frequencies of this species.

II. EXPERIMENTAL

A sample of bismuth metal with a greater than 99.999% purity was used in this study. The samples were vaporized at temperatures of 500-550 °C from a stainless steel or quartz cell, and codeposited on a



FIG. 1. The $\operatorname{Bi}_4 \tilde{A} \to \tilde{X}$ fluorescence in solid Ar at 4 K.

polished 5 K Cu or Pt surface with an excess of matrix gas. The resulting matrices were nearly colorless, and from their optical absorption spectra, we estimate their concentrations in most experiments to be less than 1:2000.

For the absorption studies a tungsten filament lamp was used as a background source. In Ne matrix experiments, the waveguide absorption technique we have recently applied to studies of molecular ions was used, 20 giving absorption paths of up to 20 mm. In solid argon the source radiation was reflected off the polished metal substrate, with resulting pathlengths of less than 0.5 mm.

A home-built Hänsch design N_2 laser pumped dye laser was used in the fluorescence studies. The sample emission, after dispersion in a SPEX 14018 monochromator, was time-resolved in a Biomation 8100 waveform recorder and further digitally processed to obtain the emission spectra, excitation spectra or lifetimes.

The temperature of the matrix was monitored using an iron-doped gold-chromel thermocouple and a calibrated carbon resistance sensor.

III. RESULTS AND DISCUSSION

A. Absorption spectra

Our absorption spectra of Ar matrix samples are in good agreement with the observations of Teichmann and Nixon.¹⁷ We observe two rather strong absorption systems in the visible, each consisting of a single vibrational progression. For both of these, the bands at the low energy end gradually disappear into the noise due to decreasing Franck-Condon factors. Since, furthermore, isotopic studies cannot be performed for bismuth (bismuth is monoisotopic ²⁰⁹₈₃Bi), the absolute vibrational numbering cannot be readily established. The higher energy system exhibits $\omega_e = 132 \text{ cm}^{-1}$ and little anharmonicity, and is apparently due to the $\tilde{X} - \tilde{A}$ transition of Bi₂. Excellent agreement of its spectroscopic constants with the gas phase values suggests that the Bi₂ is insignificantly perturbed by the solid environment. This conclusion is further strengthened by the observation that identical vibrational frequencies are also obtained in solid Ne. Large gas-matrix shifts are generally accompanied by large shifts from matrix to matrix.

In situations where the 0-0 band is Franck-Condon forbidden and undetected, one can often, if emission is also observed, still establish the absolute vibrational numbering by extrapolating the absorption and fluorescence spectra to the common origin. In the case of the bismuth doped matrices, excitation of the absorption bands of the $\tilde{X} - \tilde{A}$ transition leads to no observable visible or near-infrared emission. The excitation energy of the \tilde{A} state is well below the Bi₂ dissociation limit and the absence of emission cannot be due to Bi₂ dissociation. We conclude that the A state levels of Bi₂ are efficiently depopulated by nonradiative transitions into some lower lying electronic state. The observation of the $\tilde{X} \rightarrow \tilde{A}$ absorption in 4 K matrix samples implies clearly that \tilde{X} state is the ground state of the Bi, molecule.

Relatively little can be said about the lower energy absorption progression. The vibrational frequency of 143 cm⁻¹ is quite reasonable for an excited electronic state of Bi₂. The two visible progressions maintain reasonably constant relative intensities over a rather large concentration range, supporting assignment to the same species. They also appear with approximately the same relative intensities in solid Ne and maintain this constant ratio during annealing of the samples. The lower energy progression may therefore well be due to a new low lying electronic state of Bi₂.

B. Laser induced fluorescence

A typical fluorescence spectrum produced by excitation of the Ar matrix samples containing bismuth in the visible region is shown in Fig. 1. It consists of a series of sharp zero phonon lines (ZPLs) in the near infrared with approximately 152 cm^{-1} spacing. Teichman and



FIG. 2. Two sections of the Bi_4 excitation spectrum in solid Ar. The intensities are not corrected for laser power variation.

Nixon¹⁷ have previously observed the same fluorescent progression and assigned it to Bi₂. They conclude that the Bi₂ ground state frequency is lowered by the solid environment by $\approx 13\%$. As a supporting evidence they note that similar frequency lowering occurs in matrix isolated Pb₂.²¹ We have since reexamined the Pb₂ matrix spectroscopy and shown that the discrepancy they observe was due to incorrect analysis of the gas phase Pb₂ spectrum²² and that in reality the matrix constants exhibit less than 1% matrix shifts.²³ A 13% matrix shift in vibrational frequency of a stable, covalently bound molecule would be without precedent. In particular, the excellent agreement of the A state vibrational potential with that of the free molecule makes such a perturbation of Bi₂ ground state exceedingly unlikely.

Useful information about the emitting species can be derived from the fluorescence excitation spectra, and a portion of such a scan is shown in Fig. 2. This spectrum was obtained by monitoring the intensity of one of the sharp near-infrared vibronic bands and scanning the laser wavelength. In the visible region an intense spectrum characterized by a strong progression in a vibrational frequency of 132 cm⁻¹ is observed, with first band at 15250 cm⁻¹. A section of a second progression is observed at lower energies in the near infrared. While we had no dyes available operating below $\approx 13000 \text{ cm}^{-1}$ and could not observe the entire progression, the measured vibronic bands can be extrapolated in such a way that the first band in excitation coincides with the first band of the fluorescent progression at 12396 cm⁻¹. The two progressions appearing in the excitation spectrum must clearly correspond to two different electronic states of the fluorescing species.

On the other hand, there is no enhancement in the infrared fluorescence when the laser is tuned through the strong vibronic bands of Bi_2 in the visible. With the present assignment of the emission to Bi_2 , one would have to argue that the population of the $Bi_2 \tilde{A}$ state relaxes nonradiatively into the ground electronic state, bypassing both of the two lower lying electronic states. The Franck-Condon factors which are of key importance in relaxation of matrix isolated molecules, would surely favor nonradiative transitions into the nearby lowerlying states over direct relaxation into the ground state. Considering all this evidence we conclude that the carrier of the fluorescence and of the two low energy spectra is not Bi_{2} .

We have considered carefully the possibility of impurity involvement. Replacement of the bismuth by a sample of lower purity had no effect on the fluorescence intensity. Similarly, comparable results were obtained with samples vaporized from stainless steel, monel and quartz cells. Deliberate addition of small amounts of air resulted in a decrease, rather than an increase of the fluorescence intensity.

The dependence of the emission intensity upon sample concentration is informative. With increasing bismuth concentration, the fluorescence intensity increases more rapidly than that of the Bi₂ absorption. Also interesting are changes in the spectra with thermal history of the sample. Annealing of Ar matrices to ≈ 30 K for 10–15 min generally resulted in a slight decrease in the Bi₂ absorptions accompanied by sharpening of the individual vibronic bands. On the other hand, the same treatment increased the fluorescence intensity by more than an order of magnitude.

These results suggest that the spectra should be assigned to Bi_n cluster with n > 2. Unfortunately, in the absence of isotopic data, it is difficult to establish the number of Bi atoms in the carrier unambiguously. Phosphorus and the heavier VA subgroup molecules are known to form tetramer molecules readily. Indeed, Kohl et al.²⁴ have established that also bismuth vapor near 1000 K contains $\approx 1\%$ of Bi₄ molecules. We will therefore at this time tentatively assume that the observed fluorescence is due to the bismuth tetramer. In a later section we will consider the possibilities of alternative assignments. The data then indicate that the emitting species possesses two electronic states in the near-infrared region of the spectrum with origins in solid Ar at 12 396 and 15 250 cm⁻¹ which we will refer to as \tilde{A} and \tilde{B} states, respectively. Excitation of either of the two states results in the identical $\overline{A} - \overline{X}$ fluorescence, suggesting that in solid Ar the $ilde{B}$ state undergoes an efficient nonradiative transition into the lower lying \tilde{A} state.

$Bi_4 \quad \widetilde{X} \rightarrow \widetilde{B} \quad EXCITATION \quad SPECTRUM \quad Ne, 5 K$



FIG. 3. $\operatorname{Bi}_4 \tilde{X} \to \tilde{B}$ excitation spectrum in solid Ne. Spectrum is not corrected for laser power variation. The vibrational assignments shown are based on the assumed Bi_4 interpretation with T_d symmetry. Only v_1 numbering is shown for the main v_1 progression, while v_1 , v_2 , v_3 assignments are given above some of the weaker bands.

C. Vibronic structure and Bi₄ molecular constants

What is the structure of the Bi₄ molecule? The structure of the related P₄ molecule is known from electron diffraction studies to be tetrahedral.²⁵ Unlike several other possible structures, regular tetrahedral arrangement will result in only one totally symmetric vibrational frequency, fitting well the diatomic-like appearance of the observed spectra. As a starting hypothesis one can therefore assume also for Bi₄ tetrahedral symmetry. In the T_d Bi₄ molecule one expects, in addition to the totally symmetric ν_1 , one doubly degenerate E vibration, ν_2 , and triply degenerate ν_3 of F symmetry.

Best resolved and least perturbed molecular spectra are usually obtained in Ne matrix. Excitation of the bismuth containing neon matrices in the region of the Bi₄ \tilde{B} state produces no $\tilde{A} - \tilde{X}$ emission near 12 000 cm⁻¹, but a rather strong fluorescence in the 14 000-15 000 cm⁻¹ region is observed. The highest energy band in emission occurs at 15 307 cm⁻¹. The excitation spectrum of this emission is identical to the $\tilde{X} - \tilde{B}$ excitation spectrum in solid Ar, except for an overall blue-shift of approximately 60 cm⁻¹ and slightly better resolution. The lowest energy band again occurs at 15 307 cm⁻¹, coincident with the first band in emission. Clearly in neon the $\tilde{B} - \tilde{A}$ nonradiative transition does not have unity quantum yield and appreciable fluorescence occurs directly from the \tilde{B} state.

The excitation spectrum of the fluorescence is reproduced in Fig. 3. In addition to the main progression in the 130 cm⁻¹ frequency, numerous weaker bands are observable in the spectrum. Excitation of any of these weaker, sharp bands, produces the same emission spectrum as excitation of the main progression. This shows that matrix site effects are not involved and that all the bands are due to vibronic transitions of the same species All the observed bands can be arranged into a regular array involving, in addition to the main 130 cm⁻¹ mode, vibrational intervals of 166 and 212 cm⁻¹. The presence of several vibrational frequencies confirms that the spectra must be due to a polyatomic molecule. Both of these new frequencies appear too high for a molecule containing only atoms as heavy as Bi, and we assign them as overtones of the nontotally symmetric vibrations, $2\nu_2 = 165$ cm⁻¹ and $2\nu_3 = 212$ cm⁻¹. The even overtones of the degenerate vibrations contain totally symmetric a_1 components which can appear in the spectrum. The bands of the excitation spectrum and their assignments are summarized in Table I.

The fluorescence spectrum is shown in Fig. 4 and its analysis is quite analogous. The subsidiary progressions involving nontotally symmetric vibrations are weaker than in the excitation. In excitation, one can easily saturate the strong bands of the main progression and thus increase the relative intensities of the weaker bands. In emission the intensities are always controlled by the Franck-Condon factors. The emission spectrum again contains bands involving $2\nu_2$ and $2\nu_3$. The observed emission bands are listed in Table II. Analysis of the

TABLE I. Bi₄ $\tilde{X} \rightarrow \tilde{B}$ excitation bands in solid Ne (cm⁻¹).

$v_1'/v_2', v_3'$	0,0	2,0	4,0	0,2	2,2
0	15 312	15476	•••	15 522	•••
1	15441	15603	• • •	15649	15 811
2	15 569	15730	15890	15775	15 936
3	15696	15855	16016	15 901	16061
4	15823	15 982	16139	16030	16183
5	15 952	16107	16 260	16154	• • •
6	16077	$16\ 230$	•••	16279	• • •
7	16203	•••	• • •	•••	• • •
8	16328	•••	• • •	•••	• • •

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spectrum yields the vibrational constants for the ground electronic state of Bi_4 .

The vibrational constants of Bi4 are summarized in Table III. For comparison, the last column gives constants predicted a few years ago for the ground state of tetrahedral Bi₄ by Kohl *et al.*²⁴ The frequencies were obtained by scaling the known P_4 fundamentals by the ratio of Bi2 and P2 vibrational frequencies. The agreement between the observations and the predicted frequencies is quite spectacular. Also included in Table III is the v_1 vibration in the \tilde{A} state. As noted, we have not observed any $\tilde{A} - \tilde{X}$ fluorescence following \tilde{B} state excitation. This may either mean that the $\tilde{B} \rightarrow \tilde{A}$ nonradiative transition does not take place in solid Ne, or that the \tilde{A} state relaxes further and its emission quantum yield is extremely small. We have also attempted to excite the A state in solid Ne directly, but again, no $\tilde{A} \rightarrow \tilde{X}$ emission was observed. In the absence of the better resolved Ne matrix data we have not been able to establish the ν_2 and ν_3 vibrations in the \bar{A} state.

Superficially, the sum of the evidence from the vibrational structure would appear to be quite consistent with assigning the observed spectra to the Bi_4 molecule with tetrahedral geometry in all three electronic states observed. Difficulties with this interpretation only become

TABLE II. $\operatorname{Bi}_{4} \tilde{X} \leftarrow \tilde{B}$ emission bands in solid Ne (cm⁻¹).

v1 /v2', v3'	0,0	2,0	0,2
0	15 312	15132	15 070
1	15 162	14 982	14 921
2	15013	14832	14771
3	14864	•••	14621
4	14715	•••	14 471
5	14 566		14 321
6	14 418	•••	14173
7	14271		•••
8	14 123	• • •	•••

apparent when one considers the electronic structure of Bi_4 and attempts specific assignments for the observed transitions, and we will discuss this in a later section. The appearance of long progressions in the symmetric ν_1 mode would then indicate that substantial expansion of the metal-metal bonds accompanies the electronic excitation.

D. The \tilde{A} state lifetime and nonradiative processes

The \overline{A} state of Bi₄ exhibits in the 5 K matrix a lifetime of $\approx 1.5 \ \mu$ sec. The lifetime shows a pronounced temperature dependence, as shown in Fig. 5, where the total decay rate (radiative + nonradiative) is plotted as a function of temperature. The rates are relatively constant for lowest temperatures and increase dramatically above ≈ 10 K. Such a behavior is characteristic of multiphonon relaxation processes.^{26,27} This would suggest that the relaxation does not occur into quasiresonant levels of the ground state, but that at least part of the

TABLE III. Spectroscopic constants of Bi₄ (cm⁻¹).

	ĩ			Ã		
	Arª	Ne ^b	Calc	Ar	Ar	Ne ^d
ν_{00}	0	0	0	12 396	15250	15311.7
νı	151	149.7	141 ± 20	123	131	129.1
ν_{2}		89.8	85 ± 20			82.4
ν_3		120.4	108 ± 20			104.9

^aActually only $2\nu_2$ and $2\nu_3$ intervals are observed in the spectrum.

^bLeast square fit of the observed emission bands in Ne gives also the anharmonic constants $X_{1,1}^{\prime\prime} = -0.14$, $X_{1,2}^{\prime\prime} \sim 0.3$, $X_{1,3}^{\prime\prime} \sim 0.4$.

^cThe calculated values were obtained in Ref. 11 as described in the text.

⁶The upper state anharmonic constant obtained from the fit are $X'_{1,1} = -0.25$, $X'_{1,2} = -0.97$, $X'_{1,3} = -0.69$, $X'_{2,3} = -0.3$. The constants reproduce the ≈ 50 bands observed in Ne matrix with a mean square deviation of less than 0.6 cm⁻¹.



FIG. 5. Temperature dependence of the total (radiative+non-radiative) decay rate of the vibrationless level of the \tilde{A} state in solid Ar.

energy is channeled directly into the harmonic delocalized lattice modes. At 4 K the decay of the \tilde{A} state is dominated by fluorescence, and the measured 1.5 μ sec lifetime is probably close to the radiative value.

The \tilde{B} state emission in solid Ne has a lifetime shorter than our experimental resolution (≈ 20 nsec). It is quite likely that this value is also shortened by nonradiative processes, since the $\tilde{X} \rightarrow \tilde{A}$ and $\tilde{X} \rightarrow \tilde{B}$ absorptions seem to have comparable intensities.¹⁷ One might therefore expect similar radiative lifetimes associated with these transitions. Within the range studied (4–9 K), there appears to be no significant change in the \tilde{B} state emission intensity. One does observe, however, upon prolonged irradiation a gradual decrease in the Bi₄ fluorescence intensity in solid Ne. The energy needed for the dissociation according to the equation

$$\operatorname{Bi}_4(g) \to 2\operatorname{Bi}_2(g) \tag{1}$$

was reported to be 15300 ± 400 cm⁻¹. It appears likely that this process is responsible for the observed signal bleaching.

The observation of fluorescence of metal cluster with four atoms is rather remarkable. While numerous diatomic metal molecules have been seen in fluorescence, in larger clusters nonradiative processes and fragmentation usually appear to prevail over radiation. In Bi_4 , not only the lowest state, but also higher lying states apparently fluoresce with appreciable yields. Perhaps the high symmetry of the molecule leads to the reduced efficiency of nonradiative relaxation channels.

E. Bi₄ electronic structure

As we noted previously, all molecules of group VA seem to have a strong tendency to form four-atomic molecules which, at least in the case of P_4 , are known to have tetrahedral geometry. We have tentatively assigned the emission observed here to Bi_4 and all the evidence presented thus far seems to be consistent with this assignment. It is reasonable to assume that, like in the case of P_4 , the Bi₄ ground will have A_1 symmetry. The vibrational structure present in the observed matrix spectra suggests that the transitions involved are orbitally allowed, and the upper states would have to be of F_2 symmetry.

Since the F_2 state is triply degenerate, one could expect it to be subject to Jahn-Teller instability.²⁸ In fact, both the *E* vibration, ν_2 , and the F_2 species, ν_3 , should be Jahn-Teller active. Occurrence of Jahn-Teller distortions is usually manifested by the appearance of nontotally symmetric modes in the spectrum and by a perturbed, irregular vibrational structure. Yet all the transitions observed here are characterized by astonishingly regular and harmonic vibrational progressions and only even overtones of the nontotally symmetric modes seem to be present. We conclude that the spectra exhibit no evidence of Jahn-Teller distortion.

In a molecule containing the heavy Bi atoms the spin orbit coupling will be large and spin selection rules will not be very important. It is therefore possible, that the observed transitions may be due to components of low lying triplet states. This would also be consistent with the relatively long, 1.5 μ sec lifetime found for the $\tilde{A} - \tilde{X}$ fluorescence in Ar matrix. If this is the case, then the large spin-orbit splitting may lead to quenching of the Jahn-Teller effect.

In view of the existing difficulties with the assignment to tetrahedral Bi4, it is however, perhaps useful to consider possible alternative interpretations. We have already noted that all the control experiments designed to test if impurity atoms can be involved, gave negative results. This suggests strongly that the emitting species is a Bi, cluster. The bismuth vapors at the temperatures used for vaporization are known to contain a substantial fraction of atoms, and Bi3 molecules could form readily in the matrix. The observed spectra are clearly inconsistent with bent Bi3. In bent molecules, the valence angle is usually most sensitive to electronic excitation and one observes progressions in the low frequency bending vibration. In the present spectra the observed dominant progressions are apparently due to Bi-Bi stretching, and the remaining intervals are clearly also too high for assignment to the v_2 bend.

In linear centrosymmetric Bi₃ the assymmetric stretching vibration, ν_3 , would be expected to have the highest frequency and could only appear in the spectrum in increments of 2. If one thus assigned the present spectra to the linear centrosymmetric Bi₃ species, one would have to conclude that $\nu_1 > \nu_3$. While the reverse is much more likely, one can not rigorously exclude this possibility.

For most alternative Bi_4 geometries, as well as for even larger clusters, more than one totally symmetric vibration and more complex spectra could be expected. Also chemically they appear to be less likely possibilities. In spite of the inherent difficulties, tetrahedral Bi_4 seems to fit the observed spectra best. A linear, centrosymmetric Bi_3 would perhaps appear to be the most reasonable alternative.

F. Comparison with previous studies

Several puzzling aspects of earlier studies now become clarified. Gerber et al. have noted that the intensity of emission involving their ${ar X}'$ state decreases with increasing temperature relative to the $\tilde{A} - \tilde{X}$ Bi₂ fluorescence, and estimated from the temperature dependence that this state must lie $\approx 1500 \text{ cm}^{-1}$ below the \tilde{X} state. With the present reassignment, the decrease of \tilde{X}' population with rising temperature is readily explained in terms of Bi4 thermal dissociation. One can also understand why transitions involving the \tilde{X}' state were not observed in previous absorption studies. At the high temperatures usually employed, the absorption spectrum of Bi4 will be extremely complex and may appear nearly continuous. Furthermore, due to thermal decomposition the Bi4 concentration will be low. In a laser fluorescence experiment only a small subset of molecules in direct resonance with the laser is excited, the same way one can select only a narrow wavelength region out of an inhomogeneously broadened linewidth in a condensed phase. In either case, a sharp spectrum is observed, explaining the observation of Bi₄ in the laser fluorescence experiments.

IV. SUMMARY

In this paper we reexamine the species contained in bismuth vapor using matrix fluorescence techniques. We show that the $\tilde{X} \rightarrow \tilde{A}$ transition of Bi₂ exhibits both in the Ne and Ar matrices negligible perturbation by the host. The \tilde{A} state is very efficiently deactivated nonradiatively and no fluorescence is observed. A second, lower lying transition characterized by $\omega_e = 143$ cm⁻¹ and $T_e = 17376$ cm⁻¹ is tentatively also assigned to the Bi₂ species.

Emission and excitation spectra of a larger bismuth cluster are also observed and analyzed. We show that they are probably due to Bi₄ and determine its vibrational fundamentals. The spectra are consistent with a T_d symmetry for the Bi₄ species. The vibrational structure appears surprisingly regular and is dominated by the totally symmetric ν_1 mode. No evidence is found for Jahn-Teller distortion in any of the observed states. Both the first and second excited electronic states are seen to fluoresce in the low temperature matrices with high quantum efficiency.

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