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Matrix-isolated bismuth. II. New fluorescence band systems and resonance Raman spectra of Bi_2 and Bi_4 in solid argon

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For Bi_2 molecules in argon matrices, a new laser-induced fluorescence system with origin at 16 893 cm^{-1} has been observed. The upper state A' lies 826 cm^{-1} below the well-established A state. A progression of six bands of the resonance Raman spectrum of Bi_2 is also reported. More concentrated matrices display an extremely weak fluorescence which is very probably the $B-X$ system of Bi_4, previously observed in absorption. A sequence of resonance Raman bands with an irregular intensity pattern is attributed to an unknown Bi_n molecule.

I. INTRODUCTION

In a recent paper on bismuth in argon matrices[1] we reported about 135 bands of the weak $A \rightarrow X$ fluorescence system of Bi_2, which we observed as vibrationally unrelaxed emission produced by dye laser pumping into the $V' = 0-6$ levels of the A state. Our analysis of the system gave $\nu_{00} = 17\,719$, $\omega_e'' = 174.3$, $\omega_e' = 133.4$ cm^{-1}, values which are each within 1 cm^{-1} of those for the gaseous molecule.[2,3]

Further work has now revealed a second weaker fluorescence system which corresponds to an absorption system observed earlier.[4] The new data confirm that this system also belongs to Bi_2 and that it involves an excited state not yet detected in Bi_2 vapor. Resonance Raman bands extending through the fifth overtone have been measured for Bi_2.

Our new results include a fluorescence system due presumably to Bi_4 and some Raman bands which belong to some unidentified species.

II. EXPERIMENTAL METHODS

Matrices were prepared by our usual method of condensing onto a copper finger (10 K) mixtures of argon gas and the vapor issuing from a Knudsen-type furnace containing bismuth metal (99.98% assay). All of the spectral features reported here for the Bi_2 species were observed in very pale pink matrices with estimated Ar/Bi ratios of 1500 : 1. The matrix showing the weak fluorescence attributed to Bi_4 [Fig. 2(A)] was a more reddish one with an Ar/Bi ratio of about 150 : 1.

In our experiments excitations were produced by fixed frequencies of an 8 W argon laser and by a tunable dye laser containing Exciton 560 pumped by the Ar laser. All spectra were recorded on a Spex Ramacomp system.

III. DISCUSSION OF RESULTS

A. Bi_2–16 893 cm^{-1} emission system

Our earlier studies of argon matrix-isolated bismuth[4] showed an absorption system in the 18 000 cm^{-1} region with 11 bands fitting an ω_e' value of about 145 cm^{-1}. We assumed then that the system belonged to Bi_2, although no corresponding system had been observed for Bi_2 vapor. Very recently, in a paper which clarifies several aspects of the spectra of matrix-isolated bismuth, Bondybey and English[5] have also reported the same absorption system and concluded that the ω_e value is reasonable for an excited state of Bi_2.

The five lowest frequency bands observed in that absorption system have reasonably sharp zero-phonon lines (ZPL's) at 17 336, 17 479, 17 623, 17 666, and 17 908 cm^{-1}. In the present work we carried out some 20 experiments in which matrices were irradiated with dye laser frequencies covering the range 17 363–17 907 cm^{-1}. The new weak emission system was stimulated most clearly when the laser excitation approached the frequency of one of the aforementioned absorption ZPL's. The kind of results obtained is typified by those with dye laser frequencies near 17 500 cm^{-1} (Fig. 1). One notes first that the emission bands are strongest and sharpest in the case of the 17 492 cm^{-1} excitation, although the 17 485 and 17 497 cm^{-1} laser lines also produce well defined bands. These three excitations lie slightly above the ZPL at 17 479 cm^{-1} in the absorption spectrum and extend 6–18 cm^{-1} into the phonon sideband associated with that absorption. As the excitation is shifted to lower (17 477 cm^{-1}) or higher (17 505 cm^{-1}) frequencies, the emission system becomes weaker and less distinct (Fig. 1).

A second notable feature in the observed emission is that the ZPL frequencies vary with the excitation in a manner consonant with fluorescence narrowing of inhomogeneously broadened absorption. For example, the ZPL's shift upward by 4–6 cm^{-1} in going from the 17 485 cm^{-1} laser line to the one at 17 492 cm^{-1} and another 5–6 cm^{-1} upward with 17 497 cm^{-1} excitation.

The highest frequency ZPL observed in the new vibrationally relaxed emission system lies at 16 893 cm^{-1} [Fig. 1(D)]. If we assume that this is the 0–0 band, then values of $\omega_e'' = 174$ and $\omega_e x_e'' = 0.5$ cm^{-1} best fit the 11 observed bands and provide strong evidence that this is a Bi_2 system terminating in its ground X state. This assignment of the ν_{00} for the system, which we shall label $A' \rightarrow X$, is the only one which fits both emission and absorption and it identifies the 17 336 cm^{-1} absorption band[4] as the $3 \leftarrow 0$ transition.

The new state A' lies only 826 cm^{-1} below A. The latter is thought to be the $^1\Sigma_u^+(0_u^+)$ state[6] arising from
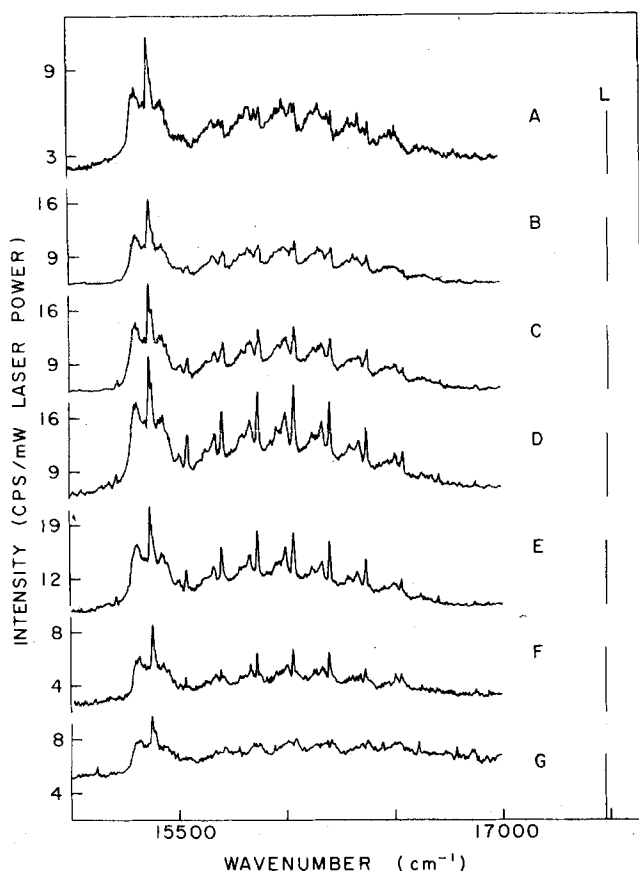
0021-9606/81/130110-04$01.00

FIG. 1. The $A' \rightarrow X$ system of Bi_2 in solid argon matrix at 10 K and $M/A = 1500$. Fluorescence is stimulated by about 200 mW from a dye laser containing Exciton 560 dye pumped by 3.5 W in the 514.5 nm line of argon laser. The dye laser is tuned to (A) 17 505, (B) 17 501, (C) 17 497, (D) 17 492, (E) 17 485, (F) 17 480, and (G) 17 477 cm^{-1}. The 0−0 band of system is at 16 893 cm^{-1}. Results illustrate resonance absorption and inhomogeneous broadening effects. The relatively intense emissions at 15 315, 15 370, and 15 425 cm^{-1} are due to atomic bismuth.

the configuration ... $(6_p \sigma_g)^2 (6_p \pi_u)^3 (6_p \pi_g)$. The matrix results do not, of course, determine the symmetry of A' and we can only speculate that it is one of the several other states $^3\Sigma_u^+$, $^3\Sigma_u^-$, $^1\Sigma_u^-$, $^3\Delta_u$, or $^1\Delta_u$ which are represented by the same electron configuration.

We noted in the $A \rightarrow X$ study[1] that pumping the $V' = 2$ level of the A state with 18 024 cm^{-1} laser radiation produced an extraneous series of five weak sharp peaks (15 067, 14 911, 14 754, 14 600, 14 446 cm^{-1}) on the low frequency side of the observed sequence of $V' = 2$ fluorescence bands. The series has a single intensity maximum at the 14 911 cm^{-1} band. The spacings of about 155 cm^{-1} are close to the 151 cm^{-1} assigned by Bondybey and English[5] to the ν_1 fundamental of the ground state of Bi_4 in argon but the five bands do not fit into the $B \rightarrow X$ emission of Bi_4, whose origin is placed at 15 250 cm^{-1}.

The spacings do match reasonably well the vibrational levels in the neighborhood of $V'' = 20$ of the ground state of Bi_2 (see Table I of Ref. 1), so we shall consider a possible explanation involving these levels. The 18 024 cm^{-1} laser line which gave rise to this series of five peaks falls between the $V' = 7$ and $V' = 8$ levels of the

A' state. We have seen that when the A' state is pumped in the range 17 363−17 907 cm^{-1} we observe only vibrationally relaxed emission. If for some reason vibrational relaxation from higher levels of the A' manifold were sufficiently slower, then pumping directly into the $V' = 7$ level of A' with the 18 024 cm^{-1} laser frequency or populating the $V' = 7$ level by intersystem crossing from the $V' = 2$ level of the A state could result in observable unrelaxed emission and our five bands could then be interpreted as the $V' = 7 \rightarrow V'' = 17-21$ transitions. The rest of the bands of the unrelaxed emission from $V' = 7$ would be obscured by the more intense $A \rightarrow X$ system. If we take $V' = 7$ of the A' state at about 17 915 cm^{-1}, then the agreement between calculated and observed frequencies for the five bands in good. While this 17 915 cm^{-1} value is 7 cm^{-1} higher than the 7 ← 0 ZPL observed in absorption, it is not at all unreasonable in view of the inhomogeneous broadening effect we have just seen in the $A' \rightarrow X$ emission.

As a final aspect of our proposed identification of the series of five bands, consider the intensities. The empirical relation $r_e^2 \omega_e$ = constant for electronic states of a given diatomic molecule, together with an $r_e = 2.66$ Å for the ground X state,[2] yields 2.91 Å as the r_e value for the A' state. Equating the vibrational energy to the classical potential energy expression

$$(V' + \tfrac{1}{2}) \, \omega_e = 2\pi^2 \, \mu c^2 \, \omega_e^2 (r - r_e)^2 \qquad (1)$$

gives a bond length r of 3.04 Å as the outer turning point of the A' potential function at the $V' = 7$ level. This r value corresponds to the outer turning point at $V'' = 23$ in the potential for the X state.[2] Our interpretation of the observed bands assigns the most intense one as $V' = 7 \rightarrow V'' = 18$. In view of the crude approximations in estimating the most intense vibronic transition from $V' = 7$, the disagreement between $V'' = 23$ and $V'' = 18$ seems tolerable.

B. Bi_2—resonance raman

We noted in the paper on the $A \rightarrow X$ fluorescence of Bi_2 in argon that several of the excitation frequencies in the 18 000−18 400 cm^{-1} range also brought out the Raman fundamental and two overtones of the molecule. A more extensive sequence involving five overtones is produced by the 19 436 cm^{-1} laser line, which lies in a more strongly absorbing region of the $A \leftarrow X$ system. The bands with shifts of 172, 345, 517, 688, 858, and 1028 cm^{-1} are shown in Fig. 2(B).

During the course of this work we received a preprint of a paper by K. Manzel, U. Engelhardt, H. Abe, W. Schulze, and F. W. Froben in which these authors report resonance Raman spectra of two species of matrix-isolated bismuth. One species with $\omega_e = 172$ cm^{-1} is assigned to Bi_2. Their most likely choice for the other progression with $\omega_e = 152$ cm^{-1} was Bi_4.

C. The 122 cm^{-1} raman progression

In our earlier work[1] we also reported that a pair of Raman bands with shifts of 370 and 490 cm^{-1} accompanied the $V' = 0$ and $V' = 1$ series of $A \rightarrow X$ emission bands of Bi_2. We now find that laser frequencies cover-
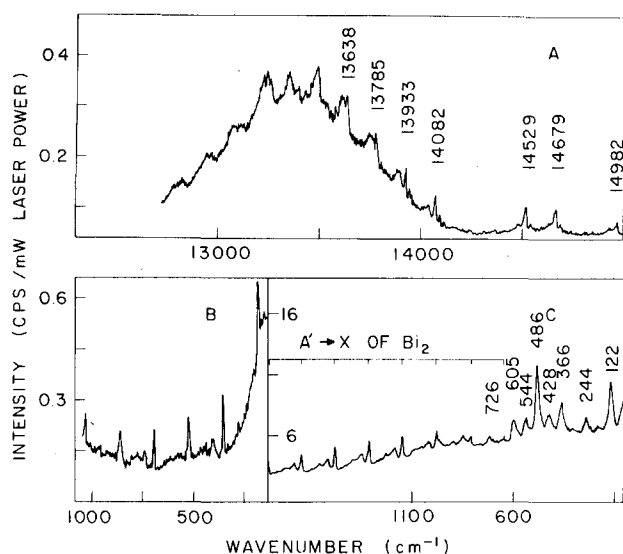
FIG. 2. (A) Fluorescence system, attributed to Bi_4, obtained by irradiating an argon matrix containing an Ar/Bi ratio of 150 at 10 K with 3 W of $19\,436$ cm^{-1} laser line. (B) Raman bands for Bi_2 in argon at 10 K and Ar/Bi = 1500. Shifts are measured with 2.9 W of the $19\,436$ cm^{-1} laser line. (C) Raman bands of bismuth species in argon matrix at 10 K with Ar/Bi = 1500, accompanied by a portion of the $A' \to X$ fluorescence of Bi_2. The spectrum is measured with 60 mW at $17\,373$ cm^{-1} from the dye laser.

ing the range $17\,360$–$17\,900$ cm^{-1} produce not only these two Raman bands but also six weaker ones, to give a series with Raman shifts of 122, 244, 366, 428, 486, 544, 605, and 726 cm^{-1} [Fig. 2(C)]. The range of the exciting laser lines covers the region from the $3 \to 0$ to the $7 \to 0$ transition in the $A' - X$ absorption of Bi_2, but it is clear from the spectral profile[4] that a broad absorption background underlies this part of the $A' - X$ system. The Raman shifts and the relative intensities of the bands, within the accuracy of our measurements, do not change over the range of the dye laser frequencies, so the scattering would appear to be a resonance Raman spectrum produced by excitation into a continuum absorption of a single species. This set of bands is two to three times as broad as the Raman bands of the Bi_2 molecule, a condition which may be the result of inhomogeneous matrix environments.

The Raman shifts are all multiples of 61 cm^{-1} and, except for the weak 428 and 544 cm^{-1} bands, they are multiples of 122 cm^{-1} bands. The irregular intensity pattern of the bands, essentially independent of the excitation, is not characteristic of a diatomic molecule.

These Raman bands are many times more intense than those due to Bi_2, which leads us to believe that the scatterer is a species composed of bismuth atoms rather than an impurity. We note that frequencies close to 122 cm^{-1} have been observed by Bondybey and English[5] in matrix-isolated bismuth and assigned to a molecule which they think is probably Bi_4 (tetrahedral), although they do not rule out other possibilities such as linear Bi_3. In particular, these authors give a value of 120.4

cm^{-1} for the ν_3 vibration of Bi_4 in its ground electronic state in solid neon.

To assign our 122 cm^{-1} as ν_3 of Bi_4 in argon would raise questions as to why intensity maxima occur at $\nu_3(122$ cm$^{-1})$ and $4\nu_3(486$ cm$^{-1})$, and how to assign the 428 and 544 cm^{-1} bands. The intensity pattern would require an effect such as Jahn–Teller splitting of a degenerate ground electronic state, but such a degenerate ground state is not expected for Bi_4, and Bondybey and English[5] did not observe any evidence of Jahn–Teller distortion in their spectra.

If the fundamental frequency in this Raman progression is 61 cm^{-1}, instead of 122 cm^{-1}, and the observed bands correspond to 2ν, 4ν, 6ν, 7ν, 8ν, 9ν, 10ν, and 12ν, we would conclude that a bending mode is activated in some molecule with a distorted ground state.

In the absence of isotopic data and on the basis of the observed broad bands, identification of the Raman scatterer is not possible.

D. $15\,000$ cm^{-1} emission system of Bi_4

Relatively concentrated matrices display an extremely weak emission system in the $15\,000$ cm^{-1} region. In our work, the spectrum of fairly sharp bands trailing off into a broad background emission centered at about $13\,500$ cm^{-1} appeared most clearly with $19\,436$ cm^{-1} laser excitation [Fig. 2(A)]. If there are missing bands at $14\,831$, $14\,380$, and $14\,231$ cm^{-1}, then the progression of some 10–12 ZPL's can be regarded as a system with a regular spacing of 150 cm^{-1}. This is the same as the ν_1 spacing observed in the vastly more intense $A \to X$ fluorescence of Bi_4 and suggests that this new emission may be the $B \to X$ system corresponding to the $B \to X$ transitions reported by Teichman and Nixon[4] from direct absorption measurements and by Bondybey and English[5] using excitation techniques.

The ν_{00} for the $B \to X$ system for Bi_4 in solid argon has been assigned as $15\,246$ and $15\,250$ cm^{-1} in the two studies.[4,5] In interpreting the new emission system as $B \to X$, the closest agreement in the band system origin would be given by assigning the highest frequency band at $14\,982$ cm^{-1} in the emission as the $0 \to 2$ transition. This would place ν_{00} at about $15\,283$ cm^{-1}. The halfwidths of the ZPL's in both the emission and absorption spectra are 10–15 cm^{-1}, so that the difference in the ν_{00} values ($15\,250$ cm^{-1} from absorption and $15\,283$ cm^{-1} from fluorescence) as measured from intensity maxima of the ZPL's may not be significant, even though the apparent ν_{00} for emission lies at the higher frequency. We should note, however, that essentially exact agreement with $\nu_{00} = 14\,982$ cm^{-1} in both absorption and emission would result if the $15\,246$ cm^{-1} absorption band[4] were actually $2 \to 0$. In view of the intensity profile of the $B \to X$ excitation spectrum of Bondybey and English,[5] this assignment would appear possible but not probable.

If indeed the new system is $B \to X$ for Bi_4, then the reason for the missing three bands in the progression would probably involve perturbations with higher vibrational levels of the A state.

ACKNOWLEDGMENTS

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