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Laser-induced fluorescence measurements of radiative lifetimes of the low lying electronic excited states $B(0^+)$ and 2(III) of the BiI molecule

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Abstract

Laser-induced fluorescence of the BiI molecule in the 4160-4770 Å region was observed and band transitions of the $B(0^+)$-$X(0^+)$ and 2(III)-$X(0^+)$ systems assigned. The nature of the low-lying excited states of BiI is discussed and measured fluorescence lifetimes used in order to establish the character of the states involved in these transitions.

Fluorescence lifetimes for emission from specific (v', J') rovibrational levels of the $B(0^+)$ ($v'=0$-4) and 2(III) states have been measured for the first time by laser-induced fluorescence. The fluorescence lifetimes for emission from the B state were in the range of 0.25-0.5 μs and a slight decrease in the fluorescence lifetimes when the vibrational energy of this molecule increases was observed and no dependence with the rotational energy was appreciated.

A collision-free fluorescence radiative lifetime of $\tau_0 \geq 0.6$ μs is proposed for emission from the BiI 2(III) state what has been characterized experimentally for the first time. No significant variations were found for fluorescence lifetimes of rotational transitions within the same vibrational level of the BiI 2(III) state.

Keywords: Laser-induced fluorescence; Radiative lifetimes; Bismuth iodide

1. Introduction

To our knowledge, the literature on the spectroscopy of BiI is rather scarce. Morgan [1] was the first to study the absorption spectra of BiI, bands in the region 4150-4300 Å were observed and attributed to the $B(0^+)$-$X(0^+)$ band system of BiI. Rao [2] observed the first emission spectrum for BiI in the 5650-5900 Å wavelength range. Singh et al. [3] analyzed several vibrational bands of the B-X system and gave for the first time several molecular constants for this molecule. Two new bands systems, A-X and A'-X, were reported by Yamdagni [4], and attributed to states below (around 3000 cm^{-1}) the well established B state of BiI. In a recent work [5], Alekseyev et al. developed a spin-orbit configuration interaction method based on relativistic effective core potentials (RECPs) to describe the potential energy curves of the electronic states of systems containing heavy atoms as bismuth and iodine, with particular attention to determine the location of the lowest-lying excited states of BiI, and where Yamdagni's assignment [4] for the A and A' states have been questioned.

Studies of the dynamics of the excited states of the bismuth halides BiCl and BiBr have recently been carried out in our laboratory [6-8] and more extensive information on BiF has been published [9-12] since the interest raised by the A-X transition of BiF as a chemical laser. A complete investigation has been made on the various low-lying electronic states of the bismuth fluoride molecule by employing relative effective core potentials including spin-orbit effects, where it has been observed that the lowest 0^+ excited state ($A0^+$) of this system contains a large contribution from the π^*-$\sigma^{*3}\Pi\lambda$-s state, especially at bond distances which are equal to or greater than the equilibrium value for the X (0^+) ground state [13]. An investigation of the electronic transitions of the BiI molecule is clearly needed in order to state the nature of the low-lying electronic states of this molecule. Alekseyev et al. [5] have computed the intensities of transitions between different electronic states and calculated radiative lifetimes of excited states of BiI for transition to $X_1\,{}^3\Sigma^-{}_0$, $X_2\,{}^3\Sigma^-{}_1$ and ${}^1\Delta_2$ states and discussed the calculated values depending of the nature of the states connected by transition. However, no experimental values for radiative lifetimes from the excited states of BiI have been reported and, therefore, a knowledge of these lifetimes is fairly necessary and can be useful to clarify the nature of these states.

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No previous laser spectroscopy studies of the BiI molecule exist. We report here the first laser-induced fluorescence (LIF) spectra of the BiI molecule on several bands of electronic BiI transitions. In this work time-resolved laser-induced fluorescence has been used to measure lifetimes of emission from (v', J') rovibrational levels of low-lying electronic states of BiI, which are given for the first time. The nature of the states involved in these transitions is discussed.

2. Experimental

The experimental set-up has been described in previous publications [6–8,14,15]. The fluorescence from rovibrational levels of the $B(0^+)$ and 2(III) states of BiI molecule was excited by a QUANTEL TDL-50 dye laser (pumped by a Nd–YAG laser) giving pulses of 6 ns duration with a narrow linewidth of 0.08 cm^{-1} and 2–6 mJ of energy in the 4160–4750 Å region, using methanol solutions of several dyes (Stilbene 420, Coumarin 440 and Coumarin 460).

Bismuth monoiodide molecules were prepared by heating BiI_3 (Aldrich Chem. Co., 99.999%) and metallic bismuth (Aldrich Chem. Co., 99.999%) inside an evacuated stainless steel cell in an double oven at different temperatures (400–500 °C) to control BiI pressure according to the following equilibrium [16,17]:

$$\frac{1}{3}\mathrm{BiI_3(g)}+\frac{2}{3}\mathrm{Bi(l)}\rightleftarrows\mathrm{BiI(g)} \qquad (1)$$

where the equilibrium constant is $K=p_{(\mathrm{BiI})}/a^{2/3}_{(\mathrm{Bi})})p^{1/3}_{(\mathrm{BiI3})}$. The activity of the liquid bismuth, $a_{(\mathrm{Bi})}$, is assumed to be unity. The BiI vapor pressure was calculated from the equilibrium constants and the BiI_3 vapor pressures at different temperatures were obtained by Cubicciotti and Keneshea [16,17].

The equilibrium governing the I_2 pressure can probably be represented by the equation [16]:

$$\mathrm{BiI_3(l)}\rightleftarrows\frac{3}{2}\mathrm{I_2(g)}+\mathrm{Bi(l)} \qquad (2)$$

BiI_3 and metallic bismuth were deoxygenated before use. Small amounts of BiI_3, Bi_2 and I_2 were present in the detection chamber, however the partial vapour pressure of BiI should be somewhat higher, according to the equilibrium constant of reaction (1), and must be responsible for the observed spectra. The pressure was controlled by a capacitance manometer (Leybold Inficon CM100-G10A) operating in the 10^{-3} to 10 Torr range.

When the laser was used in the wavelength scanning mode and undispersed fluorescence was collected, excitation spectra of the B–X and 2(III)–X band systems were obtained. Alternatively fixed-frequency laser excitation was used, and the fluorescence decay from the (v', J') excited levels of $B(v'=0\text{–}4)$ and 2(III)(v') states was recorded in real time.

Laser-induced fluorescence was detected perpendicularly to the laser beam axis by a high-gain fast photomultiplier tube (EMI 9816B). Cut-off filters were placed between the fluorescence cell and the photomultiplier tube in order to block the scattered laser light. Laser excitation spectra were obtained by recording fluorescence as a function of the laser wavelength, using a boxcar integrator (Stanford Research Systems SR250) and a strip chart recorder. A Tektronix 2432A digital oscilloscope was used to acquire the fluorescence decays from the photomultiplier tube output. Fluorescence lifetimes were obtained after averaging and processing the signals with a microcomputer connected to the system by means of a S3FG100 GURU II PLUS interface.

3. Results and discussion

Laser excitation spectra obtained by scanning the laser wavelength between 4170 and 4330 Å were observed. No other explanation that transitions of the B–X electronic spectrum of the BiI molecule could be given in this spectral region where Bi_2 is not expected to appear, especially for wavelengths shorter than 450 nm, I_2 should be dissociated and the structure of the spectrum is not compatible with other possible non-diatomic molecules. No other coherent assignment could be given, in this spectral region, different from that transition from the ground state X to a low lying electronic state of the BiI molecule. Several lines of the 0–0, 0–1, 1–0, 1–1, 1–2, 2–0, 2–1, 2–2, 2–3, 3–1, 3–2, 3–4, 4–2, 4–3, 4–4 and 4–5 bands of the BiI B–X system were observed. Vibrational assignment was made using the molecular parameters given by Kuijpers et al. [18] and Singh et al. [3], where good agreement was found. Fig. 1 shows the observed laser excitation spectrum between 4200 and 4300 Å, for the BiI B system. Because of the overlapping observed between different bands, precise rotational assignment was not possible in any of these bands. This work completes the information given previously by other authors [1,4] for 25 $(v'\text{–}v'')$ vibrational bands with $v' \leq 14$ and $1 \leq v'' \leq 7$.

BiI molecules were excited to rovibrational levels of the $B(0^+)$ state by tuning the laser wavelength to a suitable absorption line of the B–X transition. Fluorescence decay curves showed exponential behaviour, being possible to distinguish signals with a monoexponential deactivation from others with a biexponential deactivation. Fig. 2 shows examples of both types of deactivation: (a) monoexponential deactivation, and b) biexponential deactivation for emission from the (a) $v'=0$ and (b) $v'=2$ vibrational levels of the $B(0^+)$ state of BiI ($P_{\mathrm{Total}}=30$ mTorr), respectively.

Table 1 shows a summary of the lifetimes observed in the fluorescence decay curves with monoexponential behaviour and bandheads observed in our spectra, in good accordance with Singh et al. [3]. Fluorescence lifetimes between 400 ± 15 ns for emission from $v'=0$ and 170 ± 20 ns for emission from $v'=4$ vibrational levels of the BiI B state were obtained, with a decrease of the observed fluorescence lifetimes when the vibrational level v' increases.

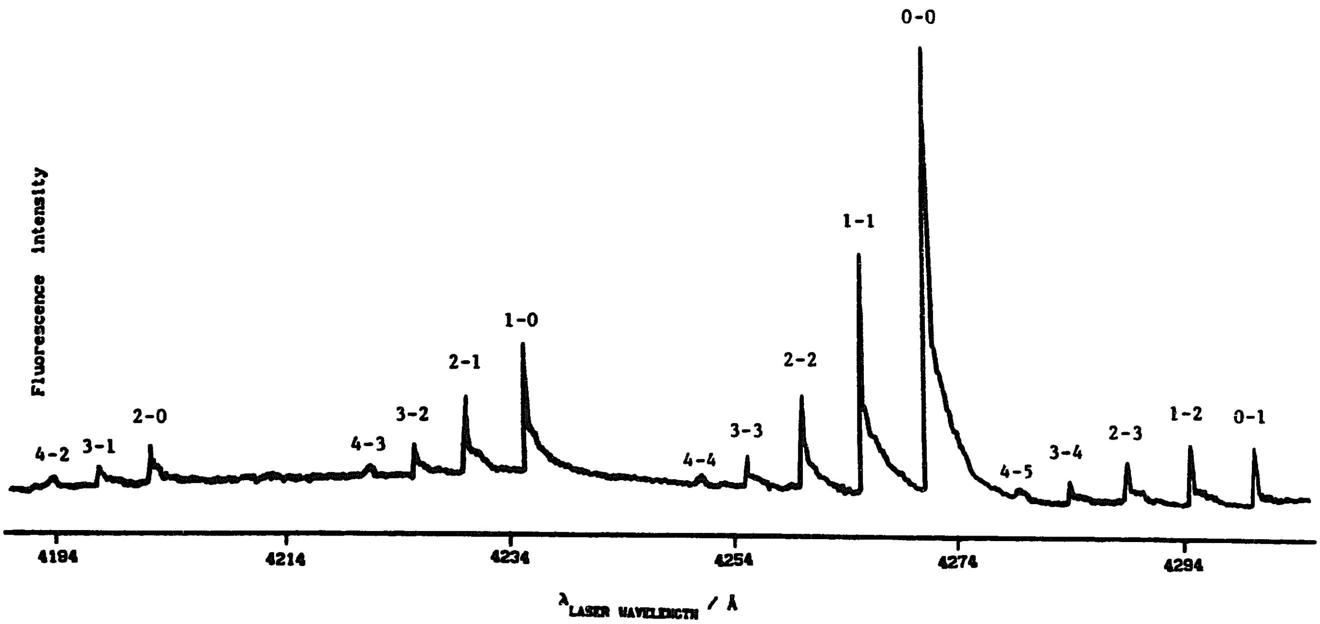
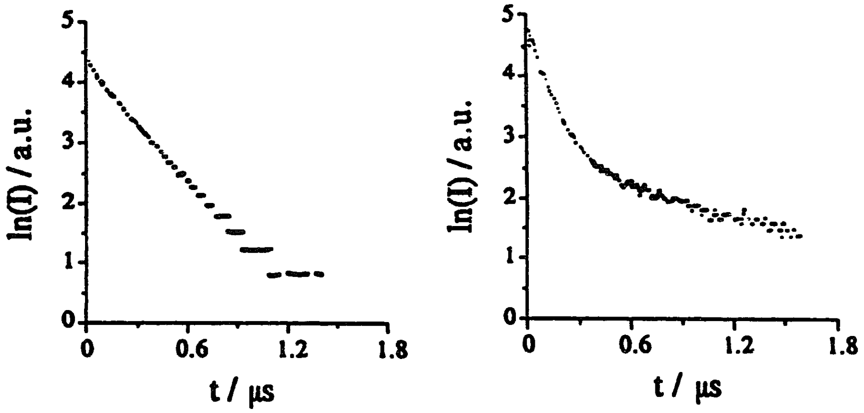


Fig. 1. Laser excitation spectrum for different (v'–v'') bands of the BiI B–X system between 4200 and 4300 Å.



a) v' = 0

b) v' = 2

Fig. 2. Semilogarithmic plot of the variation of the fluorescence intensity (arbitrary units) for emission from the (a) $v'=0$ and (b) $v'=2$ vibrational levels of the B(0^+) state of BiI ($P_{Total}=30$ mTorr) against time.

Table 1
Fluorescence lifetimes (τ) values for emission from different vibrational levels of the BiI B(0^+) state ($P_{Total}=10$ mTorr). Second and third columns specify the studied bands of the B(0^+)–X(0^+) system and their observed bandheads position (in cm^{-1}) respectively.

v'	v'–v''	ν_{vac} (cm^{-1})	τ_{OBS} (ns)
0	0–0	23409	400 ± 15
1	1–1	23439	300 ± 20
	1–0	23600	330 ± 30
2	2–2	23467	270 ± 15
	2–1	23631	270 ± 20
3	3–3	23495	200 ± 20
	3–2	23656	210 ± 20
4	4–4	23518	160 ± 20
	4–3	23681	180 ± 20

Biexponential curves showed two lifetimes: a short lifetime obtained when we analyzed the first part of the decay and a long one when we analyzed the second part. In this case, the lifetime corresponding to the short component of the decay is similar to the lifetime observed in the monoexponential decays obtained. The long component varies between 0.8 and 1.7 μs. Several monoexponential curves, observed in all the spectral region, showed lifetimes around 1 μs and are attributed in this work to the emission from the $B^3\Pi(0u^+)$ state of I_2 molecule originated by recombination of iodine atoms.

When scanning the laser wavelength in the range 4330–4770 Å, a new band system of the BiI molecule was observed, laser excitation spectra were obtained and several lines were observed. As an example, Fig. 3 shows a short section

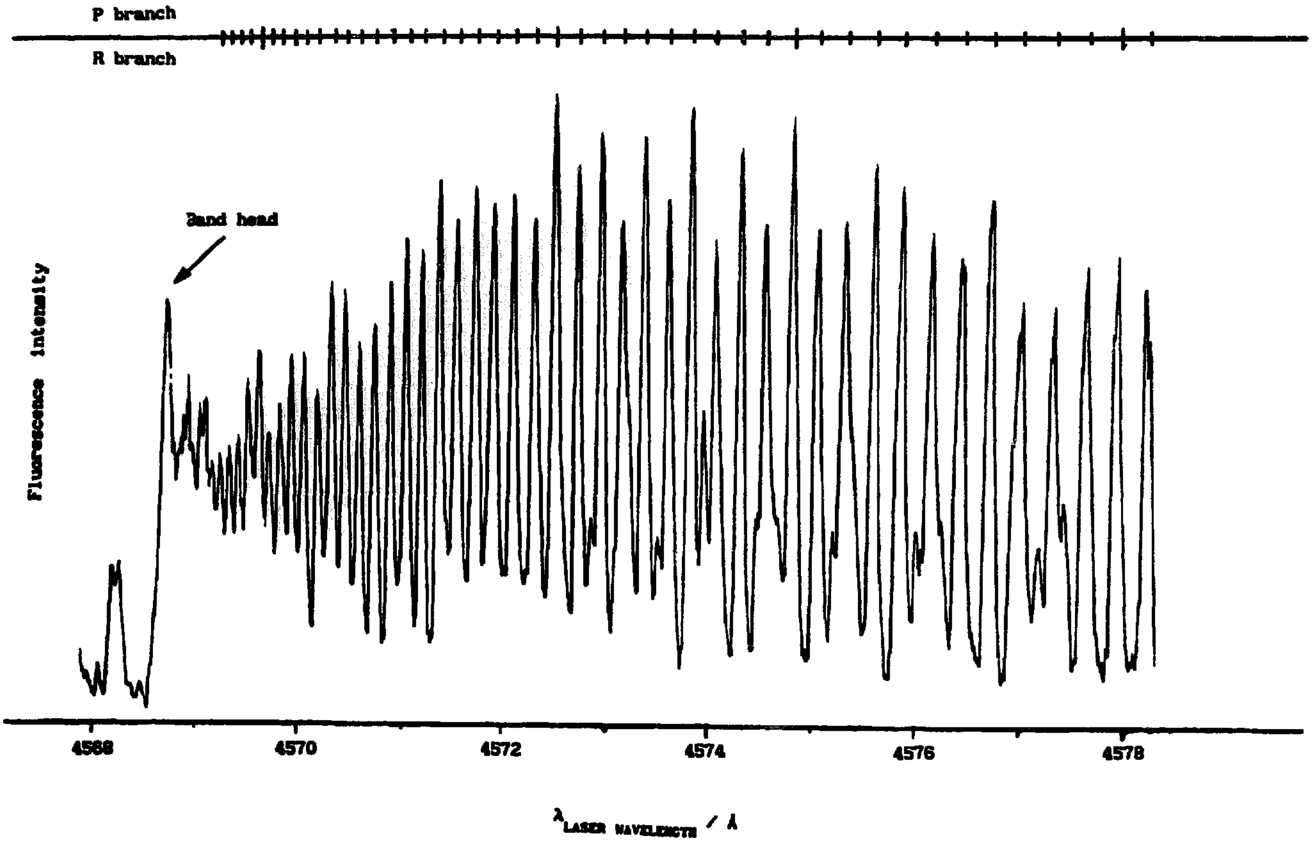


Fig. 3. Laser excitation spectrum of the so-called $(v'+5)-0$ band of the BiI 2(III) system.

Table 2
Wavenumbers of the observed bandheads (in cm^{-1}) of the 2(III)–X(0^+) system and fluorescence lifetimes (τ) values for emission from different vibrational levels of the BiI 2(III) state ($P_{\text{Total}} = 10$ mTorr).

v'–v'' band	ν_{vac} (cm^{-1})	τ_{OBS} (μs)
v'–0	21369	0.58 ± 0.02
(v' + 5)–0	21882	0.61 ± 0.03
(v' + 6)–0	21975	0.57 ± 0.03
(v' + 10)–0	22394	0.62 ± 0.03
(v' + 12)–0	22593	0.61 ± 0.03
(v' + 14)–0	22790	0.60 ± 0.03
(v' + 16)–0	22976	0.58 ± 0.03

between approximately 4568 and 4578 Å of a typical band excitation spectrum.

No assignment for bands in this spectral region has been possible in base to the reported band system published in the literature, including the so-called A'(0^+)–X observed by Yamdagni [4] in absorption. Table 2 shows the observed bandheads in the 2(III)–X transition of BiI molecule. Even though the obtained spectroscopic information is not enough to give an assignment of the observed bands, the observation of a vibrational ladder with approximate spacing of 100 cm^{-1} is clearly perceivable which allows one to make an assignment attempt as proposed in Table 2. Different attempts of rotational assignment has been made using the method of combination differences. Unfortunately, it was not possible to give a precise rotational numbering in this assignment. Line sequences of the branches R and P are clearly perceptible. Once bandheads were identified, fluorescence lifetimes of different vibrational levels of the bands of the 2(III) state were measured and their values showed in Table 2. Table 2 shows measured lifetime values, at $P_{\text{Total}} = 10$ mTorr, for different vibrational levels of the 2(III) state. However, because of the presence of others molecules, it was not possible to obtain values at lower pressures and these values should be taken not as collision-free lifetimes but as a minimum limit of these values.

Fluorescence decay curves obtained from the time dependence of the BiI emission of the 2(III) state showed a monoexponential behaviour characterized by a single lifetime of around $\tau = 0.6$ μs for low BiI pressures (≤ 10 mTorr). This value is proposed as a minimum limit of the radiative lifetime of the 2(III) state of BiI. Statistical analyses to obtain the lifetimes were carried out over a time period greater than three fluorescence lifetimes. The lifetime errors were evaluated as twice the standard deviation ($\pm 2\sigma$) of the measurements. When accidental overlapping of the P and R lines existed, it was not possible to resolve the P and R doublets. However, the mixed decay was monoexponential, indicating that the emission from these rotational levels did not produce different lifetimes. Within the experimental error no significant variation of the lifetimes with rotational energy was observed for different vibrational levels of BiI 2(III) excited state.

Potential energy curves of the low-lying Ω states of BiI can be seen in Fig. 2 of Ref. [5] and computed spectroscopic data of the lowest BiI electronic states of interest to our work in Table 5 of that reference. The well known $B(0^+)$ state, suffers a second avoided crossing with the $0^+(IV)$ state, giving place to a maximum and then later a second minimum before dissociating to $Bi(^4S_{3/2})$ and $I(^2P_{3/2})$. The characterization and assignment of the B–X transition have been made and fluorescence lifetimes from the first five vibrational levels of the $B(0^+)$ state measured. However, the other excited state involved in the band system observed in the 4330–4770 Å region is not at first sight evident, where the states 2(III) and 0^-(III) might be responsible for absorption and further emission of fluorescence.

The experimental value for ω_e around 103 cm^{-1} could be compatible with the calculated values of 127 cm^{-1} for the 2(III) and of 100 cm^{-1} for the 0^-(III) by Alekseyev et al. [5], having taken into account the accuracy of the calculations, where differences of 28 cm^{-1} between the experimental and calculated values have been found for the $B(0^+)$ state. The calculated value of Te (excitation energy) for the 0^-(III) is 23 175 cm^{-1} and has been calculated in excess for at least 2000 cm^{-1} or the transition $0^-(III)–X_1\ {}^3\Sigma^-_0$ cannot give account of the experimental band system found from 4330 Å upwards. On the other hand, it is quite likely that a similar difference encountered between the calculated and experimental value of Te of the $B(0^+)$ state, namely 759 cm^{-1} higher for the calculated value, ought to be expected for the 2(III), in such a case the observed bands should be attributed to the $2(III)–X_1\ {}^3\Sigma^-_0$ system. Furthermore, the 0^-(III) state has been described as a state with a very shallow well and the progression of bands observed could not been explained (see Table 2), and, however, the 2(III) potential well is the deepest.

As reported by Alekseyev et al. [5] the 2(III) state has strong transitions down to the a $^1\Delta_2$ state, and a calculated radiative lifetime for depopulation of the 2(III) of 4.1 μs have been calculated. That would be in good agreement with our measured fluorescence lifetime of 0.6 μs, especially having taken into account that our experimental value is not a collision-free value and, therefore, our reported value should be taken as minimum, i.e. $\tau \geq 0.6$ μs. On the other hand, it is also likely that the 2(III) state undergoes heterogeneous predissociation by the 1(IV) state [5], so this process may compete with radiative emission, giving fluorescence lifetimes smaller than the calculated ones.

The measured fluorescence lifetimes for emission from the $B(0^+)$ state (0.4 μs for $v'=0$) is also in good agreement with the calculated of 10.1 μs. In any case, with the cautions above mentioned for non-collision-free measurements, our reported values should be taken into account as the only experimental values available for the radiative lifetime of the $B(0^+)$ state, i.e. $\tau \geq 0.4$ μs.

When comparing the radiative lifetime obtained for the $A'(0^+)$ electronic state of BiI with values previously reported for the lying electronic states of the BiCl molecule, i.e. $\tau = 0.64$ μs for the $A(0^+)$ state and $\tau = 2.75$ μs for the $A'(0^+)$ state [5], the $A(0^+)$ state of the BiBr molecule, i.e. $\tau = 0.52$ μs [7], and the $A(0^+)$ state of BiF molecule, i.e. $\tau \cong 1.4$ μs [8] similar lifetimes are observed. So, from these results it is concluded that no significant dependence on the molecular mass of the halogen atom in BiX (X = F, Cl, Br, I) is observed for the radiative lifetimes of the lowest electronic excited states.

The measured lifetimes of 0.4–0.2 μs and 0.6 μs for the $B(0^+)$ and 2(III) excited states of BiI, suggest a relatively large value for the electric dipole transition moment for the involved B–X and 2(III)–X transitions. This may be attributed to a large amount of $^3\Pi$ character in the B and 2(III) excited states of the BiI molecule, as published by Alekseyev et al. [5] for the excited states of the BiI molecule.

In conclusion, fluorescence lifetimes for emission from the well known $B(0^+)$ state of the BiI molecule are reported, the 2(III)–X transition has been characterized by laser-induced fluorescence and fluorescence lifetimes for emission from the 2(III) state have been reported, where the reported values of lifetimes should be taken as a minimum limit of the radiative lifetime of these excited states of the BiI molecule from which experimental values had not been published.

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References

[1] F. Morgan, *Phys. Rev.*, *49* (1936) 41.
[2] P.T. Rao, *Indian J. Phys.*, *23* (1949)379.
[3] O.N. Singh, B.P. Asthana and N. Singh, *Spectrosc. Lett.*, *8* (1975) 101.
[4] R. Yamdagni, *Spectrochim. Acta*, *26A* (1970) 1071.
[5] A.B. Alekseyev, K.K. Das, H.-P. Liebermann, R.J. Buenker and G. Hirsch, *Chem. Phys.*, *198* (1995) 333
[6] E. Martínez and M.R. López, *J. Phys. B: Atom. Mol. Opt. Phys.*, *28* (1995)773.
[7] E. Martínez, M.R. López and A. Ortiz de Zarate, *J. Mol. Struct.*, *349* (1995) 261.
[8] E. Martínez, M.R. López, A. Notario and F. Poblete, *Chem. Phys.*, *199* (1995) 305.
[9] R.F. Heidner III, H. Helvajian, J.C. Holloway and J.B. Koffend, *J. Chem. Phys.*, *84* (1986) 2137.
[10] A. J. Ross, R. Bacis, J. D'Incan, C. Effantin, B. Koffend, A. Topouzkhanian and J. Vergs, *Chem. Phys. Lett.*, *166* (1990) 539.
[11] M.D. Oberlander and J.M. Parson, *J. Chem. Phys.*, *97* (1992) 150.
[12] M.D. Oberlander and J.M. Parson, *J. Chem. Phys.*, *99* (1993) 2365.
[13] A. B. Alekseyev, H.P. Liebermann, I. Boustani, G. Hirsch and R. J. Buenker, *Chem. Phys.*, *173* (1993) 333.
[14] E. Martínez, F.J. Basterrechea, J. Albaladejo, F. Castaño and P. Puyuelo, *J. Phys. B: Atom. Mol. Opt. Phys.*, *24* (1991)2765.
[15] E. Martínez, M.R. López, F.J. Basterrechea and P. Puyuelo, *Laser Chem.*, *11* (1991) 279.
[16] D. Cubicciotti and F.J. Keneshea, *J. Phys. Chem.*, *63* (1959) 295.
[17] D. Cubicciotti, *J. Phys. Chem.*, *65* (1961)521.
[18] P. Kuijpers, T. Torring and A. Dynamus, *Chem. Phys.*, *12* (1976)309.