

Multiphoton Excitation in Molecular Bismuth

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Two new molecular emissions have been observed at 400 nm and 250 nm in bismuth vapour after visible and infrared multiphoton absorption. A new state of even parity, labelled *W* and lying at more than 37600 cm^{-1} from the ground state, has been evidenced. Known atomic lines are also excited via dissociation of repulsive states.

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Diatomic bismuth has proved to be a very efficient medium for laser oscillations [1]. Accordingly extensive spectroscopic investigations have been carried out recently, utilizing continuous wave Ar^+ or Kr^+ lasers [2]. This paper reports the fluorescence of Bi_2 induced by a pulsed laser emitting in the infrared, visible and ultraviolet by frequency doubling and tripling.

Bismuth vapour, contained in a cross-shaped heat pipe at 940°C , has been excited by a YAG laser (pulse duration $\sim 11\text{ ns}$, linewidth $\sim 0.7\text{ cm}^{-1}$ at $1.064\text{ }\mu\text{m}$, repetition rate: 10 Hz). The fluorescence, observed perpendicular to the laser beam, has been recorded using a Boxcar averager. The input energy was 850 mJ for the fundamental infrared radiation ($1.064\text{ }\mu\text{m}$). Second and third harmonics were also utilized, pure or mixed (350 mJ at 532 nm and 130 mJ at 355 nm). Known single-photon laser-induced fluorescence series have been excited in the systems $\text{A} \rightarrow \text{X}$ and $\text{V} \rightarrow \text{X}$ respectively, when the visible and ultraviolet components were focused separately in the heat pipe [2]. Moreover, two new molecular emissions as well as atomic lines have been observed, due to multiphoton excitation.

Table I. Atomic emission lines of bismuth via multiphoton absorption and dissociation.

Excited level		Emission line		Relative intensity ^g				
Configura- tion	Energy ^a (cm^{-1})	Transition	Wavelength ^b (\AA)	Excitation				
				Pure IR	Pure Vis.	IR + Vis.	IR + UV	IR + Vis. + UV
$10\text{ s } \left\{ \begin{smallmatrix} 2\text{P}_{1/2} \\ 4\text{P}_{3/2} \end{smallmatrix} \right\}$	67 826.8	$2\text{P}_{1/2} - 2\text{P}_{3/2}^0$	2883.81 ^c				vw	
$7\text{ d } 1/2$	64 236.9	$7\text{ d } 1/2 - 2\text{P}_{1/2}^0$	2347.89	vw				
$8\text{ s } 2\text{P}_{3/2}$	64 020.8	$2\text{P}_{3/2} - 2\text{P}_{1/2}^0$	(2360.1)				vw	
$8\text{ s } 4\text{P}_{3/2}$	60 812.1	$4\text{P}_{3/2} - 2\text{D}_{5/2}^0$	2203.12	vw				
$6\text{ d } 5/2$	58 274.5	$6\text{ d } 5/2 - 2\text{D}_{3/2}^0$	2133.63	vw				
$6\text{ d } 1/2$	57 607.8	$6\text{ d } 1/2 - 2\text{P}_{1/2}^0$	2781.26 ^d					w
$10\text{ d } 2\text{D}_{3/2}$	56 329.8	$2\text{D}_{3/2} - 2\text{P}_{1/2}^0$	2883.81 ^c				vw	
$9\text{ d } 2\text{D}_{3/2}$	55 424.7	$2\text{D}_{3/2} - 2\text{D}_{5/2}^0$	2499.51				vw	
$7\text{ d } 2\text{D}_{3/2}$	51 018.6	$2\text{D}_{3/2} - 2\text{P}_{1/2}^0$	3405.66			w		
$7\text{ s } 2\text{P}_{3/2}$	49 460.6	$2\text{P}_{3/2} - 2\text{D}_{3/2}^0$	2627.91				vw	
$7\text{ s } 4\text{P}_{5/2}$	48 489.6	$4\text{P}_{5/2} - 2\text{D}_{5/2}^0$	3024.64			w	w	m
$8\text{ s } 4\text{P}_{1/2}$	47 373.2	$4\text{P}_{1/2} - 2\text{D}_{3/2}^0$	2780.52 ^d					w
$7\text{ s } 2\text{P}_{1/2}$	45 916.0	$2\text{P}_{1/2} - 4\text{S}_{3/2}^0$	2176.62	vw				
		$2\text{P}_{1/2} - 2\text{D}_{3/2}^0$	2897.98	vw		m	w	m
		$2\text{P}_{1/2} - 2\text{P}_{1/2}^0$	4121.53					s
$7\text{ s } 4\text{P}_{3/2}$	44 865.3	$4\text{P}_{3/2} - 4\text{S}_{3/2}^0$	2228.25 ^e	vw				
		$4\text{P}_{3/2} - 2\text{D}_{3/2}^0$	2989.03 ^f	vw		m	w	m
		$4\text{P}_{3/2} - 2\text{D}_{5/2}^0$	3397.21			m	m	s
$6\text{ d } 2\text{D}_{5/2}$	44 817.1	$2\text{D}_{5/2} - 4\text{S}_{3/2}^0$	2230.61 ^e	vw				
		$2\text{D}_{5/2} - 2\text{D}_{3/2}^0$	2993.34 ^f	vw		m	w	m
$7\text{ s } 4\text{P}_{1/2}$	32 588.0	$4\text{P}_{1/2} - 4\text{S}_{3/2}^0$	3067.72	vw	m	m	m	s
		$4\text{P}_{1/2} - 2\text{D}_{3/2}^0$	4722.55		vs	vs	vs	vs

^a Levels measured by Joshi and Srivastava (Ref. 4).

^b Values given by A. N. Saidel et al., H. F. Clearman or S. Mrozowski (Ref. 5).

^c Both transitions correspond to the same wavelength, and it was not possible to know which one is involved.

^{d, e, f} The resolution of the monochromator used was not sufficient to determine if either or both of these two lines are excited.

^g vs: very strong; s: strong; m: mean; w: weak; vw: very weak.

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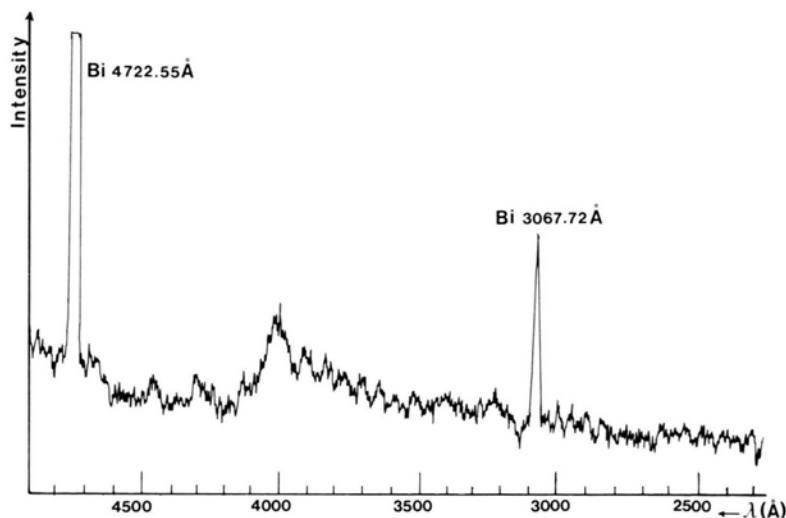


Fig. 1. Part of fluorescence spectrum of bismuth upon pure visible excitation (532 nm).

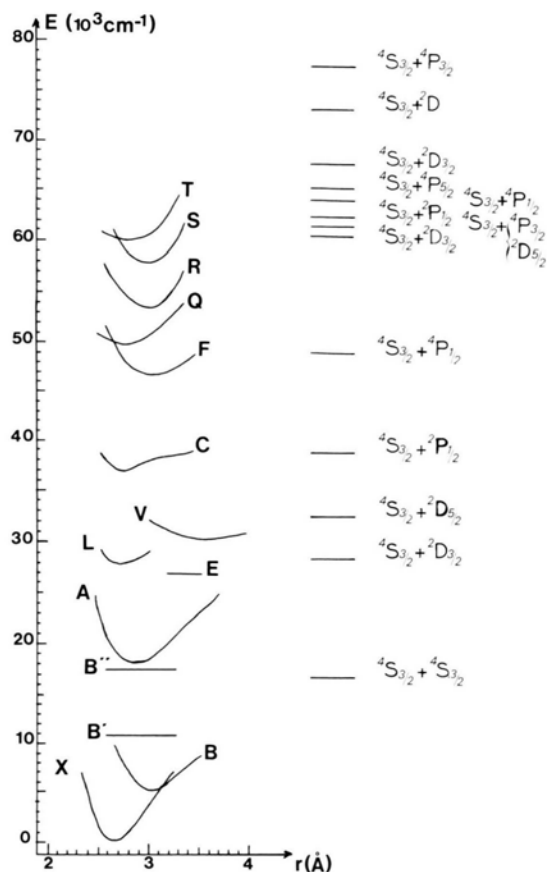


Fig. 2. Potential energy curves for the best observed states of Bi_2 (after ref. 2).

The visible light (532 nm) gives rise to a weak molecular structure at roughly 400 nm (Fig. 1). Its origin may be explained in the following manner: a first photon raises a bismuth molecule to state A (see Figure 2). The absorption of a second photon excites the latter to a new state of even parity, called W_g , which radiates to the low-lying odd state B_u . W_g is thus situated at least at 37600 cm^{-1} from the ground state X_g . When both infrared and visible laser

radiations enter the vapour zone, another molecular structure appears at 250 nm approximately. It is due to the further absorption of an infrared photon by a molecule in the W_g state. The final state attained in this manner is of odd parity, and lies at more than 47000 cm^{-1} from the X state. It may be one of the already known F or Q states (see Fig. 2), or a new one. The molecular emission observed at 250 nm is due to a transition towards the low-lying even states X or B' .

Atomic lines have been observed in any case of excitation (see Table 1). At least two photons are absorbed by a bismuth molecule which is thus excited to a repulsive state [3]. The subsequent dissociation yields an atom in the ground state ($4S_{3/2}$) and an excited atom, which gives rise to the atomic emission. The lines observed upon absorption of infrared photons are comparatively very weak, because at least 6 photons are involved. $7s^4P_{1/2}$ is the first excited level populated, and the lines originating from it (3067.72 Å and 4722.55 Å) are the strongest ones. 3 visible or 2 ultraviolet photons are absorbed in the process leading to this level. The other levels are not populated by visible photons alone. One further infrared photon must be absorbed (after 3 visible or 2 U.V. photons) in order to yield the $6d^2D_{5/2}$, $7s^4P_{3/2}$, $7s^2P_{1/2}$ and $7s^4P_{5/2}$ levels, whereas the $8s^4P_{1/2}$ level is excited only in the presence of both visible and U.V. radiations (2 photons from the former and one photon from the latter are required).

To sum up, two new molecular emissions have been observed in bismuth. They originate from a new bound state W of even parity, lying at more than 37600 cm^{-1} , and another one of odd symmetry, having an energy greater than 47000 cm^{-1} . Besides, several even or odd repulsive states lie at more than 50000 cm^{-1} and are optically connected to the ground state. By multiphoton absorption they yield ground and excited atoms of different energies, the latter giving rise to several known emission lines.

The molecular fluorescence is rather weak in the type of excitation used. A dye laser would be better suited to reach higher intensities; otherwise, no laser action can be expected.

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