Two photon optogalvanic spectrum of the D–X system of HgBr

G ULLAS, V KUMAR and S B RAI

Laser and Spectroscopy Laboratory, Department of Physics, Banaras Hindu University, Varanasi 221 005, India

Abstract. Two photon laser optogalvanic spectrum of the D–X system of HgBr molecule has been recorded using Nd–YAG laser pumped dye laser for the first time. A large number of new bands involving higher vibrational levels have been observed. Isotopic heads due to the two bromine isotopes have been observed and used in fixing the vibrational assignment. Vibrational constants for the X and D states of the two isotopic molecules have been determined.

1. Introduction

The spectrum of diatomic mercury bromide has been a subject of study for several decades (Rai et al 1983; Kumar et al 1987 and references therein). Broad band lasing transition in the B–X system of this molecule is known since several years. However the mechanism of population inversion is not well understood as yet. It is supposed that $HgBr_2$ molecule in the excited states ($^1\Sigma^+, ^3\Sigma^+$) dissociates into Br and HgBr in the $B^2\Sigma^+$ state, a transition from $V = 0$ level of this to the higher vibrational levels in the ground state ($X^2\Sigma^+$) give rise to the lasing action. Most of these studies have been concerned with the $B \to X$ emission (Nighan 1980; Nighan and Brown 1982; Megeoch et al 1983a, b) and very little attention has been devoted to the higher lying excited states of HgBr (e.g. C, $D^2\Pi$ states etc.) which are energetically closer to the $^1\Sigma^+$ and $^3\Sigma^+$ states of $HgBr_2$. The role of such levels cannot be neglected as they may provide efficient pathways for energy transfer from $HgBr_2$ to HgBr.

Recently we have studied the bands involving these states under moderately high resolution (Rai et al 1983). However these studies are limited in scope since only few low lying vibrational levels could be studied because of unfavourable vibrational intensity distribution. The study of high lying levels of these states are very important for energy transfer.

Studies of molecular species by the optogalvanic technique had shown that bands involving low Franck-Condon factors could be detected using this technique. It was therefore felt that use of this technique might result in more detailed information about these states of HgBr. In view of the short wavelengths involved we used the two photon optogalvanic technique and the results of these studies are presented here.
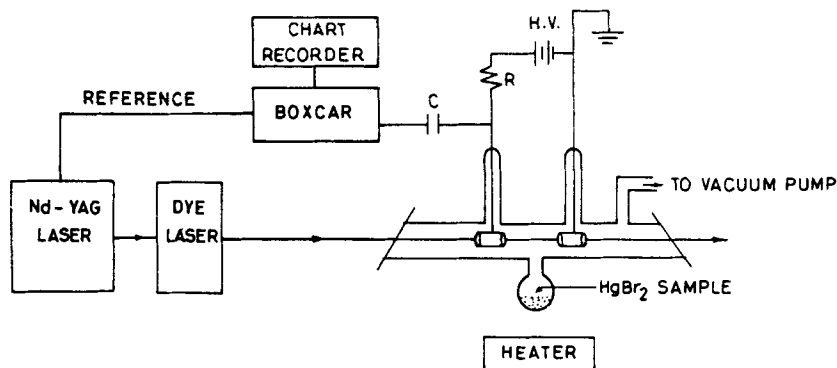
Figure 1. Schematic diagram of the LOG experimental set up.

2. Experimental details

The experimental set up used in the present study is shown in figure 1. It consists of a glass discharge tube of 15 cm length with ends cut at Brewsters angle and a small bulb in the centre to keep the sample. The tube is fitted with two cylindrical electrodes of Ni, 0·5 cm in diameter and 1 cm in length, which are kept 1·5 cm apart. The tube was first evacuated and then heated up to about 200°C so as to give HgBr vapour at a pressure of a few torr in the tube. When voltage of 700–1000 V from a stabilized D.C. power supply was applied across the electrodes, a stable and silent bluish colour discharge resulted. A dye laser with coumarine 500 dye pumped by third harmonic of a Nd–YAG laser was used as a source of radiation. This gave a continuously tunable laser radiation from 485–545 nm. The energy output of the dye laser at 500 nm is 8·5 mJ/pulse. Polarization of the laser beam was kept linear. The dye laser output was tightly focussed in the central part of the cell with a 50 cm focal length convex lens. The signal was processed through a EG & G boxcar average model 162 with a gate width of 5 ns and time constant of 1 μs. The optogalvanic signal was finally fed to a double pen recorder (omniscribe). A small part of the laser beam was directed onto the slit of a 0·5 m monochromator for wavelength calibration. The spectra were also recorded by varying the laser power. We have also checked the fluctuation of discharge which was very stable. Our measured bands are accurate to $\pm 1 \, \text{cm}^{-1}$.

3. Results

From the previous spectroscopic studies it has been concluded that the X, B, C, D and E states in HgBr are of $^2\Sigma^+$, $^2\Sigma^+$, $^2\Pi_{1/2}$, $^2\Pi_{3/2}$ and $^2\Pi$ type respectively. Another $^2\Pi$ state labelled as A state has also been reported by Lapatovitch *et al* (1982) and Megeoch *et al* (1983) though it is almost unstable and combines only with the $B^2\Sigma^+$ state. The longest wavelength band system arising from the $B^2\Sigma^+-X^2\Sigma^+$ transition in HgBr extends up to 508 nm, while the remaining $C^2\Pi_{1/2}-X^2\Sigma^+$, $D^2\Pi_{3/2}-X^2\Sigma^+$ and $E^2\Pi-X^2\Sigma^+$ transitions cover the spectral range 294–243 nm. No discrete bands have been observed in HgBr emission or absorption spectrum in the region with $\lambda > 508$ nm. When we looked at the optogalvanic signal in HgBr in the region $\lambda > 508$ nm, at smaller laser power (less than 1 mJ) no signal corresponding to
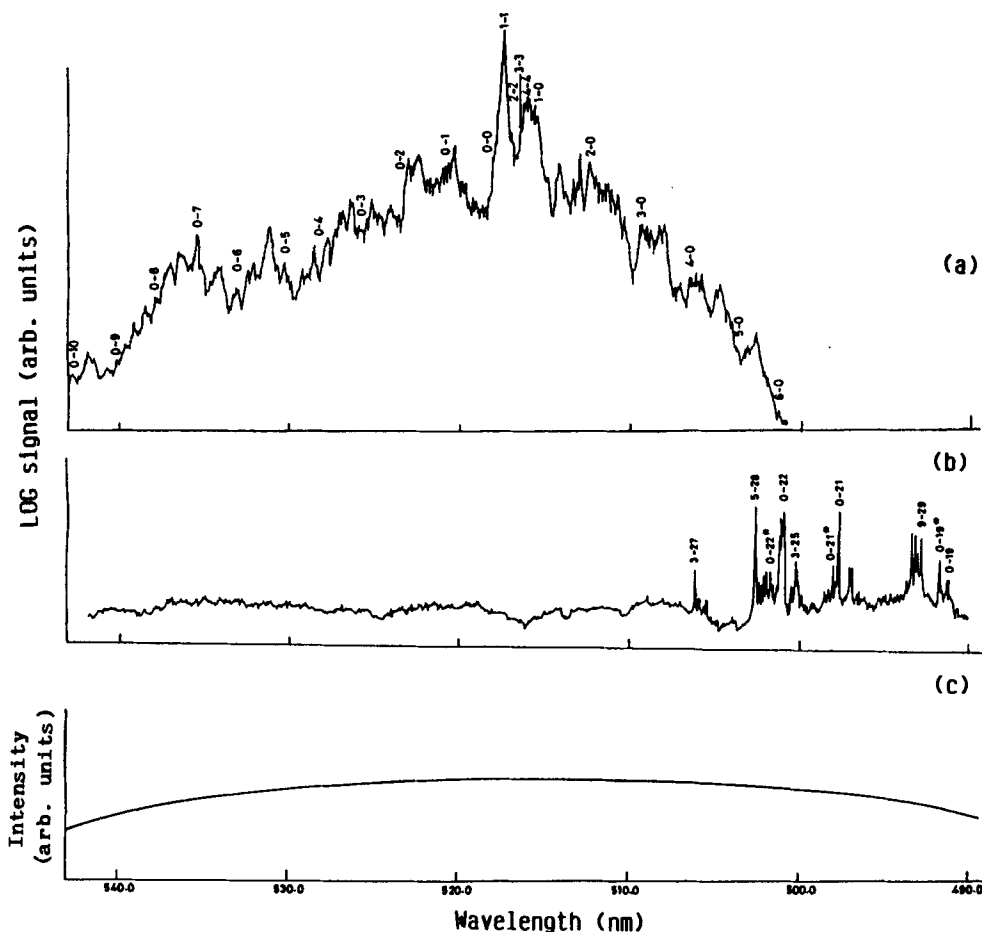
Figure 2. (a) Two photon optogalvanic spectrum of the $D-X$ system of HgBr (laser power 8 mJ/pulse); (b) Optogalvanic signal in the wavelength region 545–490 nm at 1 mJ laser power; (c) Laser profile.

discrete transition was observed (see figure 2b). On the other hand when the laser power was increased, large number of bands were seen with $\lambda > 506$ nm (see figure 2a). We found from our measurements of the laser power and the estimated size of the focussed spot that the bands are observed only when the photon density exceeds 3.5×10^{19} photons/cm^2. Since the lasing efficiency of the dye goes down considerably towards the two ends of the tunable range therefore only a rather limited spectral region could be explored. However, the variation of the optogalvanic signal with laser power (see figure 3) confirms that these are due to a two photon absorption process and belong to the $D^2\Pi_{3/2}-X^2\Sigma^+$ transition. Some of the bands observed at the shorter wavelengths obviously belong to the $B-X$ system and corresponds to one photon transition.

3a. *Analysis of the bands of the D–X system*

The two photon optogalvanic spectrum corresponding to the $D-X$ system of HgBr is shown in figure 2a which also shows the dye laser profile (figure 2c). No
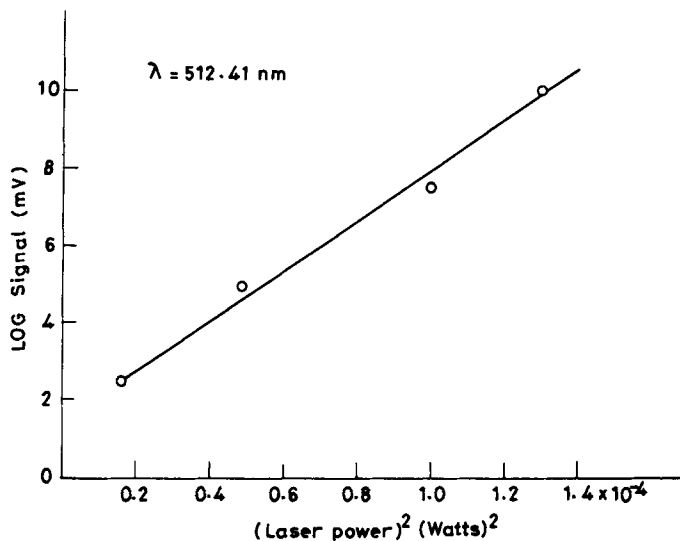
Figure 3. Variation of LOG signal with (laser power)^2.

normalization of the spectrum was performed. The spectrum shows a large number of bands superposed on the dye laser emission profile. A comparison of the optogalvanic spectrum with the emission spectrum recorded earlier (Rai *et al* 1983) helped us in identifying the bands of 0,0 and other sequences. In the emission measurements we could observe bands belonging to $\Delta V = 0$, ± 1, ± 2, ± 3 and ± 4 sequences only, however, in the optogalvanic study bands belonging to $\Delta V = 5$, 6 and $\Delta V = -5$, -6, -7, -8 and -9 have also been detected. In addition new bands involving vibrational levels with high quantum number, both in the upper and the lower electronic states have also been observed in the sequences known earlier. The new bands of the D–X system as measured in the present work are given in table 1.

As mentioned earlier, the D–X system in the HgBr arises due to $^2\Pi_{3/2}$–$^2\Sigma^+$ transition. Unlike the atoms, the selection rules for two photon transition in molecules are $\Delta\Lambda = 0$, ± 1, ± 2, $\Delta J = 0, \pm 1$, ± 2, $g \rightarrow g$ and $s \rightarrow a$. The intensity of the different branch lines depend on the polarization characteristics of the laser beam. If both the photons absorbed by the molecule are right handed circularly polarized a transition with $\Delta\Lambda = 2$ will be allowed but not with $\Delta\Lambda = 0$. However if one photon is right hand polarized and other left, $\Delta\Lambda = 0$ will appear with large intensity compared to $\Delta\Lambda = 2$. With linearly polarized light it is $\Delta\Lambda = 0$ which is allowed. However $\Delta\Lambda = \pm 1$ transition appears in both the cases. In two photon transition the parity of the excited state is always preserved. In the present spectrum the rotational structure in different bands are not resolved. Even the two band heads also lie very close to each other and could not be resolved. The HgBr molecule has several isotopic constituents and while the isotopic shifts due to the different mercury isotopes are too small to be resolved the two different heads due to the ^{79}Br and ^{81}Br isotopes could be clearly identified in many cases. The measured isotopic separations which are within our error limit to the calculated isotopic shifts helped in confirming the vibrational assignments. We have now arranged all the known bands of the D–X system including the new ones presently measured in the Deslandre's scheme for the two isotopic molecules and determined the vibrational constants for the two states. These new

Table 1. Vacuum wave numbers (cm^{-1}) vibrational assignment and the vibrational isotopic shift due to bromine isotope in the $D-X$ system of Hg ^{81}Br.

Observed λ (nm)	Observed ν (cm^{-1})	$\nu \times 2$ (cm^{-1})	Assignment of the bands	Isotopic shift	
				Obs. (cm^{-1})	Cal. (cm^{-1})
500·81	19962·084	39924·168	6–0	—	11·7
501·52	19933·835	39867·650	10–5	—	10·9
501·67	19927·746	39855·492	9–4*	—	10·7
502·13	19909·609	39819·218	8–3*	11·6	10·4
502·79	19883·475	39766·950	12–8	—	10·2
503·10	19871·223	39742·446	6–1	—	9·9
503·61	19851·100	39702·200	10–6	—	9·4
504·06	19833·378	39666·756	9–5	—	9·2
504·52	19815·295	39630·590	8–4	7·7	8·9
504·73	19807·051	39614·102	12–9*	—	8·5
505·89	19761·634	39523·268	10–7	7·3	8·0
506·15	19751·482	39502·964	9–6*	—	7·7
506·51	19737·445	39474·890	11–11	8·3	7·5
507·12	19713·703	39427·406	12–10	—	7·2
507·32	19705·932	39411·864	7–4	8·5	7·2
507·58	19695·838	39391·676	11–9	6·3	6·9
508·03	19678·315	39356·630	10–8	6·3	6·6
509·36	19627·010	39254·020	7–5*	—	5·7
510·07	19599·690	39199·380	6–4	5·7	5·4
511·29	19552·924	39105·848	8–7	5·1	4·6
512·41	19510·186	39020·372	6–5	4·2	3·9
			10–10		3·6
514·04	19448·321	38896·642	11–12	—	3·1
			7–7*		2·8
514·45	19432·822	38865·644	2–1*	—	2·5
514·70	19423·383	38846·766	6–6*	—	2·4
515·26	19402·273	38804·546	5–5	2·3	2·0
515·56	19390·933	38781·866	12–14	2·5	2·3
515·80	19381·961	38763·922	8–9	—	1·8
			4–4		1·7
516·07	19371·821	38743·642	11–13	—	1·8
516·38	19356·443	38712·886	7–8	—	1·4
516·81	19344·083	38688·166	10–12	—	1·4
516·99	19337·348	38674·696	6–7	—	0·9
517·54	19316·798	38633·596	5–6*	—	1·3
517·65	19312·693	38625·386	12–15	—	1·1
518·05	19297·782	38595·564	8–10	—	0·1
518·20	19292·047	38584·094	4–5	—	0·2
			11–14		0·7
518·67	19274·714	38549·428	7–9	—	0·1
519·02	19261·717	38523·434	10–13	—	0·2
519·63	19239·105	38478·210	9–12	—	0·2
519·84	19231·333	38462·666	5–7	—	0·8
520·29	19214·700	38429·400	8–11	—	0·7

(Continued)

Table 1. (*Continued*)

Observed λ (nm)	Observed ν (cm⁻¹)	ν × 2 (cm⁻¹)	Assignment of the bands	Isotopic shift Obs. (cm⁻¹)	Cal. (cm⁻¹)
520·55	19205·103	38410·206	4–6	—	1·2
521·26	19181·152	38362·304	10–14	—	0·1
521·61	19166·076	38332·152	6–9	—	1·7
521·72	19162·035	38324·070	9–13	—	1·4
521·82	19158·363	38316·726	2–4	—	2·1
522·23	19143·322	38286·644	5–8	—	2·1
522·43	19135·993	38271·986	8–12	—	2·0
523·20	19107·831	38215·662	7–11	—	2·5
523·55	19095·057	38190·114	3–6	—	2·4
523·90	19082·302	38164·604	6–10	3·7	3·4
524·00	19078·659	38157·318	9–14	—	2·6
524·57	19057·928	38115·856	5–6	3·7	3·5
524·70	19053·206	38106·412	8–13	3·5	3·2
525·19	19035·430	38070·860	4–8	3·9	4·0
525·39	19028·184	38056·368	7–12	3·8	3·7
526·17	18999·977	37999·954	6–11	3·4	4·3
			9–15		3·8
526·88	18974·374	37948·748	5–10	5·0	5·2
			8–14		4·4
527·61	18948·121	37896·242	4–9	—	5·4
			7–13		4·9
528·38	18920·508	37841·016	6–12	5·9	5·5
529·07	18895·833	37791·666	8–15	6·3	5·5
			5–11		6·1
529·77	18870·866	37741·732	1–6	—	6·3
529·87	18867·304	37734·608	7–14	7·2	6·1
			4–10		7·1
530·47	18845·965	37691·930	0–5	7·3	7·6
530·66	18839·217	37678·434	6–13	7·2	6·7
			3–9		7·3
531·46	18810·505	37621·010	5–12	8·9	7·4
			2–8		7·9
532·16	18786·115	37572·230	7–15	7·3	7·3
			1–7		8·5
532·96	18757·917	37515·834	6–14	—	7·9
			0–6		9·0
			3–10		9·0
533·89	18726·294	37452·588	5–13*	8·6	8·6
534·54	18702·472	37404·944	4–12	10·6	9·2
			1–8		9·8
535·19	18679·758	37359·516	6–15	10·3	9·1
535·39	18672·780	37345·560	3–11	10·1	9·9
			0–7		
536·04	18650·138	37300·276	5–14	10·6	9·8
536·23	18643·530	37287·060	2–10	10·5	10·9
536·93	18619·224	37238·448	4–13	10·7	10·4
537·20	18609·866	37219·732	1–9*	10·5	11·2

Table 1. (*Continued*)

Observed λ (nm)	Observed ν (cm^{-1})	$\nu \times 2$ (cm^{-1})	Assignment of the bands	Isotopic shift	
				Obs. (cm^{-1})	Cal. (cm^{-1})
537·83	18588·068	37176·136	3–12	10·5	11·1
538·00	18582·194	37164·388	0–8	12·2	11·8
528·32	18571·148	37142·296	5–15	10·5	10·9
538·76	18555·981	37111·962	2–11*	—	11·8
539·12	18543·591	37087·182	4–14	11·5	11·6
539·52	18529·843	37059·686	1–10	13·9	12·9
540·12	18509·601	37019·202	3–13	13·1	12·4
540·56	18494·193	36988·386	0–9	13·8	13·2
541·06	18477·102	36954·204	2–12	13·6	13·1
541·56	18460·043	36920·086	4–15	13·8	12·8
541·86	18449·823	36899·646	1–11	13·9	13·8
542·70	18421·266	36842·532	0–10	14·0	14·9

*Bands due to Hg^{79}Br

constants are very close to the values obtained in our earlier work (Rai *et al* 1983). This establishes that the constants reported earlier by us are sufficient to reproduce the bands involving $V' \leqslant 13$ and $V'' \leqslant 15$.

Acknowledgements

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