

## On the C-X system of diatomic mercury chloride

A K RAI, S B RAI and D K RAI

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

MS received 10 October 1980; revised 17 January 1981

**Abstract.** The C-X system of diatomic mercury chloride has been re-investigated in emission. The previous vibrational assignments of this system by Horne and others have been confirmed by measurement of the chlorine isotopic shift and improved vibrational constants for the 'C' state determined.

**Keywords.** Vibrational structure; isotopes; vibrational constant; mercury chloride.

### 1. Introduction

The spectral study of diatomic mercury halides has gained importance due to the observation of lasing transitions in some of their bands [HgCl (558 nm), HgBr (502 nm), Park 1977, Eden 1977b; and HgI (443 nm) Park 1977]. The nature of the ground state with its weak binding in these molecules makes them a possible material for obtaining broad band high power lasers. Both experimental and theoretical work is under way to characterize the molecular states of these compounds in various laboratories (Wadt 1980; Husain *et al* 1980). Spectroscopic studies on these molecules are still in a very unsatisfactory state and the rotational constants corresponding to none of the molecular states are known with high precision. In several cases even the vibrational assignment are still uncertain (Huber and Herzberg 1979). As part of our programme to study the spectra of these compounds we have investigated the emission spectrum of D-X system of HgCl (Rai *et al* 1981). The results of our investigation on the C-X system are presented here.

The earlier vibrational assignments for the C-X system, made on the basis of emission studies (Wieland 1929; Cornell 1938; Howell 1943 and Krishnamurthy 1958) have been shown to be in error by Horne *et al* (1968) who photographed the bands in absorption in a flash photolysis experiment. The overall intensity of absorption spectrum so obtained was very poor resulting in a not too consistent vibrational assignment. We have now succeeded in obtaining a good emission spectrum under moderate resolution and dispersion which has enabled us to confirm the later assignments by Horne *et al* (1968).

### 2. Experimental

A sample of mercuric chloride with a purity 99.9% (Merck) is excited in an uncondensed transformer discharge. It is found that even in a low wattage discharge

HgCl gives very intense whitish glow and all the three known systems B-X, C-X and D-X develop very well. The bands have been photographed on a Hilger large quartz spectrograph (6.8 Å/mm reciprocal dispersion near 2800 Å). The intensity of bands in the C-X system is relatively poor and therefore exposure times as long as 20–30 min were found essential to record them on panchromatic film. Several spectrograms with different exposures were recorded and each was measured a number of times. The measured wavelength is expected to be accurate to within 0.2 Å for sharp bands and to within 1 Å for diffuse bands.

### 2.1. Structure of bands and vibrational analysis

The bands of the C-X system of HgCl are relatively weak and show a rather diffuse pattern. The different sequences overlap with each other making the spectrum look quite complex. The absorption experiment of Horne *et al* (1968) shows that this

Table 1. Band head of C-X system of <sup>35</sup>HgCl

Band	Relative intensity	Observed wavenumber (cm <sup>-1</sup> )	Calculated wavenumber (cm <sup>-1</sup> )	Obs.—Cal. (cm <sup>-1</sup> )	Vibrational isotopic shift for <sup>35</sup> HgCl and <sup>37</sup> HgCl	
					observed (cm <sup>-1</sup> )	calculated (cm <sup>-1</sup> )
(0, 0)	9	35843.03	35843.03	0.0	—	—
(0, 1)	7	35550.33	35549.18	+1.15	— 7.10	— 5.82
(0, 2)	2	35257.00	35257.96	-0.96	-14.00	-12.97
(1, 0)	6	36243.26	36242.06	+1.20	+ 8.26	+10.39
(1, 1)	9	35950.00	35948.21	+1.79	—	+ 3.37
(1, 2)	5	35656.00	35656.99	-0.99	—	- 3.77
(1, 3)	1	35364.00	35368.41	-4.42	—	-11.05
(1, 4)	2	35079.67	35082.47	-2.80	-20.33	-18.44
(2, 0)	4	36639.75	36636.57	+3.17	+20.75	+19.38
(2, 1)	5	36345.33	36342.72	+2.60	+13.71	+12.36
(2, 2)	6	36050.00	36051.50	-1.50	—	+ 5.20
(2, 3)	4	35760.00	35762.93	-2.93	—	- 2.07
(2, 4)	1	35475.00	35476.99	-1.99	—	- 9.45
(2, 5)	2	35193.00	35193.68	-0.68	-16.00	-16.97
(3, 0)	3	37025.00	37026.56	-1.56	—	+28.16
(3, 1)	2	36733.00	36732.71	+0.28	+26.00	+21.13
(3, 2)	4	36439.00	36441.50	-1.50	—	+13.98
(3, 3)	5	36149.00	36152.92	-3.92	—	+ 6.71
(3, 4)	4	35863.50	35866.98	-3.48	—	- 0.68
(3, 5)	1	35578.00	35583.67	-5.67	-10.00	- 8.19
(3, 6)	1	35295.00	35303.00	-8.00	—	-15.83
(3, 7)	2	35018.00	35024.97	-6.97	—	-23.58
(4, 3)	3	36537.70	36538.40	-0.70	—	+15.28
(4, 4)	3	36248.50	36252.46	-3.96	—	+ 7.88
(4, 5)	3	35964.70	36969.15	-4.45	—	+ 0.37
(4, 6)	1	35683.33	35688.48	-4.93	—	- 7.26
(4, 7)	1	35403.33	35410.45	-7.12	—	-15.01
(5, 3)	2	36920.67	36919.36	+1.31	+22.67	+26.78
(5, 4)	3	36633.00	36633.41	-0.41	—	+16.25
(5, 5)	2	36348.70	36350.11	-1.41	—	+ 8.73
(5, 6)	4	36067.00	36069.44	-2.44	—	+ 1.10
(5, 7)	1	35788.00	35791.41	-3.41	—	- 6.66

system involves the ground state of HgCl. The band lying near 2790 Å has the maximum intensity in our emission spectrum as it has in the absorption experiment; we took it as the (0, 0) band. The bands lying at successive separations of  $\sim 290 \text{ cm}^{-1}$  from this band on the longer wavelength side could be marked easily and were assigned to the (0,  $v$ ) progression. The separation of the (1, 1) and (0, 1) bands gives us an idea of  $\Delta G_{1/2}$  in the upper state of this system. Taking this into consideration the bands of the (1, 0) sequence could be marked easily. The bands belonging to other sequences were then sorted out and their wave numbers along with their vibrational assignments are given in table 1.

## 2.2 Isotopic shift

Mercury contains six isotopes with percentage abundances of 6.85% ( $^{204}\text{Hg}$ ), 10.20% ( $^{198}\text{Hg}$ ), 13.22% ( $^{201}\text{Hg}$ ), 16.84% ( $^{199}\text{Hg}$ ), 23.13% ( $^{200}\text{Hg}$ ), 29.8% ( $^{202}\text{Hg}$ ) and chlorine has two isotopes with abundances 75.53% and 24.47%. There are twelve isotopic molecules in all present in natural mercury chloride. However, the isotopic shift corresponding to the different isotopes of Hg is so small [the largest value is  $\sim 2.70 \text{ cm}^{-1}$  for [(3,0)]] that the separate isotopic bands could not be resolved in the present investigations. However the effect of this is that most of the bands appear with a diffuse and broad appearance. This is probably the reason for the difference in calculated and observed wavenumbers of band heads (see table 1). The isotopic shifts corresponding to two isotopes of chlorine is however appreciable and they could be easily marked in the observed spectrum. A good agreement is obtained between the calculated and the observed isotopic shift (see table 1) corresponding to  $^{35}\text{HgCl}$  and  $^{37}\text{HgCl}$ .

## 3. Discussion

Horne *et al* (1968) could observe only 14 bands in their spectrum whereas we could detect more than 30 bands. The  $\Delta G(v + \frac{1}{2})$  values obtained in the present work are much more regular than those reported by Horne *et al* (1968). The vibrational constants obtained in our study are given in table 2. The constants for the excited state is appreciably different from those obtained by Horne *et al* (1968).

Table 2. Vibrational constants of C-X system of mercury chloride

	Present value $\text{cm}^{-1}$	Values reported by Horne <i>et al</i> (1968) $\text{cm}^{-1}$
$\omega'_e$	403.547	383.0
$\omega''_e$	296.486	292.2
$\omega'_e x'_e$	2.259	—
$\omega''_e x''_e$	1.318	—
$\nu_e$	35789.735	35784.0

**References**

- Burnlam R L 1978 *Appl. Phys. Lett.* **33** 156  
Cornell S D 1938 *Phys. Rev.* **54** 341  
Eden J G 1977 *Appl. Phys. Lett.* **31** 448  
Horne D G, Gosavi R and Strausz O P 1968 *J. Chem. Phys.* **48** 4758  
Howell H G 1943 *Proc. R. Soc. (London)* **A182** 95  
Huber K P and Herzberg G 1979 *Constants of diatomic molecules* (New York: Van Nostrand Reinhold)  
Husain J, Wiesenfeld J R and Zare R N 1980 *J. Chem. Phys.* **72** 2479  
Krishnamurthy V G 1958 *Z. Phys.* **150** 287  
Parks J H 1977 *Appl. Phys. Lett.* **31** 192, 297  
Rai A K, Rai S B and Rai D K 1981 *Curr. Sci.* **50** 178  
Schimitschek E J and Celto J E 1978 *Opt. Lett.* **2** 64  
Wadt W R 1980 *J. Chem. Phys.* **72** 2469  
Wieland K 1929 *Phys. Acta* **2** 77