SHORT COMMUNICATIONS

VAPOUR PRESSURE EQUATION FOR METAL HALIDES USED IN DOUBLE PULSE LASERS

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THE use of metal halides to provide substantially reduced operating temperatures in metal vapour lasers has been established with copper chloride and copper iodide as the starting materials[1, 2]. This approach to metal vapour lasers is especially attractive since it can lead to the development of practical efficient high energy laser devices in the visible portion of the spectrum[3–5]. The higher vapour pressure (P) of these metal halides in comparison to the corresponding metals is the main reason for using metal halides as lasents. The vapour pressures of metal halides are available in literature at a few temperatures[6], but no vapour pressure equation of the form $\log P = A + B/T$ is reported for the metal halides except for CuCl, CuBr and CuI for which experimental vapour pressure equations have been obtained for $P < 10^{-2}$ mm of Hg[7] and for $PbCl_2$ and $PbBr_2$, the equations have been reported for the temperature ranges 773–1223 K and 1008–1191 K respectively[8].

The purpose of this note is to present the vapour pressure equations for CuCl, CuBr, CuI, $PbCl_2$, $PbBr_2$, PbI_2 and $MnCl_2$ which are of interest to those working with metal vapour lasers using metal halides as lasents, by least square fitting of reported vapour pressures and temperatures. Table 1 gives the A and B values in vapour pressure equation of the above mentioned metal halides along with the already reported A and B values. These equations will be useful for the estimation of the populations of the metal atoms in laser levels and ground states using $N = P/KT$, where P is the molecular vapour pressure at temperature T, N the molecular vapour density and K the Boltzmann constant.

The extended life-time of upper laser levels in double pulse metal vapour lasers have been obtained using relevant equations[5] and Holstein's theory of resonance radiation trapping[9]. The trapping threshold temperatures have been calculated theoretically using the temperature-life time data[10], and these are compared with existing experimental values of the laser starting temperatures of the metal halide lasers. For example in CuCl, CuBr and CuI the calculated trapping threshold temperatures are 585 K and 695 K which are in excellent agreement with the experimental values 590 K[11], 693 K[12] and 685 K[5] respectively. The results suggest that the present vapour pressure equations are very much consistent and applicable to double pulse metal vapour lasers using metal halides as lasents.

Table 1 *Least square fitting of* $\log P = A + B/T$

Substance	A	B	T in °K	Reference
CuCl	6.115	−5003.21	819–1111	Present work
	5.306	−4103.43	1112–1522	"
	4.649	−3118.61	1523–1763	"
	5.454	−4214.96	1151–1642	8
	11.235	−8156.00	548–657	7
CuBr	6.604	−5574.01	845–1117	Present work
	5.702	−4560.24	1118–1628	"
	9.693	−7674.00	578–657	7
	8.298	−6756.00	670–704	7
	7.787	−6309.00	>743	7
CuI	5.720	−4378.52	900–1180	Present work
	5.329	−3925.81	1181–1610	"
	11.141	−9463.00	<629	7
	9.409	−8351.00	642–670	7
	8.677	−7853.00	680–769	7
$PbCl_2$	8.998	−7375.87	820–998	Present work
	8.405	−6867.45	999–1227	"
	8.961	−7411.44	773–1223	8
$PbBr_2$	8.906	−6995.51	786–959	Present work
	8.262	−6386.67	960–1187	"
	8.064	−6163.14	1008–1191	8
PbI_2	8.933	−6712.60	752–917	Present work
	8.081	−5936.02	918–1145	"
$MnCl_2$	6.937	−6181.50	953–1152	"
	7.619	−6930.33	1153–1463	"

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SPECTROSCOPIC EVIDENCE FOR STERIC ENHANCEMENT OF RESONANCE IN COMPLEXES

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THE phenomenon of steric enhancement of resonance was discovered by Baliah and Uma[1] while studying the electric dipole moments of some substituted anisoles and acetophenones. Since its discovery, several physico-chemical investigations have been carried out in support of this view[2-6]. In the present work the electronic, infrared and ^{1}H NMR spectral data of a few palladium(II) complexes with suitable substituted phenyl methyl sulphides as ligands synthesized[7-9] are taken for substantiating this phenomenon.

It is observed that the electron-releasing substituent present in the ligand decreases the ν(Pd-S) stretching frequency, whereas electron withdrawing group increases[10,11]. The ν(Pd-S) stretching frequency in the complex trans-$PdCl_2(p\text{-}OCH_3C_6H_4SCH_3)_2$ is at 277 cm^{-1} (table 1) which is much less than the corresponding frequency in trans-$PdCl_2(C_6H_5SCH_3)_2$[7,12,13]. This decrease is caused by p-OCH_3, an electron-releasing group. The ν(Pd-S) stretching frequency in trans-$PdCl_2(m\text{-}CH_3C_6H_4SCH_3)_2$ is 297 cm^{-1} which is almost the same as that of the parent compound. The ν(Pd-S) stretching frequency in trans-$PdCl_2(4\text{-}OCH_3\text{-}3\text{-}CH_3C_6H_3SCH_3)_2$ is at 270 cm^{-1}, which is less than that of trans-$PdCl_2(p\text{-}OCH_3C_6H_4SCH_3)_2$, because the 3-methyl group in 4-methyoxy-3-methylphenyl methyl sulphide exerts an accelerating influence of the conjugation of methoxy group with the phenyl ring. The methyl group makes the methoxy assume a trans-orientation and hence the probability of the methoxy group attaining planarity with the aromatic ring increases. There can, therefore, be enhanced interaction of the methoxy group with the aromatic

Table 1 *Infrared, electronic and ^{1}H NMR spectra of the complexes*

Complex	IR ν(Pd-S) cm^{-1}	Electronic spectra λ_{max} nm	Electronic spectra ϵ	^{1}H NMR $-SCH_3$ (δ)	^{1}H NMR $-CH_3$ (δ)	^{1}H NMR $-OCH_3$ (δ)	^{1}H NMR Ph protons (δ)
trans-$PdCl_2(C_6H_5SCH_3)_2$	298	332 277	11,600 7,100	2.66	—	—	7.2–7.86
trans-$PdCl_2(m\text{-}CH_3C_6H_4SCH_3)_2$	297	335 277	11,900 6,600	2.49	2.26	—	7.09–7.49
trans-$PdCl_2(p\text{-}OCH_3C_6H_4SCH_3)_2$	277	365 277	10,000 6,800	2.52	—	3.69	6.69–7.67
trans-$PdCl_2(4\text{-}OCH_3\text{-}3\text{-}CH_3C_6H_3SCH_3)_2$	270	372 277	10,800 8,700	2.52	2.18	3.80	6.66–7.66
trans-$PdCl_2(3,5\text{-di-}CH_3\text{-}4\text{-}OCH_3C_6H_2SCH_3)_2$	312	356 277	10,400 5,700	2.46	2.18	3.60	7.12–7.32

The solvent in all cases was C_6H_6.