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THE 3250 A He-Cd LASER EXCITED RESONANCE RAMAN EFFECT OF $PdBr_4^{2-}$

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The rigorous resonance Raman effect was observed for the square planar $PdBr_4^{2-}$ ion, using the ultraviolet line of a He-Cd laser as the exciting source. The overtone progression of the totally symmetric vibration was observed up to the fourth.

For the study of the resonance Raman effect the laser having the shorter wavelength lines is useful as the exciting source. For this reason we used the 3250 A line of a He-Cd laser and measured the Raman effect for a group of compounds which have the electronic absorption in this region. Especially we tried to study simple and highly symmetrical molecules or ions and the results for $PdBr_4^{2-}$ are given in this report.

An NEC model GLG-2018 He-Cd laser and a Spex model 1401 double monochromator equipped with 5000 A blazed gratings are used. The detection system is composed of an HTV R-585 photomultiplier and a handmade photon counting circuit[1]. The focusing lens of the laser beam and the collecting lens of the scattered light are both made of quartz.

K_2PdBr_4 was prepared from the solution of $PdCl_2$ and KBr in concentrated hydrobromic acid.[2] The visible and ultraviolet absorption spectrum of the sample in 2M hydrobromic acid is shown in Fig. 1. It is in agreement with that of $PdBr_4^{2-}$.[3]

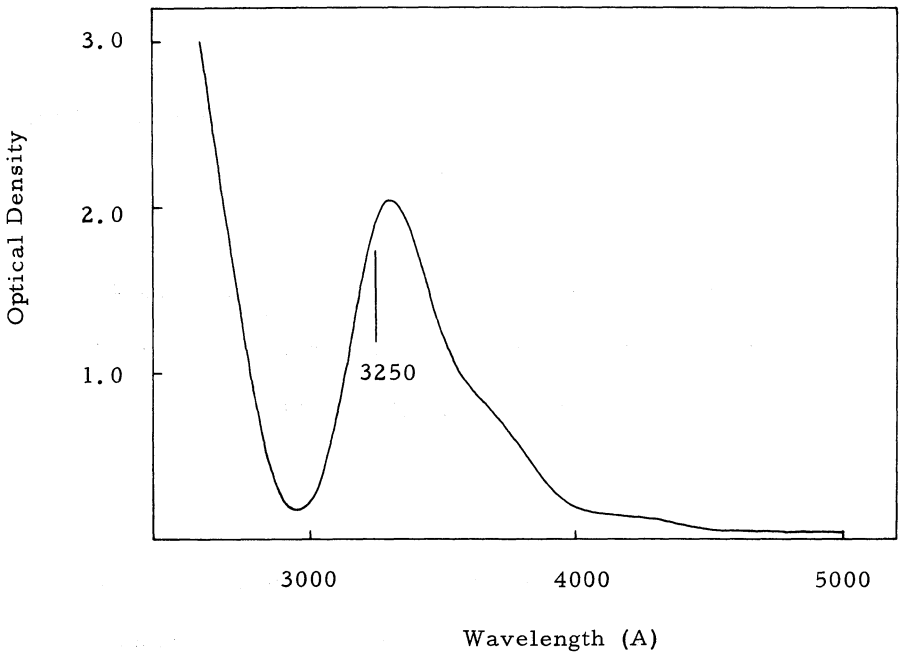

Fig. 1. The visible and ultraviolet absorption spectrum of $PdBr_4^{2-}$ in 2M hydrobromic acid. Concentration 2.0×10^{-3}M.

$PdBr_4^{2-}$ in solution has two strong absorption bands in the ultraviolet region. They are both caused by the charge transfer from Br^- to Pd^{2+}.[3] The longer wavelength band has a maximum at 3323 A, which is close to the 3250 A line of the He-Cd laser. The molar extinction coefficient at the peak of this band is 11500 and high enough for giving rise to the rigorous resonance Raman effect.[4]

Fig. 2 shows the Raman spectrum of the dilute solution (3.9×10^{-4}M) of K_2PdBr_4 in 2M hydrobromic acid. The Raman spectrum of the solid K_2PdBr_4 in the KBr disk is shown in Fig. 3. In order to obtain the spectrum of the solid state with better signal to noise ratio, the pressed pellet (K_2PdBr_4 and KBr in the ratio of 1:260), 1.3 cm in diameter, was rotated by a DC motor as described by Kiefer and Bernstein.[5]

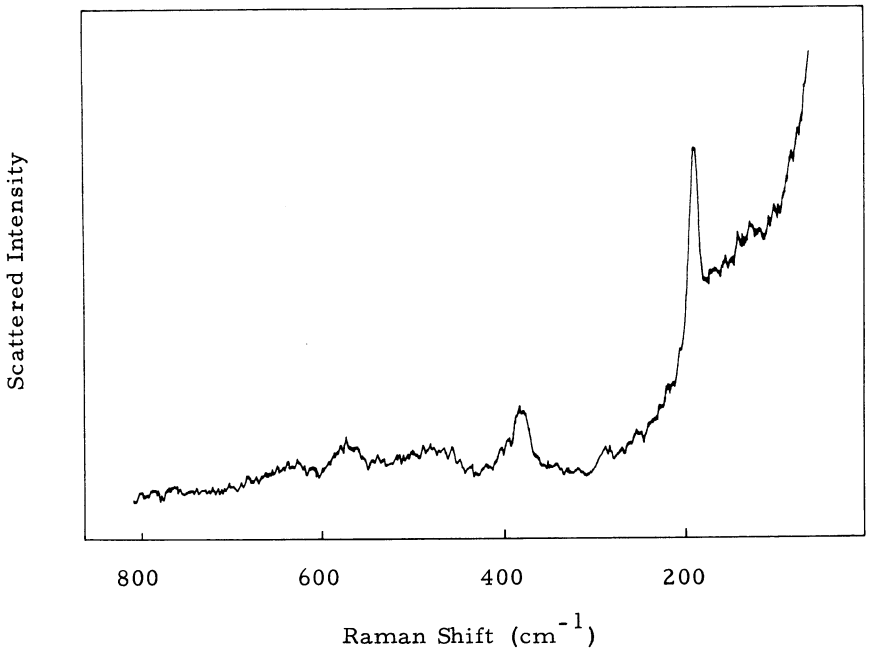

Fig. 2. The Raman spectrum of $PdBr_4^{2-}$ in 2M hydrobromic acid. Concentration 3.9×10^{-4}M. Slit 5 cm^{-1}. Scan speed 8.3 cm^{-1}/min. Time constant 15 sec. The broad peaks near 500 cm^{-1} and 620 cm^{-1} are due to quartz cell.

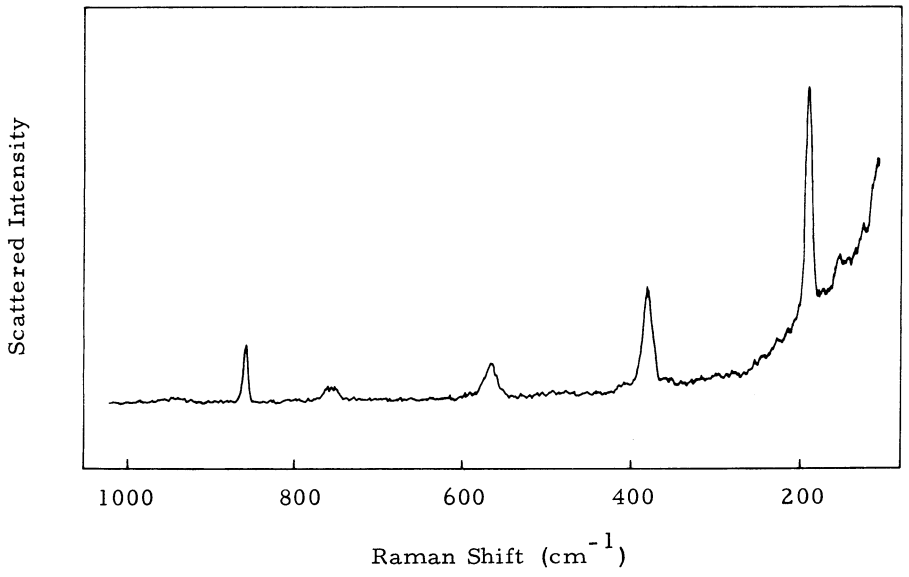

Fig. 3. The Raman spectrum of the solid K_2PdBr_4 in the KBr disk. The ratio of K_2PdBr_4 to KBr is 1:260. Slit 6.5 cm^{-1}. Scan speed 8.3 cm^{-1}/min. Time constant 15 sec. The peak at 856 cm^{-1} is a spontaneous emission line of the He-Cd laser.

The observed Raman shifts are listed in the first and second columns of Table 1. Hendra measured the Raman effect of the solid K_2PdBr_4 using a He-Ne laser as the exciting source and observed three Raman bands.[6] His results are also listed in the third column of Table 1. $PdBr_4^{2-}$ is a square planar ion with D_{4h} symmetry and has three Raman active vibrations, $\nu_1(a_{1g})$, $\nu_2(b_{2g})$ and $\nu_5(b_{1g})$. The assignments of the observed bands are shown in the last column of Table 1. The band at 190 cm^{-1} in the spectrum of the solution is polarized and is assigned to the ν_1 vibration, the shift being in agreement with that by Hendra. The shoulder at 152 cm^{-1} in the spectrum of the solid might be assigned to ν_2, but the shift is 13 cm^{-1} smaller than that obtained by Hendra. It is more probable that the band is due to the impurity such as Br_3^-, which may be formed by the decomposition of the sample.

Table 1

The Observed Raman Shifts of $PdBr_4^{2-}$ (cm^{-1})[a]

This Work		Hendra	Assignment
solid	solution	solid	
124	(125)	125	$\nu_5(b_{1g})$
		165	$\nu_2(b_{2g})$
190	190	192	$\nu_1(a_{1g})$
376	383		$2\nu_1$
563	(570)		$3\nu_1$
748			$4\nu_1$
(940)			$5\nu_1$

[a] All the values are accurate within 2 cm^{-1}, except the broad bands given in parentheses.

Table 2 gives the change of the half bandwidths of the ν_1 vibration and its overtones. The increase in bandwidth with the vibrational quantum number was observed both in the spectra of the solid and solution. The widths of the Raman bands are about two times larger in solution than in solid. This may be the reason why the overtones higher than the second were not observed in the spectrum of the solution.

So far, the observations of the rigorous resonance Raman effect for simple polyatomic molecules or ions have been reported in several cases, including $MnO_4^-(T_d)$[7], $CrO_4^{2-}(T_d)$[4], $S_3^-(C_{2v})$[8] and $I_3^-(C_{\infty v})$[9) 10]. There exist two characteristic features in the spectra of these compounds. One is the enhancement of the totally symmetric vibration and its overtones and the other is the increase in the bandwidths of the overtones with the vibrational quantum number. The present results for $PdBr_4^{2-}(D_{4h})$ give another example for such a profile of the rigorous resonance Raman effect.

Table 2

The Observed Half Bandwidths
for the ν_1 Vibration and its Overtones (cm^{-1})

	solid	solution
ν_1	7 (5.0)[a]	12 (4.0)[a]
$2\nu_1$	11 (6.5)	23 (4.0)
$3\nu_1$	15 (8.5)	
$4\nu_1$	19 (10.0)	

[a] Values in parentheses are slit widths used.

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