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# Electronic Absorption Spectra of Square-Planar Chloro-Aqua and Bromo-Aqua Complexes of Palladium(II) and Platinum(II)

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Visible and UV aqueous solution spectra for the square-planar complexes  $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$ ,  $\text{PdCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$ , and  $\text{PdBr}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0, 1, 2, 3, 4$ ) have been recorded and calculated. The difference in blue shift within each family of spectra when halide is substituted by water is two to three times smaller for the d-d bands than for the symmetry-allowed high-intensity bands. This variation of blue shift and the variation of band intensity due to the different symmetry of the complexes within each series together with previous magnetic circular dichroism and polarized crystal spectra have made possible unambiguous assignments of the bands in the  $\text{MX}_4^{2-}$  spectra ( $X = \text{Cl}, \text{Br}$ ). Thus, the shoulders at  $3.79 \mu\text{m}^{-1}$  ( $\text{PtCl}_4^{2-}$ ) and  $3.03 \mu\text{m}^{-1}$  ( $\text{PtBr}_4^{2-}$ ) are probably due to  $2a_{2u} \leftarrow 2b_{2g}$  and the shoulders at  $2.9 \mu\text{m}^{-1}$  ( $\text{PdCl}_4^{2-}$ ) and  $2.35 \mu\text{m}^{-1}$  ( $\text{PdBr}_4^{2-}$ ) to  $3b_{1g} \leftarrow a_{2g}$ , i.e., these shoulders are probably not associated with d-d transitions as often previously assumed. The symmetry-allowed high-intensity bands in the UV  $\text{PtCl}_4^{2-}$  spectrum at  $4.65$  and  $4.34 \mu\text{m}^{-1}$  ( $3.73$  and  $3.37 \mu\text{m}^{-1}$  for  $\text{PtBr}_4^{2-}$ ) are described as metal-to-ligand charge transfer transitions  $2a_{2u} \leftarrow 3a_{1g}$  and  $2a_{2u} \leftarrow 2e_g$  whereas the symmetry-allowed bands in the  $\text{PdCl}_4^{2-}$  spectrum at  $4.50$  and  $3.74 \mu\text{m}^{-1}$  ( $4.05$  and  $3.02 \mu\text{m}^{-1}$  for  $\text{PdBr}_4^{2-}$ ) are described as ligand-to-metal charge transfer  $3b_{1g} \leftarrow 2e_u$  and  $3b_{1g} \leftarrow b_{2u}, 3e_u$ . The results also suggest that the  ${}^1B_{1g} \leftarrow {}^1A_{1g}$  and  ${}^1E_g \leftarrow {}^1A_{1g}$  transitions overlap both in the platinum and palladium complexes, i.e., the  $d_{z^2}$  metal orbital is probably very close in energy to the degenerate  $d_{xz}$  and  $d_{yz}$  orbitals. These conclusions are summarized in the simplified energy level diagrams in Figure 8.

## Introduction

Transition assignments for electronic spectra of square-planar halide complexes of palladium and platinum have been based on experimental solution spectra,<sup>1-8</sup> polarized<sup>9-15</sup> and luminescence<sup>16</sup> crystal spectra, and measurements of circular dichroism (CD<sup>4</sup> and MCD<sup>3,5</sup>). Crystal and ligand field theory<sup>1,2,12,16</sup> and MO theory<sup>17-21</sup> have been used for the interpretation of these experiments. Martin<sup>13</sup> has reviewed the literature on the platinum complexes up to about 1970. However, there are still several ambiguities concerning the assignments both of the high-intensity bands in the UV and the less intense d-d bands in the near visible region.

The high-intensity bands in the UV spectra of both  $\text{PdCl}_4^{2-}$  and  $\text{PtCl}_4^{2-}$  have generally been described as ligand-to-metal charge transfer transitions (to  $3b_{1g}$ ).<sup>4,6,17,18,22</sup> However, Anex and Takeuchi<sup>14</sup> recently reported a strong out-of-plane polarization for the  $4.6\text{-}\mu\text{m}^{-1}$  ( $1 \mu\text{m}^{-1} = 10 \text{ kK}$ ) band of  $\text{K}_2\text{PtCl}_4$ , whereas the  $3.6\text{-}\mu\text{m}^{-1}$  band of  $\text{K}_2\text{PdCl}_4$  was found to be in-plane polarized. The authors therefore concluded that the  $4.6\text{-}\mu\text{m}^{-1}$  absorption in the  $\text{PtCl}_4^{2-}$  spectrum is due to  $5d_{z^2} \rightarrow 6p_z$ , i.e., a transition to  $2a_{2u}$ . This is not consistent with the previous assignment scheme for  $\text{PtCl}_4^{2-}$  developed by Gray et al.<sup>17,18</sup> Simultaneous MO calculations by Messmer et al.<sup>21</sup> also indicate that the  $4.6\text{-}\mu\text{m}^{-1}$  band of  $\text{PtCl}_4^{2-}$  probably is associated with a transition  $8a_{2u} \leftarrow 5e_g$  ( ${}^1E_u$ ). (This is equivalent to  $2a_{2u} \leftarrow 2e_g$  using the nomenclature of Basch and Gray.<sup>18</sup> In the following text, the energy levels will be denoted according to ref 18). Accordingly, the band should be in-plane polarized.

As far as the low-intensity d-d transitions are concerned, there seems now to be general agreement that the order both for  $\text{PdCl}_4^{2-}$  and  $\text{PtCl}_4^{2-}$  is  $3b_{1g} (d_{x^2-y^2}) \gg 2b_{2g} (d_{xy}) > 2e_g (d_{xz}, d_{yz})$ , whereas the position of  $3a_{1g} (d_{z^2})$  still is unclear. Recent MO calculations<sup>18,19,21</sup> generally support the order  $d_{xz}, d_{yz} > d_{z^2}$ , but van der Lugt<sup>20</sup> arrives at  $d_{z^2} > d_{xz}, d_{yz} > d_{xy}$ . The semiempirical ligand and crystal field

calculations give various results for the order between  $d_{z^2}$  and  $d_{xz}, d_{yz}$ . For instance, Chatt et al.<sup>1</sup> and Patterson et al.<sup>16</sup> conclude that  $d_{z^2}$  has the lowest energy, whereas Fenske et al.<sup>2</sup> place  $d_{z^2}$  above  $d_{xz}, d_{yz}$ . Martin, Tucker, and Kassman<sup>12b</sup> discuss two alternatives: A, having  $d_{xz}, d_{yz} > d_{z^2}$ , and B, which was considered to be the most probable by the authors, with  $d_{xz}, d_{yz} \approx d_{z^2}$ .

Obviously, the results of some of the ligand and crystal field calculations are strongly dependent on the chosen assignments for the observed bands in the d-d region, which is by no means univocal. For instance, the shoulder at  $3.65 \mu\text{m}^{-1}$  in the crystal spectrum and at  $3.79 \mu\text{m}^{-1}$  in the solution spectrum of  $\text{PtCl}_4^{2-}$  has sometimes been associated with  $3b_{1g} \leftarrow 3a_{1g} (d_{x^2-y^2} \leftarrow d_{z^2})$ <sup>6,8,13,16,18,21,23</sup> and sometimes with a spin-forbidden charge transfer transition.<sup>12,17</sup> Similarly, the shoulder at  $2.9 \mu\text{m}^{-1}$  in the solution spectrum of  $\text{PdCl}_4^{2-}$  has alternatively been described as  $3b_{1g} \leftarrow 3a_{1g} (d_{x^2-y^2} \leftarrow d_{z^2})$ ,<sup>18</sup> a mixture of  $3b_{1g} \leftarrow 2b_{2g} (d_{x^2-y^2} \leftarrow d_{xy})$  and  $3b_{1g} \leftarrow 2e_g (d_{x^2-y^2} \leftarrow d_{xz}, d_{yz})$ ,<sup>21</sup> charge transfer  $3b_{1g} \leftarrow a_{2g}$ ,<sup>7</sup> or recently as due to the presence of small concentrations of dinuclear complexes.<sup>15</sup>

We here report solution spectra for three series of halo-aqua complexes, viz.  $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$ ,  $\text{PdCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$ , and  $\text{PdBr}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0, 1, 2, 3, 4$ ), which together with previous MCD<sup>3,5</sup> and polarization<sup>10-12,14,15</sup> data, might be helpful for the spectral assignments. The assignments for the  $\text{MX}_4^{2-}$  complexes with  $D_{4h}$  symmetry can be transferred to the other complexes in the family  $\text{MX}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  having lower symmetry (cf. Chatt et al.<sup>1</sup>). A comparison of the energies and intensities for corresponding bands in such a series of spectra will furnish a possibility to check the spectral assignments. For instance, the stepwise displacement of the d-d bands toward the UV when halide is substituted by water in  $\text{MX}_4^{2-}$  is much smaller than the corresponding displacement for the high-intensity bands. Moreover, bands which are symmetry forbidden in the  $D_{4h}$  complexes can be allowed in complexes having lower symmetry, so observed changes

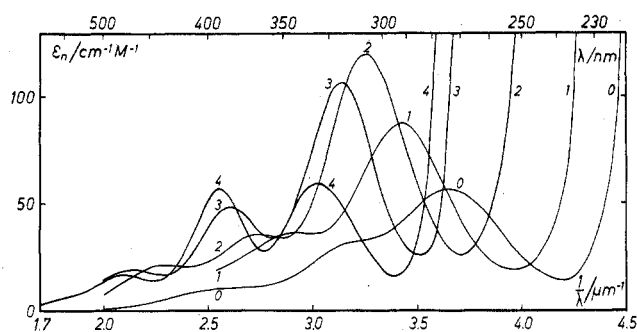


Figure 1. d-d spectra for  $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0, 1, 2, 3, 4$ ). The spectrum for  $n = 2$  represents the equilibrium mixture of cis and trans isomers (55% cis).

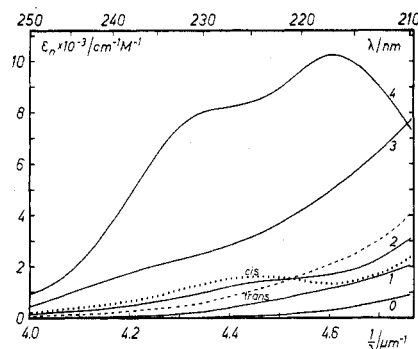


Figure 2. High-intensity bands for  $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0, 1, 2, 3, 4$ ).  $\text{PtCl}_2(\text{H}_2\text{O})_2$  has been resolved into cis and trans spectra.

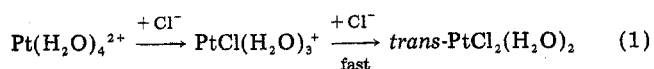
in intensity might also give useful information.

### Experimental Section

**Chemicals and Apparatus.**  $\text{K}_2\text{PtCl}_4$  (Johnson and Matthey) was the same as used previously.<sup>24</sup> Solutions of platinum(II) perchlorate and palladium(II) perchlorate were prepared by published methods.<sup>7,24</sup> Perchloric acid (Baker p.a.), hydrochloric acid (Merck p.a.), freshly distilled hydrobromic acid (Merck p.a.), and water, doubly distilled from quartz vessels, were used to prepare the solutions. Perchloric acid was the supporting electrolyte. The ionic strength was 1.00 M. The hydrogen ion concentration of 1.00 M is sufficient to suppress protolysis both of palladium and platinum aqua ions.<sup>7,24</sup> Spectra were recorded at 25.0 °C using a Cary 15 recording spectrophotometer and Hellma Quartz Suprasil cells.

**$\text{PtCl}(\text{H}_2\text{O})_3^+$ .** After equilibration for 75–150 h at 25 °C spectra for ten solutions having  $C_{\text{Pt}} = 7.18$  mM and  $0 \leq C_{\text{Cl}} \leq 2.8$  mM and seven solutions with  $C_{\text{Pt}} = 4.08$  mM and  $0 \leq C_{\text{Cl}} \leq 1.6$  mM were recorded between 400 and 210 nm. The half-life for the equilibration is about 18 h for  $C_{\text{Pt}} = 4$  mM.<sup>25</sup> The molar absorptivity for  $\text{PtCl}(\text{H}_2\text{O})_3^+$ ,  $\epsilon_1$ , was obtained from the equation  $e = \epsilon_0 C_{\text{Pt}} + (\epsilon_1 - \epsilon_0) C_{\text{Cl}}$ , where  $e$  denotes the absorptivity of the solution and  $\epsilon_0$  the molar absorptivity for  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ , determined previously.<sup>24</sup> Concentrations of other complexes were negligible.

**trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$ .** Solutions of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  (4.12 or 0.412 mM) containing hydrochloric acid (50 mM) were aged for 75–100 min at 25 °C and their spectra subsequently recorded between 550 and 205 nm. The following reaction to trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$  occurs quantitatively:<sup>25</sup>



Consecutive chloride anations of  $\text{PtCl}(\text{H}_2\text{O})_3^+$  to cis- $\text{PtCl}_2(\text{H}_2\text{O})_2$  and of trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$  to  $\text{PtCl}_3\text{H}_2\text{O}^+$  are slow.<sup>26</sup> The half-life for the rate-determining anation of  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  is 9 min for 50 mM chloride.<sup>25</sup>

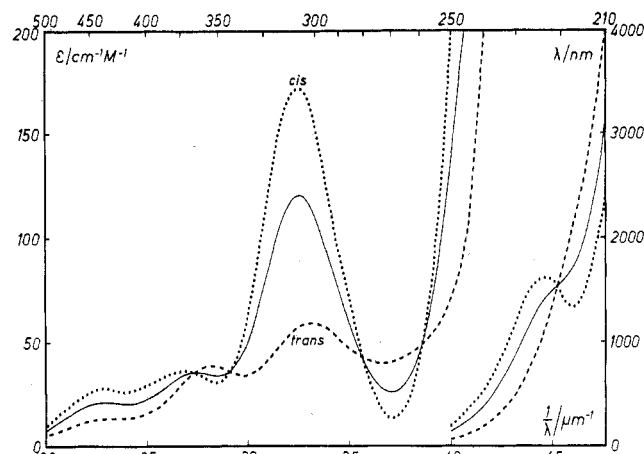


Figure 3. d-d and first high-intensity bands for the equilibrium mixture cis/trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$  resolved into its components.

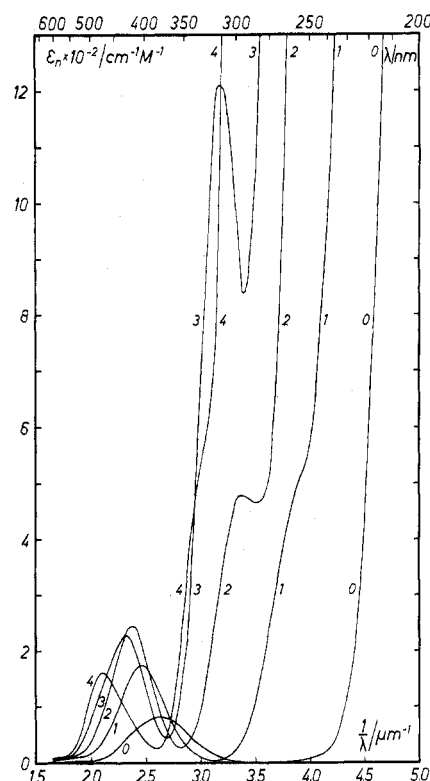


Figure 4. d-d and first charge transfer bands for  $\text{PdCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0, 1, 2, 3, 4$ ). The spectrum for  $n = 2$  represents a mixture of 68% cis, 32% trans.

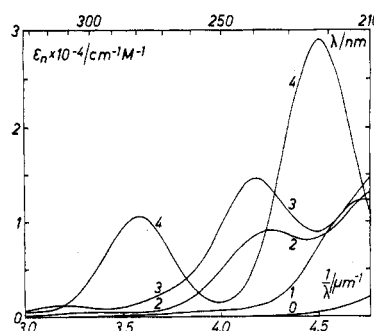


Figure 5. Charge transfer spectra of  $\text{PdCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0, 1, 2, 3, 4$ ). The spectrum for  $n = 2$  represents a mixture of 68% cis, 32% trans.

**cis- $\text{PtCl}_2(\text{H}_2\text{O})_2$ .** Spectrum for cis- $\text{PtCl}_2(\text{H}_2\text{O})_2$  was calculated from the spectrum of the equilibrium mixture of cis- and trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$  recorded previously<sup>27</sup> and

TABLE I: Wavenumbers,  $\lambda^{-1}/\mu\text{m}^{-1}$ , and Molar Absorptivities,  $\epsilon_n/\text{cm}^{-1} \text{ M}^{-1}$ , for  $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0, 1, 2, 3, 4$ )

$\text{PtCl}_4^{2-}$ <sup>b</sup>	$\text{PtCl}_3(\text{H}_2\text{O})^-$ <sup>b</sup>	<i>cis</i> - $\text{PtCl}_2(\text{H}_2\text{O})_2$	<i>trans</i> - $\text{PtCl}_2(\text{H}_2\text{O})_2$	$\text{PtCl}(\text{H}_2\text{O})_3^+$	$\text{Pt}(\text{H}_2\text{O})_4^{2+}$ <sup>c</sup>	Assignment ( $D_{4h}$ )	Excited state ( $D_{4h}$ )
1.78 (3)	- <sup>a</sup>	-	-	-	-	d-d singlet $\rightarrow$ triplet	
2.10 (17)	2.14 (19)	2.25 (20)	2.25 (10)	-	2.57 (10)	d-d singlet $\rightarrow$ triplet	
2.56 (56)	2.61 (48)	2.69 (25)	2.81 (35)	2.85 (25)	3.13 (15)	$3b_{1g}(d_{x^2-y^2}) \leftarrow 2b_{2g}(d_{xy})$	$^1A_{2g}$
3.02 (59)	3.14 (107)	3.25 (170)	3.31 (40)	3.43 (87)	3.66 (57)	$3b_{1g}(d_{x^2-y^2}) \leftarrow 2e_g(d_{xy}, d_{xz})$ , $3a_{1g}(d_{z^2})$	$^1E_g, B_{1g}$
3.79 (~400)	4.3 (1500)	4.45 (900)	Absent	-	-	$2a_{2u} \leftarrow 2b_{2g}$	$^1B_{1u}$
4.34 (7200)	4.8 (8000)	-	-	-	-	$2a_{2u} \leftarrow 2e_g$	$^1E_u$
4.65 (9050)	-	-	-	-	-	$2a_{2u} \leftarrow 3a_{1g}$	$^1A_{2u}$

<sup>a</sup> A dash denotes not observable. Proposed assignments for  $D_{4h}$  symmetry ( $\text{PtCl}_4^{2-}$ ,  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ ) included. <sup>b</sup> Reference 27. <sup>c</sup> Reference 24.

TABLE II: Wavenumbers,  $\lambda^{-1}/\mu\text{m}^{-1}$ , and Molar Absorptivities,  $\epsilon_n/\text{cm}^{-1} \text{ M}^{-1}$ , for  $\text{PdCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0, 1, 2, 3, 4$ )

$\text{PdCl}_4^{2-}$	$\text{PdCl}_3(\text{H}_2\text{O})^-$	$\text{PdCl}_2(\text{H}_2\text{O})_2$ (68% <i>cis</i> )	$\text{PdCl}(\text{H}_2\text{O})_3^+$	$\text{Pd}(\text{H}_2\text{O})_4^{2+}$	Assignment ( $D_{4h}$ )	Excited state ( $D_{4h}$ )
1.65 (8)	1.71 (10)	1.75 (10)	1.80 (8)	1.86 (2.5)	d-d singlet $\rightarrow$ triplet	
2.11 (161)	2.32 (227)	2.38 (243)	2.46 (175)	2.64 (82.8)	d-d bands (cf. Table I)	$^1A_{2g}, ^1E_g, ^1B_{1g}$
2.9 (200)	3.18 (800)	3.4 (400)	3.9 (200)	-	$3b_{1g} \leftarrow a_{2g}$	$^1B_{2g}$
3.58 (10300)	4.18 (14500)	4.25 (5000)	4.72 (12000)	-	$3b_{1g} \leftarrow 3e_u, b_{2u}$	$^1E_u, ^1A_{2u}$
4.50 (29000)	- <sup>a</sup>	-	-	-	$3b_{1g} \leftarrow 2e_u$	$^1E_u$

<sup>a</sup> A dash denotes not observable. Proposed assignments for  $D_{4h}$  symmetry included.

TABLE III: Wavenumbers,  $\lambda^{-1}/\mu\text{m}^{-1}$ , and Molar Absorptivities,  $\epsilon_n/\text{cm}^{-1} \text{ M}^{-1}$ , for  $\text{PdBr}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0, 1, 2, 3, 4$ )

$\text{PdBr}_4^{2-}$	$\text{PdBr}_3(\text{H}_2\text{O})^-$	$\text{PdBr}_2(\text{H}_2\text{O})_2$ (86% <i>cis</i> )	$\text{PdBr}(\text{H}_2\text{O})_3^+$	$\text{Pd}(\text{H}_2\text{O})_4^{2+}$	Assignment ( $D_{4h}$ )	Excited state ( $D_{4h}$ )
- <sup>a</sup>	-	-	1.8 (30)	1.86 (2.5)	d-d singlet $\rightarrow$ triplet	
1.96 (200)	2.0 (200)	2.3 (400)	2.42 (280)	2.64 (82.8)	d-d bands (cf. Table I)	$^1A_{2g}, ^1E_g, ^1B_{1g}$
2.35 (200)	2.52 (1500)	2.7 (250)	3.5 (450)	-	$3b_{1g} \leftarrow a_{2g}$	$^1B_{2g}$
2.73 (3000)	3.2 (3000)	-	-	-	$3b_{1g} \leftarrow 3e_u, b_{2u}$	$^1E_u, A_{2u}$
3.02 (10800)	3.67 (15000)	3.75 (6000)	4.38 (14800)	-	$3b_{1g} \leftarrow 3e_u$	$^1E_u, A_{2u}$
3.65 (6000)	-	-	-	-	$3b_{1g} \leftarrow 2e_u$	$^1E_u$
4.05 (30000)	4.38 (15000)	4.45 (16000)	-	-	$3b_{1g} \leftarrow 2e_u$	$^1E_u$

<sup>a</sup> A dash denotes not observable. Proposed assignments for  $D_{4h}$  symmetry included. The assignments for the bromo-aqua complexes are uncertain because of spin-orbit and symmetry splitting and mixed *cis* and *trans* spectra for  $n = 2$ .

the known spectrum of the *trans* isomer using the equilibrium constant  $K_{c/t} = [\text{cis}]/[\text{trans}] = 1.2 \pm 0.1$  determined separately.<sup>26</sup>

**Palladium Complexes.** Spectra for equilibrated solutions of palladium complexes were recorded and resolved as described previously.<sup>7</sup>

## Results and Discussion

**Spectra.** The spectra are shown in Figures 1-7. Gaussian analysis gave the results in Tables I-III. The suggested assignments have been summarized in the tables.

Two separate band systems can be recognized in each family of spectra, namely, the high-intensity bands in the UV and the weak (d-d) bands in the UV-near-visible spectral region. All these bands are displaced toward the UV when the halide ligands are exchanged for water, but the blue shift is two to three times smaller for the d-d bands than for the high-intensity bands. The spectra for the chloro-bromo complexes  $\text{PtCl}_{4-n}\text{Br}_n^{2-n}$  ( $n = 0, 1, 2, 3, 4$ ) reported elsewhere<sup>28</sup> display similar characteristics. The d-d bands of  $\text{PtCl}_4^{2-}$  at 2.56 and  $3.02 \mu\text{m}^{-1}$  are displaced to 2.42 and  $2.72 \mu\text{m}^{-1}$  in the  $\text{PtBr}_4^{2-}$  spectrum, whereas the high-intensity bands at 3.79, 4.34, and  $4.65 \mu\text{m}^{-1}$  are displaced about three times more, to 3.03, 3.37 and  $3.73 \mu\text{m}^{-1}$ , respectively, in the  $\text{PtBr}_4^{2-}$  spectrum. This means that the energy differences between the filled and excited one-electron energy levels which give rise to the high-intensity bands are much more affected by the nature of the ligands, than are the corresponding energy differences for the d-d bands. Using the MO-LCAO language, this is equivalent to saying that there is a larger mixing between those metal and ligand AOs which give rise to the energy

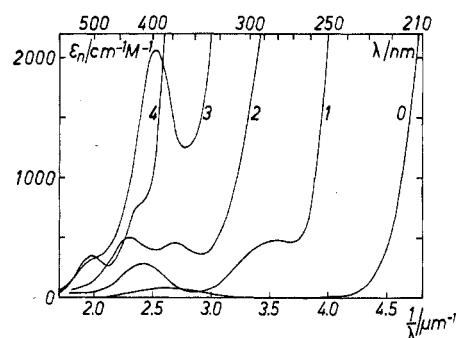


Figure 6. d-d and first charge transfer bands of  $\text{PdBr}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0, 1, 2, 3, 4$ ). The spectrum for  $n = 2$  represents a mixture of 86% *cis*, 14% *trans*.

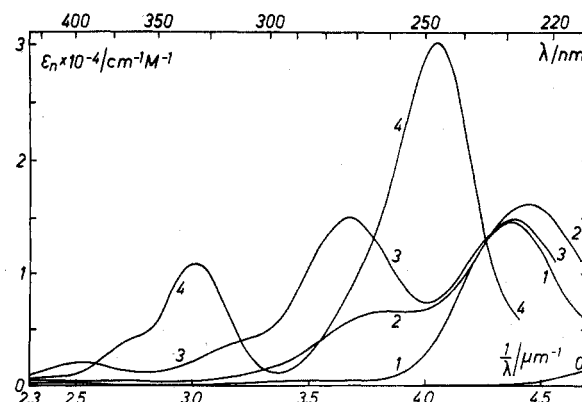


Figure 7. Charge transfer spectra for  $\text{PdBr}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  ( $n = 0, 1, 2, 3, 4$ ). The spectrum for  $n = 2$  represents a mixture of 86% *cis*, 14% *trans*.

TABLE IV: Absorption Spectra of  $\text{PtCl}_4^{2-}(\text{aq})$  and Single-Crystal  $\text{K}_2\text{PtCl}_4(\text{s})$  at Room Temperature

$\text{PtCl}_4^{2-}(\text{aq})^b$		$\text{K}_2\text{PtCl}_4(\text{s})$		Polarization <sup>a</sup>	Ref <sup>c</sup>	MCD term <sup>d</sup>	Assignment	Excited state
$\lambda^{-1}/\mu\text{m}^{-1}$	$\epsilon/\text{cm}^{-1}\text{M}^{-1}$	$\lambda^{-1}/\mu\text{m}^{-1}$	$\epsilon/\text{cm}^{-1}\text{M}^{-1}$					
1.78	3	1.73	5	xy	10		Singlet triplet d-d, cf. Martin ref 12b, alternative B	Allowed via $E_u$ vibrations
2.10	17	2.02	20	z	10, 12b			
		2.04	17.5	xy	10, 12b			
		2.34	9 (?)	xy	12b			
		2.37	5	z	12b	B	$3b_{1g}(d_{x^2-y^2}) \leftarrow 2b_{2g}(d_{xy})$	$^1A_{2g}$
2.56	56	2.57	45, 62	xy	10, 12b		$3b_{1g}(d_{x^2-y^2}) \leftarrow 3a_{1g}(d_{z^2})$	
3.02	59	2.85	57, 74	xy	10, 12b	A	$3b_{1g}(d_{x^2-y^2}) \leftarrow 2e_g(d_{xz}, d_{yz})$	$^1B_{1g}$
3.79	~400	2.93	70, 101	z	10, 12b	B	$2a_{2u} \leftarrow 2b_{2g}(d_{xy})$	$^1E_g$
		(3.65)		?	10			$^1B_{1u}$
4.34	7200	(~4.5) <sup>e</sup>		(xy)	14	A	$2a_{2u} \leftarrow 2e_g(d_{xz}, d_{yz})$	Allowed via $B_{2g}$ vibration
4.65	9050	4.41	32100 <sup>f</sup>	z	14		$2a_{2u} \leftarrow 3a_{1g}(d_{z^2})$	$^1E_u$ $^1A_{2u}$

<sup>a</sup> xy denotes in-plane polarization, z out-of-plane polarization. <sup>b</sup> cf. Table I. <sup>c</sup> Cf. also ref 11, which gives values at 5 K. <sup>d</sup> References 3 and 5. <sup>e</sup> Estimated from ref 14, Figure 1. (Cf. also the discussion<sup>14</sup> on p 4415.) <sup>f</sup> According to ref 14 this crystal  $\epsilon$  should be divided by 3 for comparison with the solution value.

TABLE V: Absorption Spectra of  $\text{PdCl}_4^{2-}(\text{aq})$  and Single-Crystal  $\text{K}_2\text{PdCl}_4(\text{s})$  at Room Temperature

$\text{PdCl}_4^{2-}(\text{aq})^b$		$\text{K}_2\text{PdCl}_4(\text{s})$		Polarization <sup>a</sup>	Ref	MCD term	Assignment	Excited state
$\lambda^{-1}/\mu\text{m}^{-1}$	$\epsilon/\text{cm}^{-1}\text{M}^{-1}$	$\lambda^{-1}/\mu\text{m}^{-1}$	$\epsilon/\text{cm}^{-1}\text{M}^{-1}$					
1.65	8	1.70	7	z	10, 15 <sup>d</sup>	A	singlet triplet d-d, cf. ref 15	Allowed via $E_u$ vibrations
		(1.80)	(19)	xy	10, 15 <sup>d</sup>			
2.11 <sup>e</sup>	161	(2.00)	(67)	xy	10, 15 <sup>d</sup>			
		2.26	128	xy	10, 15 <sup>d</sup>			
		2.30	80	z	10, 15 <sup>d</sup>	B	$3b_{1g}(d_{x^2-y^2}) \leftarrow 2b_{2g}(d_{xy})$	$^1A_{2g}$
							$3b_{1g}(d_{x^2-y^2}) \leftarrow 3a_{1g}(d_{z^2})$	$^1B_{1g}$
2.9	200 <sup>f</sup>	(2.95)	(67)	xy	10		$3b_{1g}(d_{x^2-y^2}) \leftarrow 2e_g(d_{xz}, d_{yz})$	$^1E_g$
3.56	10300	3.68	14000	xy	14		$3b_{1g}(d_{x^2-y^2}) \leftarrow a_{2g}$	$^1B_{2g}$
		3.74	388	z	15 <sup>d</sup>	A	$3b_{1g}(d_{x^2-y^2}) \leftarrow 3e_u$	$^1E_u$
4.50 <sup>g</sup>	29000	4.51	27600	xy	14		$3b_{1g}(d_{x^2-y^2}) \leftarrow b_{2u}$	$^1A_{2u}$
							$3b_{1g}(d_{x^2-y^2}) \leftarrow 2e_u$	$^1E_u$

<sup>a</sup> xy denotes in-plane polarization, z out-of-plane polarization. <sup>b</sup> Cf. Table II. <sup>c</sup> Reference 5. <sup>d</sup> Reference 15 gives values at 15 K. <sup>e</sup> Asymmetric band, cf. ref 7, Figure 9. <sup>f</sup> McCaffery et al.<sup>5</sup> and Rush et al.<sup>15</sup> report  $\epsilon \approx 500 \text{ cm}^{-1} \text{ M}^{-1}$ . <sup>g</sup> Rush et al.<sup>15</sup> report a band at  $4.078 \mu\text{m}^{-1}$  with  $\epsilon = 900 \text{ cm}^{-1} \text{ M}^{-1}$ .

levels connected with the high-intensity bands than there is between those AOs giving rise to the levels for the d-d bands. Thus, the MOs  $3a_{1g}$ ,  $2e_g$ ,  $2b_{2g}$ , and  $3b_{1g}$  can probably be considered to be rather pure metal d orbitals. This is contrary to the conclusions from the MO calculations by Messmer et al. (ref 21, pp 2852, 2853) but agrees with the calculations by Cotton and Harris.<sup>19</sup>

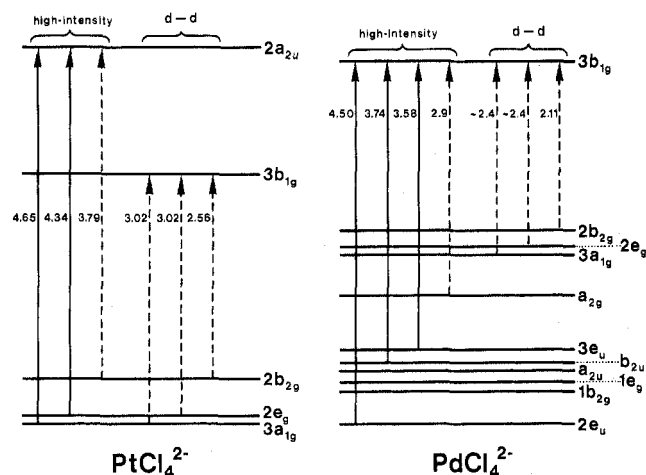
**Shoulders.** It appears from Tables I-III that the displacements of the shoulders at 3.79 ( $\text{PtCl}_4^{2-}$ ), 2.9 ( $\text{PdCl}_4^{2-}$ ), and  $2.35 \mu\text{m}^{-1}$  ( $\text{PdBr}_4^{2-}$ ) for the stepwise substitutions of the halides by water is about the same as the corresponding changes for the known symmetry-allowed high-intensity bands. It is therefore not very likely that these shoulders and the corresponding shoulder for  $\text{PtBr}_4^{2-}$  at  $3.03 \mu\text{m}^{-1}$  (cf. ref 28) are d-d bands as has often been assumed.<sup>6,8,13,16,18,21,23</sup> It is much more probable that they are due to symmetry-forbidden transitions of the same type as the high-intensity bands, which has previously been suggested by Saito et al.<sup>4</sup> Further support to this assignment is given by their relatively large intensities and by the variation of these intensities with the symmetry of the complexes within the series  $\text{MX}_n(\text{H}_2\text{O})_{4-n}^{2-n}$  (vide infra).

**d-d Bands.** The exclusion of the above-mentioned shoulders as due to the  $3b_{1g} \leftarrow 3a_{1g}(d_{x^2-y^2} \leftarrow d_{z^2})$  transition removes the main difficulty with the Martin, Tucker, and Kassman<sup>12b</sup> alternative B for the assignment of the d-d bands of  $\text{PtCl}_4^{2-}$  (cf. also Patterson et al.,<sup>16</sup> p 2875).

The two levels  $3a_{1g}(d_{z^2})$  and  $2e_g(d_{xz}, d_{yz})$  are probably so close in energy that the transition from both these levels to  $3b_{1g}(d_{x^2-y^2})$  are contained within the  $3.02\text{-}\mu\text{m}^{-1}$  band of  $\text{PtCl}_4^{2-}$  solution spectrum. The MCD results by Martin,<sup>3</sup>

McCaffery<sup>5</sup> and their co-workers show that this band contains an A term connected with the transition from the degenerate level  $2e_g(d_{xz}, d_{yz})$  to  $3b_{1g}(d_{x^2-y^2})$ , but cannot exclude the possibility that the band also contains  $3b_{1g} \leftarrow 3a_{1g}$  (cf. McCaffery et al.,<sup>5</sup> p 5732). The polarization measurements reviewed in Tables IV and V, however, suggest that the  $3.02\text{-}\mu\text{m}^{-1}$  band might contain both these transitions. The  $3b_{1g} \leftarrow 2e_g$  transition will be out-of-plane (z) polarized and the  $3b_{1g} \leftarrow 3a_{1g}$  in-plane (xy) polarized, if they are allowed via  $E_u$  vibrations (cf. Chatt et al.<sup>1</sup>). In fact Day et al.,<sup>10</sup> Mortensen,<sup>11</sup> and Martin et al.<sup>12b,15</sup> report the existence of two polarized components at about 2.85 (xy) and  $2.93 \mu\text{m}^{-1}$  (z)<sup>10,11,12b</sup> for  $\text{K}_2\text{PtCl}_4$  crystals and at about 2.26 (xy) and  $2.30 \mu\text{m}^{-1}$  (z)<sup>10,15</sup> for  $\text{K}_2\text{PdCl}_4$  crystals (cf. Tables IV and V). They correspond to the  $3.02\text{-}\mu\text{m}^{-1}$  band of  $\text{PtCl}_4^{2-}$  solutions and to the asymmetric  $2.11\text{-}\mu\text{m}^{-1}$  band of  $\text{PdCl}_4^{2-}$  solutions.

So we conclude that the broad absorptions at  $2.11 (\text{PdCl}_4^{2-})$  and  $1.96 \mu\text{m}^{-1} (\text{PdBr}_4^{2-})$  contain all the three singlet  $\rightarrow$  singlet d-d transitions, whereas the band at  $3.02 \mu\text{m}^{-1} (\text{PtCl}_4^{2-})$  contains the two singlet  $\rightarrow$  singlet transitions from  $3a_{1g}(d_{z^2})$  and  $2e_g(d_{xz}, d_{yz})$  and the  $2.56\text{-}\mu\text{m}^{-1}$  band ( $\text{PtCl}_4^{2-}$ ) the transition  $3b_{1g}(d_{x^2-y^2}) \leftarrow 2b_{2g}(d_{xy})$ . Similarly, the band at  $2.42 \mu\text{m}^{-1}$  in the  $\text{PtBr}_4^{2-}$  spectrum should be due to  $3b_{1g} \leftarrow 2b_{2g}$  and the band at  $2.72 \mu\text{m}^{-1}$  should contain both transitions from  $3a_{1g}$  and  $2e_g$  to  $3b_{1g}$  (cf. ref 28, Table X). The splitting of the filled d levels ( $d_{z^2}$ ,  $d_{xz}$ ,  $d_{yz}$ ,  $d_{xy}$ ) can be concluded to be smaller in the palladium complexes than in  $\text{PtCl}_4^{2-}$ , and the  $d_{x^2-y^2}$  orbital should lie closer to the filled levels in the palladium complexes than in  $\text{PtCl}_4^{2-}$ , since the transitions have lower energies in the former complexes. These conclusions are summarized in



**Figure 8.** Suggested simplified energy level diagrams for  $\text{PtCl}_4^{2-}$  and  $\text{PdCl}_4^{2-}$  complexes in aqueous solution. Notation of energy levels according to ref 18. The experimental wavenumbers in  $\mu\text{m}^{-1}$  ( $1 \mu\text{m}^{-1} = 10 \text{ kK}$ ) have been included. Symmetry-forbidden transitions have been marked with dashed arrows and allowed transitions with full-drawn arrows. The diagram for  $\text{PtCl}_4^{2-}$  should be applicable for  $\text{PtBr}_4^{2-}$  also, and that for  $\text{PdCl}_4^{2-}$  for  $\text{PdBr}_4^{2-}$ .

the energy level diagrams in Figure 8.

**High-Intensity Bands.** Anex and Takeuchi<sup>14</sup> concluded that the intense absorption in the  $\text{PtCl}_4^{2-}$  spectrum at  $4.65 \mu\text{m}^{-1}$  is due to a metal  $5d \rightarrow 6p$  transition ( $2a_{2u} \leftarrow 3a_{1g}$ ), in agreement with the proposed assignments by Chatt et al.<sup>1</sup> and by Jørgensen.<sup>23</sup> If we assume that the shoulder at  $4.34 \mu\text{m}^{-1}$  and the previously discussed shoulder at  $3.79 \mu\text{m}^{-1}$  in the  $\text{PtCl}_4^{2-}$  spectrum are also associated with transitions from the metal  $d$  levels to  $2a_{2u}$ , we arrive at the simple energy level diagram for  $\text{PtCl}_4^{2-}$  in Figure 8.

The bands at  $4.65$  and  $4.34 \mu\text{m}^{-1}$  are symmetry allowed. The shoulder at  $4.34 \mu\text{m}^{-1}$  contains a MCD A term<sup>5</sup> which is compatible with the assignment  $2a_{2u} \leftarrow 2e_g$ . The two bands at  $4.65$  and  $4.34 \mu\text{m}^{-1}$  differ by  $0.31 \mu\text{m}^{-1}$  whereas there is no observable difference between the two corresponding  $d-d$  transitions from  $3a_{1g}$  and  $2e_g$  at  $3.02 \mu\text{m}^{-1}$  (cf. Figure 8). This might be due to differences both in interelectronic repulsion and configurational interaction depending on whether the electron is excited to the  $2a_{2u}$  or  $3b_{1g}$  level.

The shoulder at  $3.79 \mu\text{m}^{-1}$  is symmetry forbidden but vibronically allowed via a  $B_{2g}$  vibration (cf. Chatt et al.<sup>1</sup> concerning vibrational modes). The transition must then be out-of-plane ( $z$ ) polarized, but unfortunately no data on its polarization have been published so far. This transition is also symmetry forbidden for all the mixed complexes except  $\text{cis-PtCl}_2(\text{H}_2\text{O})_2$ , which belongs to the symmetry group  $C_{2v}(C_2'')$ . The presence of a maximum at  $4.45 \mu\text{m}^{-1}$  for  $\text{cis-PtCl}_2(\text{H}_2\text{O})_2$  and the absence of any corresponding absorption for  $\text{trans-PtCl}_2(\text{H}_2\text{O})_2$  (cf. Figures 2 and 3 and Table I) supports our assignment. This band is also strong ( $\epsilon = 1500 \text{ cm}^{-1} \text{ M}^{-1}$ ) for  $\text{PtCl}_3\text{H}_2\text{O}^-$ , which belongs to  $C_{2v}(C_2')$ . One explanation might be that the transition is allowed via a  $B_1$  vibration, which corresponds not only to the  $B_{2g}$  but also to the  $E_u$  vibration in  $\text{PtCl}_4^{2-}$ . Corresponding assignments for the high-intensity bands of  $\text{PtBr}_4^{2-}$  at  $3.03$  ( $2a_{2u} \leftarrow 2b_{2g}$ ),  $3.37$  ( $2a_{2u} \leftarrow 2e_g$ ), and  $3.73 \mu\text{m}^{-1}$  ( $2a_{2u} \leftarrow 3a_{1g}$ ) can be made.<sup>28</sup>

The assignments for the two symmetry-allowed transitions at  $4.65$  and  $4.34 \mu\text{m}^{-1}$  (and also for the  $3.02 \mu\text{m}^{-1}$   $d-d$  band) are further supported by a comparison of solution and crystal spectra, see Table IV. Because of electrostatic effects in the solid state, the energy of the  $3a_{1g}$  ( $d_{x^2-y^2}$ ) orbital will be higher in the crystal than in aqueous solution both relative to the in-plane  $d$  orbitals, (including

$3b_{1g}$ ) and to the  $2a_{2u}$  orbital, at least if the latter is composed mainly of ligand  $p$  orbitals (vide infra). Transitions from  $3a_{1g}$  should therefore be expected to show a red shift in the crystal spectrum. Accordingly, the  $4.65\text{-}\mu\text{m}^{-1}$  solution band is displaced to  $4.41 \mu\text{m}^{-1}$  in the crystal spectrum and one of the components of the  $3.02\text{-}\mu\text{m}^{-1}$  band to  $2.85 \mu\text{m}^{-1}$ , whereas the other bands are much less affected.

As far as the palladium complexes are concerned, the  $4.50\text{-}(\text{PdCl}_4^{2-})$  and  $4.05\text{-}\mu\text{m}^{-1}$  ( $\text{PdBr}_4^{2-}$ ) bands have been associated with  $3b_{1g} \leftarrow 2e_u$  ( ${}^1E_u \leftarrow {}^1A_{1g}$ ) and the  $3.58\text{-}(\text{PdCl}_4^{2-})$  and  $3.02\text{-}\mu\text{m}^{-1}$  ( $\text{PdBr}_4^{2-}$ ) bands with  $3b_{1g} \leftarrow 3e_u$ ,  $b_{2u}$  ( ${}^1E_u$ ,  ${}^1A_{2u} \leftarrow {}^1A_{1g}$ ) in accordance with previous assignments by Jørgensen,<sup>22</sup> Basch and Gray,<sup>18</sup> and Rush et al.<sup>15</sup>

A comparison of the high-intensity bands in solution and crystal spectra (see Table V) shows that the position of these bands are much less affected than the bands of  $\text{PtCl}_4^{2-}$  at  $4.65 \mu\text{m}^{-1}$  (and  $3.02 \mu\text{m}^{-1}$ ), cf. Table IV. This is consistent with the description of the bands in the  $\text{PdCl}_4^{2-}$  spectrum as due to in-plane transitions.

We have previously<sup>7,29</sup> associated the shoulders at  $2.9$  ( $\text{PdCl}_4^{2-}$ ) and  $2.35 \mu\text{m}^{-1}$  ( $\text{PdBr}_4^{2-}$ ) with  $3b_{1g} \leftarrow a_{2g}$ . If this transition is allowed via an  $E_u$  vibration, it will be in-plane ( $xy$ ) polarized in the crystal spectrum, as was observed experimentally by Day et al.<sup>10</sup> The out-of-plane ( $z$ ) polarized  $3b_{1g} \leftarrow b_{2u}$  transition found by Rush et al.<sup>15</sup> in the crystal spectrum of  $\text{K}_2\text{PdCl}_4$  at  $3.74 \mu\text{m}^{-1}$  (cf. Table V) cannot be identified with the shoulder at  $2.9 \mu\text{m}^{-1}$  in the solution spectrum, since it differs too much in wave-number.

The transition  $3b_{1g} \leftarrow a_{2g}$  is symmetry forbidden for  $\text{PdX}_4^{2-}$ ,  $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ , and  $\text{trans-PdX}_2(\text{H}_2\text{O})_2$  but allowed for the other complexes in the series  $\text{PdX}_n(\text{H}_2\text{O})_{4-n}^{2-n}$ . Accordingly, the shoulder develops into a peak for  $\text{PdCl}_3\text{H}_2\text{O}^-$ ,  $\text{PdCl}_2(\text{H}_2\text{O})_2$  (68% *cis*),  $\text{PdBr}_3\text{H}_2\text{O}^-$ ,  $\text{PdBr}_2(\text{H}_2\text{O})_2$  (86% *cis*), and  $\text{PdBr}(\text{H}_2\text{O})_3^+$ , cf. Figures 4 and 6.

However, the assignment of this shoulder is tentative. Since it has lower energy than the allowed  $3b_{1g} \leftarrow 3e_u$  (metal  $d_{x^2-y^2} \leftarrow$  ligand  $p_\pi$ ) transition at  $3.58 \mu\text{m}^{-1}$  ( $\text{PdCl}_4^{2-}$ ) it is reasonable to assume that the lowest one-electron energy level for the  $2.9\text{-}\mu\text{m}^{-1}$  ( $\text{PdCl}_4^{2-}$ ) shoulder is also composed of ligand  $p_\pi$  orbitals (cf. Basch and Gray,<sup>18</sup> Figure 1). We have assumed that this orbital is  $a_{2g}$  simply because some MO calculations<sup>18,20a,21</sup> place it highest in energy among the MO set built from ligand  $p_\pi$  orbitals. The energy level diagram in Figure 8 summarizes these conclusions for  $\text{PdCl}_4^{2-}$ , and should also be applicable to  $\text{PdBr}_4^{2-}$ .

As far as the symmetry-allowed bands of the mixed chloro and bromo aqua complexes of palladium are concerned, it should in principle be possible to correlate them with corresponding bands in the  $\text{PdX}_4^{2-}$  spectrum. This is complicated by symmetry splitting of transitions to degenerate states ( ${}^1E_u \leftarrow {}^1A_{1g}$  in  $\text{PdCl}_4^{2-}$ , cf. Table II) and, in the case of the bromide complexes, by spin-orbit splitting. Moreover, the spectrum of  $\text{PdX}_2(\text{H}_2\text{O})_2$  represents a mixture of the *cis* and *trans* spectra, which cannot be so easily resolved as the  $\text{PtCl}_2(\text{H}_2\text{O})_2$  spectrum because of the rapid reaction rates of the palladium complexes. The shoulders at the low-energy sides of the symmetry allowed bands in  $\text{PdBr}_4^{2-}$  are most reasonably due to singlet  $\rightarrow$  triplet transitions ( ${}^3E_u \leftarrow {}^1A_{1g}$ ).<sup>15</sup>

The high-intensity bands blue shift in a strikingly similar manner in going from  $\text{PtCl}_4^{2-}$  to  $\text{Pt}(\text{H}_2\text{O})_4^{2+}$  and  $\text{PdCl}_4^{2-}$  to  $\text{Pd}(\text{H}_2\text{O})_4^{2+}$ . This is most simply explained if the MO levels  $2a_{2u}$  in  $\text{PtCl}_4^{2-}$  and  $2e_u$ ,  $3e_u$  in  $\text{PdCl}_4^{2-}$  are assumed

to be predominantly ligand orbitals. Since the highest occupied levels  $3a_{1g}$ ,  $2e_g$ , and  $2b_{2g}$  and the lowest unoccupied level  $3b_{1g}$  are mainly metal d orbitals, the high-intensity bands in the palladium spectra might be described as ligand-to-metal charge transfer, and those in the platinum spectra as metal-to-ligand charge transfer bands. Perhaps the charge-transfer bands of  $PtCl_4^{2-}$  might have some  $d \rightarrow p$  character as previously suggested,<sup>1,14,23</sup> but a pure  $d \rightarrow p$  transition should blue shift much less within the series than observed, as a  $\pi$  donor ligand should destabilize both  $2a_{2u}$  and the filled d orbitals.

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## Kinetic Details of a Gas-Surface System by the Frequency Response Method

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Adsorption-rate spectra of an ethylene-on-zinc oxide system maintained at  $-70$  and  $-20$  °C were observed by the frequency response method at equilibrium pressures between  $4 \times 10^{-2}$  and 1.8 Torr. The pressure dependence of the spectra stemming from two kinds of surface species, termed III and II in an earlier paper, was interpreted in a five parameter model; a kinetic equation,  $(d/dt)A_j = k_a^{(j)}PN_S^{(j)}(1 - \theta_j) \exp(-g_j\theta_j) - k_d^{(j)}N_S^{(j)}\theta_j \exp(h_j\theta_j)$ , was postulated for each individual surface species  $j$ , of which the amount is denoted by  $A_j$  and the coverage  $\theta_j$  is defined as  $A_j/N_S^{(j)}$ . All constants in the equation,  $k_a^{(j)}$ ,  $k_d^{(j)}$ ,  $N_S^{(j)}$ ,  $g_j$ , and  $h_j$ , were determined according to a theoretical procedure at each equilibrium temperature; a slight dependence of the constants on temperature was found and discussed with the Fermi-Dirac distribution for  $A_j(T_e)$ . Conclusions of  $h_j \gg g_j \sim 0$  for both species indicate that repulsive forces acting between each kind of the admolecules affect the desorption rate but not the adsorption.

## Introduction

In an earlier paper<sup>1</sup> the ethylene-on-zinc oxide system maintained at  $-20$  °C has been investigated, where the kinetic behavior for at least two kinds of surface species of ethylene has been found to be described by the Langmuir equation with sufficient accuracy. It is thought to be of further interest to study the temperature dependence of the kinetic constants in the equation. However, forces acting between admolecules which are neglected in the Langmuir model could not be overlooked at lower temperatures.

A kinetic equation taking into account these effects with the additional constants  $g_j$  and  $h_j$  (eq 1) was postulated,

$$(d/dt)A_j = k_a^{(j)}PN_S^{(j)}(1 - \theta_j) \exp(-g_j\theta_j) - k_d^{(j)}N_S^{(j)}\theta_j \exp(h_j\theta_j) \quad (1)$$

therefore, instead of the Langmuir equation for each individual surface species. Here  $A_j$  denotes the amount of

surface species  $j$ ;  $N_S^{(j)}$ , the number of sites available for adsorption;  $k_a^{(j)}$  and  $k_d^{(j)}$  are rate constants for adsorption and desorption, respectively; and  $\theta_j$  is the coverage defined by

$$\theta_j = A_j/N_S^{(j)} \quad (2)$$

The equation improperly<sup>2</sup> termed Becker-Zeldovich has been derived from the theory of rate processes by Higuchi, Ree, and Eyring.<sup>3</sup> Though the Elovich equation

$$(d/dt)A = a \exp(-\alpha A) \quad (3)$$

where  $a$  and  $\alpha$  are constants, is known to have the most general application,<sup>2,4,5</sup> it may be included in a particular case of eq 1. The second term in eq 1 is also reported to give a good representation of the rate of desorption in many cases of chemisorption.<sup>5</sup>

In the present article a method is shown for determining the five constants in eq 1 from data on the frequency