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Molecular Orbital Theory for Metal-Halides Complexes. The Electronic Structure and the Spectrum of $[PdCl_4]^{2-}$ Ion

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The electronic structure of the ground state is studied by semiempirical SCF–MO–LCAO calculations. An assignment of the electronic spectrum is given on the basis of both a configuration interaction calculation and some SCF calculations for the lowest excited states.

Introduction

During the last ten years considerable interest has been given to the electronic spectra of d^8 square-planar complexes.[1-8]

This interest has mainly concerned the energy order of the molecular orbitals (MO's) deriving from the d atomic orbitals (AO's). Several orders have been proposed and, as a consequence, different assignments of the observed bands have been given.

Calculations based on the Ligand Field theory have not given a definitive solution to the problem and, according to recent experimental results, not always correct.[9-12] The difficulty of the problem is connected with the fact that in these MO's there is some participation of the AO's of the ligands and in particular it is remarkably different in the different symmetries. The MO theory, according to the LCAO-SCF scheme, can take into account this fact.

Several authors have already investigated the d^8 square-planar complexes on the basis of rather simplified calculation schemes.[13-14]

The purpose of this work has been that of studying the ion $[PdCl_4]^{2-}$, which is a typical example of the d^8 square-planar complexes, by applying the semiempirical MO theory that we derived by a proper elaboration from the scheme of Pople-Pariser-Parr for unsaturated hydrocarbons.[15-17] Our method is more elaborated than those in[13-14] and permits the evaluation of the transition energies both by a Configuration Interaction (CI) calculation or by SCF calculations carried out for the excited states.

Outline of the Calculations

The calculation scheme has been described in previous papers.[15-17] There two main features of the method: the semi-empirical evaluation of the integrals and the « zero differential overlap » approximation. In particular for the integrals the following criteria have been used:

(a) The one-centre integrals have been evaluated from the valence state energies[16]: for Cl the data given in[16] has been used, and for Pd the values* have been obtained from the valence state energies, evaluated by means of the Slater-Condon parameters given in.[18]

(b) The two-centres coulomb repulsion integrals have been evaluated using the « uniformly charged spheres » approximation as reported in.[15-17]

(c) The off-diagonal core integrals $H_{rs} = \int \chi_r H^{core} \chi_s d\tau$ have been evaluated by applying the formula:

$$H_{rs} = -\tfrac{1}{2}(I_r + I_s)S_{rs}$$

where I_r and I_s are valence state ionization potentials and S_{rs} is the overlap integral.[15] For the calculation of S_{rs} the AO radial functions for Pd and Cl have

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* $U_d = -121.66$, $U_s = -88.25$, $U_p = -72.60$. $g(d_i,d_i) = 13.87$, $g(d_{z^2},d_{xz}) = 12.79$, $g(d_{z^2},d_{xy}) = 12.11$, $g(d_{xz},d_{yz}) = 12.34$, $g(d_{x^2-y^2},d_{xy}) = 12.99$, $g(d_i,s) = 9.02$, $g(d_{z^2},p_z) = 7.85$, $g(d_{z^2},p_x) = 7.63$, $g(d_{xz},p_z) = 7.78$, $g(d_{xy},p_z) = 7.55$, $g(s,p_i) = 6.42$, $g(p_i,p_i) = 6.22$, $g(p_i,p_j) = 5.45$, $g(s,s) = 7.46$.

been taken from[21] and[22] respectively.

(d) The neutral atom penetration integrals have been neglected.

With regard to the « zero differential overlap » approximation, Pople-Santry-Segal have pointed out[19] that this approximation gives results not invariant with respect to certain transformations of the AO basis set. In order to know how important is this fact in our case, some preliminary calculations have been performed in which we evaluated several times the integrals involving the symmetry orbitals, each time using a different orientation of the AO basis set. We found that the values vary only slightly and from this we think that the fact holds also for the SCF and CI calculations.

In this study a square-planar structure (D_{4h} symmetry) and a bond-lenght Pd–Cl of 2.30 Å have been assumed.[20]

As the results of the calculations depend on the extension of the AO basis set and since in the semiempirical approaches a larger basis does not always give results in better agreement with the experimental data,[27] we have performed the calculations twice:

(A) With the following basis set: 4d, 5s, 5p for Pd and 3p for Cl atoms.

(B) To the above set the 3s AO's of the ligands has been added.

The electrons occupying AO's not included in the above basis set have been considered part of the core.

The results of the two sets of calculations are rather close. For both cases (henceforth denoted by A and B) the following calculations have been carried out:

1. *Ground state* (Symmetry $^1A_{1g}$): evaluation of the SCF eigenvectors and eigenvalues.

2. *d–d excitations*: evaluation of the transition energies by means of the relation:

$$\Delta E_{i\rightarrow j} = \varepsilon_j - \varepsilon_i - J_{ij} + 2K_{ij} \qquad (1)$$

where ε_j and ε_i are the MO eigenvalues and J_{ij}, K_{ij} are respectively coulomb and exchange integrals.

3. *Charge transfer excitations $^1A_{1g}\rightarrow{}^1E_u$ and $^1A_{1g}\rightarrow{}^1A_{2u}$* (allowed for dipole radiation): The evaluation of the transition energies, for each symmetry, has been done in two different ways:

(i) By a CI calculation extended to all the monoexcited configurations of the same symmetry.

(ii) By an SCF calculation (only for the lowest excited state).

The transition energy is found from the difference of the total energy with respect to that of the ground state.

4. *Charge transfer excitations $^1A_{1g}\rightarrow{}^1B_{2g}$ and $^1A_{1g}\rightarrow{}^1E_g$* (forbidden for dipole radiation): The evaluation of the transition energies has been done in two different ways:

(i) As in 2. for d–d transitions by means of eq. (1).

(ii) As in 3. case (ii) by means of an SCF calculation.

All the SCF calculations have been performed according to the method proposed by M. Rossi[23] which is particularly suitable for high symmetry and, in addition, it is always covergent.

We have found that in this case the effect of the configuration interaction is rather small.

The SCF calculations concerning excited states have been performed because in previous studies we found[28] that the electron distribution in the CT excited states obtained by SCF calculations can be remarkably different from that obtained by CI calculations, unless in the latter the many-electron excited configurations are considered, but this is rather laborious. This fact has been confirmed also in this work.

For the d–d excitations no SCF calculations have been done because the above fact is less important.

Results and Discussion

(a) *The MO energies and the fractional charge distribution.* The eigenvectors and the eigenvalues of the SCF calculations for the ground state are reported in Table I.

On the basis of the eigenvalues the energy order of the antibonding d–type MO's is the following:

$$\varepsilon_{d_{z^2}} < \varepsilon_{d_{xy}} < \varepsilon_{d_{xz}} = \varepsilon_{d_{yz}} < \varepsilon_{d_{x^2-y^2}} \qquad (2)$$

However some facts have to be pointed out:

1. The degree of participation of the AO's of the ligands is small in $3a_{1g}(d_{z^2})$ and $3b_{1g}(d_{x^2-y^2})$ and rather large in $2b_{2g}(d_{xy})$ and $2e_g(d_{xz},d_{yz})$. The previous calculations of Basch and Gray[13] also agree on this point.

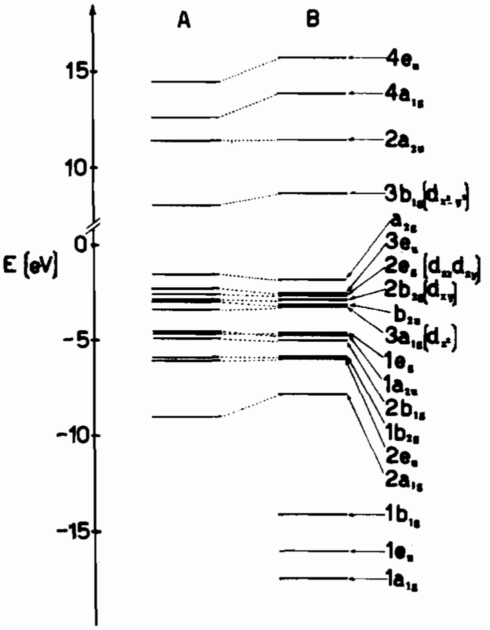

Figure 1. Molecular Orbital energy levels.

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Table I. Eigenvalues and eigenvectors for the ground state ($^1A_{1g}$)

	case A						case B						
MO	ε(eV)	5s	5p	4d	σ_L	π_L	ε(eV)	5s	5p	4d	s_L	σ_L	π_L
$1a_{1g}$							—17.48	.340		.105	.902	.244	
$1e_u$							—16.02		.273		.952	.069	.122
$1b_{1g}$							—14.11			.146	.985	—.089	
$2a_{1g}$	— 9.00	.438		.225	.870		— 7.79	.284		.169	—.362	.871	
$2e_u$	— 6.11		.354		.810	.467	— 5.97		.275		—.194	.844	.418
$1b_{2g}$	— 5.86			.694		.720	— 5.90			.630			.776
$2b_{1g}$	— 4.94			.558	.830		— 5.01			.525	—.001	.851	
$1a_{2u}$	— 4.53		.226			.974	— 4.75		.221				.975
$1e_g$	— 4.70			.781		.625	— 4.67			.703			.711
$3a_{1g}(d_{z^2})$	— 3.44	—.182		.970	—.159		— 3.22	—.180		.974	—.009	—.135	
b_{2u}	— 3.00					1.000	— 3.24						1.000
$2b_{2g}(d_{xy})$	— 2.94			.720		—.694	— 2.91			.776			—.630
$2e_g(d_{xz},d_{yz})$	— 2.58			.625		—.781	— 2.61			.711			—.703
$3e_u$	— 2.38		—.082		—.471	.878	— 2.61		—.090		—.059	—.428	897
a_{2g}	— 1.62					1.000	— 1.87						1.000
$3b_{1g}(d_{x^2-y^2})$	8.11			.830	—.558		8.67			.838	—.171	—.518	
$2a_{2u}$	11.44		.974			—.226	11.46		.975				—.221
$4a_{1g}$	12.58	.881		.089	—.466		13.78	.878		.104	—.234	—.404	
$4e_u$	14.47		.932		—.349	—.100	15.67		.918		—.231	—.316	—.073

Table II. Eigenvectors for the excited states ^1E_u and $^1A_{2u}$ - Case B

	$^1E_u(3e_u \rightarrow 3b_{1g})$						$^1A_{2u}(b_{2u} \rightarrow 3b_{1g})$					
MO	5s	5p	4d	s_L	σ_L	π_L	5s	5p	4d	s_L	σ_L	π_L
$1a_{1g}$	.319		.085	.917	.226		.320		.084	.916	.229	
$1e_u$		.266		953	.080	.122		.264		.954	.075	.123
$1b_{1g}$			.109	.990	—.086				.107	.991	—.085	
$2a_{1g}$	.296		.118	—.332	.888		.293		.113	—.335	.888	
$2e_u$		.263		—.203	.814	.477		.260		—.200	.800	.503
$1b_{2g}$			.317			.948			.274			.962
$2b_{1g}$			.321	.047	.946				.328	.046	.944	
$1a_{2u}$		.199				.980		.210				.978
$1e_g$			.303			.953			.296			.955
$3a_{1g}(d_{z^2})$	—.180		.981	—.010	—.075		—.181		.981	—.010	—.069	
b_{2u}						1.000						1.000
$2b_{2g}(d_{xy})$			.948			—.317			.962			—.274
$2e_g(d_{xz},d_{yz})$			.953			—.303			.955			—.296
$3e_u$		—.107		—.040	—.484	.867		—.115		—.038	—.509	.852
a_{2g}						1.000						1.000
$3b_{1g}(d_{x^2-y^2})$			.941	—.131	—.313				.939	—.129	—.320	
$2a_{2u}$		.980				—.199		.978				—.210
$4a_{1g}$	.882		.130	—.222	—.394		.883		.133	—.222	—.392	
$4e_u$		.921		—.222	—.311	—.070		.922		—.222	—.310	—.070

Table III. Fractional charge distributions

			case A			case B		
			q_{Pd}	q_{Cl}	Δq_{Pd}	q_{Pd}	q_{Cl}	Δq_{Pd}
Ground State		$^1A_{1g}$	.32	—.58		.57	—.64	
Excited States	from SCF	$^1B_{2g}$	—.10	—.47	—.42	.12	—.53	—.45
		^1E_g	—.08	—.48	—.40	.15	—.54	—.42
		^1E_u	—.11	—.47	—.43	.11	—.53	—.46
		$^1A_{2u}$	—.09	—.48	—.41	.13	—.53	—.44
	from CI	^1E_u	—.36	—.41	—.68	—.12	—.47	—.69
		$^1A_{2u}$	—.37	—.41	—.69	—.11	—.47	—.68

2. The above energy order cannot be compared with those given on the basis of Ligand Field treatments,[6] because the eigenvalues ε_i contain the contribution of the field of the electrons occupying the d–type MO's.

The SCF eigenvectors for the excited states $^1E_u(3e_u \rightarrow 3b_{1g})$, $^1A_{2u}(b_{2u} \rightarrow 3b_{1g})$, $^1B_{2g}(a_{2g} \rightarrow 3b_{1g})$, $^1E_g(1e_g \rightarrow 3b_{1g})$ are all rather close, independent of the excited state, but differ substantially from those of the ground state. In particular $1b_{2g}$ and $1e_g$ MO's are more localized on the ligands and $2b_{2g}$ and $2e_g$ have a larger d–character. As examples, the eigenvectors for the two excited states $^1E_u(3e_u \rightarrow 3b_{1g})$ and $^1A_{2u}(b_{2u} \rightarrow 3b_{1g})$ (case B) are reported in Table II.

Table IV. Ligand Field bands and proposed assignments

$PdCl_4^{2-}$		$PtCl_4^{2-}$		Proposed assignments			
ν (kK)	ε	ν (kK)	ε	I Ref. [1]	II Ref. [2]	III Ref. [3]	IV Ref. [5]
		17.3(xy)	5	$^3A_{2g}$		$^3A_{2g}$	
17.0(z) 18.0(xy)	7 19	20.2(z) 20.4(xy)	20 17.5	^3E_g	$(^3A_{2g},{}^3B_{1g})$	$^1A_{2g}$	$^1B_{1g}$
20.0(xy)	67	26.0(xy)	45	$^1A_{2g}$	$^1A_{2g}$	$^1B_{1g}$	$^1A_{2g}$
22.0(xy) 23.0(z)	128 80	28.5(xy) 29.3(z)	57 70	^1E_g	$^1B_{1g}$	^1E_g	^1E_g

The fractional charge distributions for the ground state and for the lowest excited states are given in Table III. The value of the fractional charge on Pd calculated for the ground state in both cases, A and B, is consistent with the values obtained for similar compounds by pure quadrupole resonance measurements:[24-25]

$$PdBr_4^{2-}: q_{Pd}=0.40 \quad PtBr_4^{2-}: q_{Pt}=0.28 \quad PtCl_4^{2-}: q_{Pt}=0.44$$

It is interesting to examine the difference of fractional charge between the lowest excited states and the ground state.

In fact it is practically independent of the AO basis set and of the symmetry of the excited state but it is different for the two different approaches, CI and SCF.

(b) *The Electronic Spectrum.*

1. *The Experimental Data and the Proposed assignments.* A remarkable amount of work has been done on the spectra of $PdCl_4^{2-}$ and $PtCl_4^{2-}$, especially with regard to the assignment of the Ligand Field bands. A summary of this work is given in Table IV.

In the last five years some of the previous proposed assignments have been excluded on the basis of accurate measurements of absorption spectra made on single crystals with polarized light at 4°K[9] and of magnetic circular dichroism (MCD).[8] In particular it has been found:

(i) The bands 20.0 kK of $PdCl_4^{2-}$ have only the xy polarization. Therefore, if we accept a vibronic mechanism, these bands must be assigned as:[9]

$$^1A_{1g}\rightarrow{}^1A_{2g}[2b_{2g}(d_{xy})\rightarrow 3b_{1g}(d_{x^2-y^2})]$$

(ii) From MCD measurements the bands 22.0 kK of $PdCl_4^{2-}$ and 30.0 kK of $PtCl_4^{2-}$ show an A term[8] and this is consistent with the assignment:

$$^1A_{1g}\rightarrow{}^1E_g[2e_g(d_{xz},d_{yz})\rightarrow 3b_{1g}(d_{x^2-y^2})]$$

It is evident that only the assignment I and IV of Table IV are compatible with the above facts.

Assignment I is supported by Ligand Field calculations[6] and by the considerations based on the different intensity of the d–d bands in K_2PtCl_4 and in the Magnus salt, $Pt(NH_3)_4PtCl_4$, of Day *et al.*[9]

On the other hand, the assignment IV is supported by the considerations given by Martin and Lenhard[5] on the basis of the shift of the maxima of the d–d bands in the z and xy polarizations.

The main objection, which is made to assignment IV, is that it neglects the inflection at 29.5 kK of $PdCl_4^{2-}$, although the intensity is of the order expected for a Ligand Field band.

2. *The Results of the Calculations.* The results of our calculations for the transition energies and the corresponding assignment of the bands are reported in Table V.

It is interesting to point out here that, whereas at a first glance from the MO energy order (2) one should expect no agreement with the assignments of Table IV, the results of the calculations support assignment IV. This can be clearly understood by considering the quantity $J_{ij}-2K_{ij}$ of eq. (1) (Table VI). In fact this quantity follows exactly the reverse order of eq. (2)

$$\begin{aligned}(J_{3a_{1g},3b_{1g}}-2K_{3a_{1g},3b_{1g}})>(J_{2b_{2g},3b_{1g}}-2K_{2b_{2g},3b_{1g}})\\ >(J_{2e_g,3b_{1g}}-2K_{2e,3b_{1g}})\end{aligned} \tag{3}$$

and as a consequence also the energy order of the d–d transitions is reversed. Order (3) depends on the following facts:

(i) The exchange integrals K_{ij} are, in our approach, very small or zero and order (3) corresponds substantially to that of the coulomb integrals I_{ij}.

(ii) Denoting with $\Phi_i=a_id_i+b_i\chi_i^L$ a d–type MO (where χ_i^L is an appropriate symmetry orbital of the ligands) we have:

$$\begin{aligned}J_{i,3b_{1g}}={}&a^2_ia^2_{3b_{1g}}J(d_i,d_{x^2-y^2})+a^2_i b^2_{3b_{1g}}J(d_i,\chi^L_{3b_{1g}})+\\ &+b_i^2a^2_{3b_{1g}}J(\chi_i^L,d_{x^2-y^2})+b_i^2b^2_{3b_{1g}}J(\chi_i^L,\chi^L_{3b_{1g}})\end{aligned}$$

The value of a J_{ij} integral is smaller when one of the involved charge clouds becomes more diffuse. In particular for the above integrals we have the order:

$$J(d_i,d_{x^2-y^2})>J(d_i,\chi^L_{3b_{1g}})\sim J(\chi_i^L,d_{x^2-y^2})>J(\chi_i^L,\chi^L_{3b_{1g}})$$

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Table V. Calculated transition energies and band assignment

	Excited State	Perturbing Vibration	Polarization	Calculated transition energies (eV) A eq.(1)	A CI	A SCF	B eq.(1)	B CI	B SCF	Observed Bands eV	kK	Polarization
d–d	$^1B_{1g}$ $3a_{1g}(d_{z^2})\rightarrow 3b_{1g}(d_{x^2-y^2})$	B_{2u}	z	1.20			1.48			2.11	17.0^1	z
		E_u	xy							2.23	18.0^1	xy
	$^1A_{2g}$ $2b_{2g}(d_{xy})\rightarrow 3b_{1g}(d_{x^2-y^2})$	E_u	xy	2.43			2.45			2.48	20.0^1	xy
	^1E_g $2e_g(d_{xz},d_{yz})\rightarrow 3b_{1g}(d_{x^2-y^2})$	E_u	z	3.06			3.04			2.80	22.6^1	xy
		A_{2u}	xy							2.85	23.0^1	z
		B_{2u}	xy									
forbidden CT	$^1B_{2g}$ $a_{2g}\rightarrow 3b_{1g}$	E_u	xy	4.00		3.42	4.78		4.26	3.66	29.5^1	xy
	^1E_g $1e_g\rightarrow 3b_{1g}$	E_u	z	4.07		5.59	5.15		6.39			
		A_{2u}	xy									
		B_{2u}	xy									
allowed CT	^1E_u $3e_u\rightarrow 3b_{1g}$		xy		4.69	4.09		5.15	4.62	4.46	36.0^1	
	$^1A_{2u}$ $b_{2u}\rightarrow 3b_{1g}$		z		5.42	4.91		5.89	5.43			
	^1E_u $2e_g\rightarrow 2a_{2u}$		xy		7.28			7.14		5.57	44.9^2	
	$^1A_{2u}$ $3a_{1g}\rightarrow 2a_{2u}$		z		7.24			6.90				
	^1E_u $2e_u\rightarrow 3b_{1g}$		xy		8.14			8.10				

[1] from ref. [9]. [2] from ref. [8].

Table VI. d-d and forbidden CT transition energies

	case	ε_j	ε_i	J_{ji}	K_{ji}	$E_i\rightarrow_j$(eV)
$3a_{1g}(d_{z^2})\rightarrow 3b_{1g}(d_{x^2-y^2})$	A	8.11	−3.44	10.37	0.01	1.20
	B	8.67	−3.22	10.43	0.01	1.48
$2b_{2g}(d_{xy})\rightarrow 3b_{1g}(d_{x^2-y^2})$	A	8.11	−2.94	8.62	0.00	2.43
	B	8.67	−2.91	9.13	0.00	2.45
$2e_g(d_{xz}d_{yz})\rightarrow 3b_{1g}(d_{x^2-y^2})$	A	8.11	−2.58	7.63	0.00	3.06
	B	8.67	−2.61	8.24	0.00	3.04
$a_{2g}\rightarrow 3b_{1g}(d_{x^2-y^2})$	A	8.11	−1.62	5.73	0.00	4.00
	B	8.67	−1.87	5.76	0.00	4.78
$1e_g\rightarrow 3b_{1g}(d_{x^2-y^2})$	A	8.11	−4.70	8.74	0.00	4.07
	B	8.67	−4.67	8.19	0.00	5.15

$J_{i,3b_{1g}}$ is smaller where the participation of the AO's of the ligands in Φ_i is larger. In particular, it is clear that order (3) is a consequence of the larger participation of the ligand AO's in $2b_{2g}$ and in $2e_g$ than in $3a_{1g}$.

It is interesting to note that the Ligand Field bands, which are found to be experimentally more intense, involve, on the basis of assignment IV, electron transitions from MO's, which have a larger participation of the ligand AO's.

With regard to CT transitions, we have considered the excitations $^1A_{1g}\rightarrow{}^1E_u$ and $^1A_{1g}\rightarrow{}^1A_{2u}$ which are the only ones allowed by an electric dipole mechanism.

At a first glance, on the basis of the results of the calculations, we should assign the band 36.0 kK as $^1A_{1g}\rightarrow{}^1E_u(3e_u\rightarrow 3b_{1g})$ and the band 44.9 kK as $^1A_{1g}\rightarrow{}^1A_{2u}(b_{2u}\rightarrow 3b_{1g})$. However it is evident from the comparison of all the calculated CT transition energies (allowed and forbidden: see Table V with those of the observed bands, that the former are slightly higher (this is probably because of the approximation of neglecting the neutral atom penetration integrals). Thus, taking this fact into account, we think it is more reasonable to assign the band 36.0 kK to both the above excitations. This agrees with the proposal of Jørgensen[29] and with the experimental results obtained by the polarized reflection spectra[8] and by the MCD measurements.

With regard to the band 44.9 kK it is difficult to make a precise assignment on the basis of the results of our calculations. The possible excitations to be considered are $^1A_{1g}\rightarrow{}^1E_u(2e_g\rightarrow 2a_{2u})$ and $^1A_{1g}\rightarrow{}^1A_{2u}$-$(3a_{1u}\rightarrow 2a_{2u})$. Their transition energies, evaluated only by CI calculations, are $1.45\div 1.71$ eV higher. The assignment as $^1A_{1g}\rightarrow{}^1E_u(2e_g\rightarrow 2a_{2u})$ is experimentally supported by MCD measurements.

In order to explain the weak shoulder at 29.5 kK, we have finally examined the lowest orbitally forbidden CT transitions which can be allowed by a vibronic mechanism. Of all the possible transitions only two have energy low enough to be considered for the assignment of the 29.5 kK band:

$$^1A_{1g}\rightarrow{}^1B_{2g}(a_{2g}\rightarrow 3b_{1g}) \qquad {}^1A_{1g}\rightarrow{}^1E_g(1e_g\rightarrow 3b_{1g})$$

The SCF calculations give a good agreement in the case of the excitation $^1A_{1g}\rightarrow{}^1B_{2g}(a_{2g}\rightarrow 3b_{1g})$ and rather poor in the case of $^1A_{1g}\rightarrow{}^1E_g(1e_g\rightarrow 3b_{1g})$. We think that it is more reasonable to assign the band as $^1A_{1g}\rightarrow{}^1B_{2g}(a_{2g}\rightarrow 3b_{1g})$. In fact the a_{2g} MO certainly has the highest energy among the filled MO's localized on the ligands (it is the only one with four nodal planes) and therefore such excitation must appear at lower than the first allowed CT transition. Furthermore this assignment is in complete agreement with the observed polarization xy.[9]

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(28) L. Oleari, L. Di Sipio, G. De Michelis, and E. Tondello, Proceeding of XII International Conference on Coordination Chemistry (ICCC), Sydney, August 20-27, 1969, pag. 76.

(29) Jørgensen, *Advan. Chem. Phys.*, 5, 119 (1963).

With regard to the fact of assigning the shoulder at 29.5 kK as a CT transition and not as a Ligand Field band, we think that there is evidence in the following facts:

(i) By replacing the Cl with Br atoms in $PdCl_4^{2-}$, the band shifts 7 kK towards lower wavenumbers, and this corresponds exactly to the difference of the optical electronegativities between Cl and Br.[30] This feature is also observed in the analogous complexes of Pt and Au:[10]

$PdCl_4^{2-}$ 30.5 kK	$PtCl_4^{2-}$ 38.3 kK	$AuCl_4^-$ 26.0 kK
$PdBr_4^{2-}$ 24.0 kK	$PtBr_4^{2-}$ 31.0 kK	$AuBr_4^-$ 19.5 kK

(ii) M. Ito *et al.* have shown[10] that by replacing the Cl atoms with 1–propilendiamine in $PdCl_4^{2-}$ and $PtCl_4^{2-}$ the d–d bands shift regularly and rather linearly with the number of the replaced Cl's. This behaviour is not shown by the shoulder at 29.5 kK.

Conclusions

From the results of the calculations the following main conclusions can be drawn:

1) The participation of the AO's of the ligands is noticeably different in the different symmetries.

2) The coulomb repulsion integrals $J_{i,3b_{1g}}$ depend remarkably on the extent of participation of the ligand AO's in Φ_i MO and they have an important contribution to the transition energy of the Ligand Field bands. In particular, from the results of the calculations, the energy order of the d–d transitions is reversed with respect to that of the MO's.

3) There is a remarkable charge distribution rearrangement in the CT excitations. The ligand→ metal charge transfer is much smaller than would be expected from the ground state MO's. This fact is very important also in the assignment of the CT bands.

4) The CT transitions, forbidden for dipole radiation but allowed through a vibronic mechanism, must be considered in the interpretation of the electronic spectra. In fact in the case of $PdCl_4^{2-}$ the shoulder 29.5 kK can be assigned as $^1A_{1g} \rightarrow {}^1B_{2g}(a_{2g} \rightarrow 3b_{1g})$.

We think that the above conclusions hold true independently of the approximations introduced in our calculations and that have to be taken into account as a basis in the interpretation of the spectrum of $PdCl_4^{2-}$.

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(30) C. K. Jørgensen, « Orbitals in Atoms and Molecules », Academic Press, London 1962, pag. 94.