Theoret. Chim. Acta (Berl.) 64, 83–96 (1983)

THEORETICA CHIMICA ACTA

Spin-orbit electronic states of octahedral Pt-group d^6 complexes as derived from reflectance spectra and ligand field calculations

Gerd Eyring, Thomas Schönherr, Hans-Herbert Schmidtke

Institut für Theoretische Chemie der Universität Düsseldorf, Universitätsstraße 1, Gebäude 26.32, D-4000 Düsseldorf 1, Federal Republic of Germany

The 90 K diffuse reflectance spectra of some octahedral Rh(III), Ir(III) and Pt(IV) complex compounds with chloride, thiocyanate and amine ligands are reported. The spectra show in the visible and near ultraviolet distinct bands due to spin-orbit components of singlet-triplet d–d transitions which are explained by ligand field calculations including spin-orbit coupling considering all possible d-electron configurations. Model parameter sets are obtained by fitting the measured band peaks to possible transitions between calculated energy levels. For some of the bands the vibrational structure could be resolved which is assigned to metal-ligand stretching vibrations of the electronically excited complex octahedra with vibrational fundamentals lower than those of the ground state.

Key words: Rh(III), Ir(III), Pt(IV) complexes—Reflection spectra—Ligand field calculations—Spin-orbit coupling.

1. Introduction

In general only few excited states of transition group complex compounds can be identified from optical measurements. This is due to the poorly resolved spectra which are usually obtained if the transitions occur between different electron configurations. Ligand field investigations can only be carried out when assignments of some of the spectral band peaks are possible which can serve as a basis for theoretical calculations. Many coordination compounds show in absorption only one or two spin allowed ligand field bands and, if at all, some nearby inflections indicating other transitions, which are forbidden to a higher degree by selection rules. The quality of these spectra is usually not good enough for carrying out band assignments and determining energy level schemes and ligand field parameters by comparing experimental results and theoretical calculations. The situation is more promising for compounds which have intraconfigurational transitions (e.g. d^3 and d^4 system as Cr^{3+}, Mn^{4+}, Re^{4+}, Os^{4+}) with highly resolved narrow line spectra. However, in octahedral d^6 compounds the ground state electron configuration has a closed shell (t_{2g}^6) which for obtaining an excited state must be broken. A transition between states belonging to different configurations leads to vibrational progressions which, except for a few single crystal spectra recorded at liquid helium temperature [1–4], could not be resolved so far. In particular, spin forbidden transitions into $t_{2g}^5e_g$ and $t_{2g}^4e_g^2$ electron configurations are expected to be very numerous, but they are difficult to identify since they occur with relatively low intensity. The chance for finding such transitions is improved by compounds of heavier metals since for these systems the spin selection rule is not strictly obeyed due to the larger spin-orbit coupling. Therefore, an investigation of Pt-group compounds would turn out to be promising. A larger spin-orbit coupling also increases the splitting of the multiplets [4] due to the higher spin-forces which improves the possibility for resolving neighboring transitions in the spectrum. Since in reflectance spectra smaller extinctions appear somewhat enhanced compared to larger ones [5], this technique seems to be superior over usual absorption measurements when looking for low intensity peaks which are located close to larger absorptions in the spectra.

In the present paper we report the diffuse reflectance spectra of some platinum group d^6-complex compounds at low temperature and try to fit the measured peaks to the energy level schemes obtained from ligand field calculations which includes complete spin-orbit coupling and considers all possible d-electron configurations. Since very little is known so far about parameter sets which apply for these compounds, the calculations were carried out for several possible band assignments until a best fit with the experiment had been obtained and at the same time maintaining the correct parameter relations within the spectrochemical and nephelauxetic series [6]. One important result which is envisaged is to obtain reliable identifications (symmetry assignments and energy intervals) of the lowest excited levels which have parent state of multiplicities different from the ground state. These levels are responsible for the luminescence behavior and the photochemical properties of the compounds. Due to the growing interest in this field [7–9] an investigation of these level systems seems to be useful at this time.

2. Experimental

2.1. Materials

The compounds K_3PhCl_6, K_3IrCl_6 and K_2PtCl_6 are commercially available, they were recrystallized several times before being used as samples for recording the spectra. The other compounds (cf. Table 1) were prepared and purified by methods given in the literature [10–13].

2.2 Reflectance spectra

Diffuse reflectance spectra furnish information on the light absorption properties of powdered materials if regular reflection on the surface of the crystalline particles can be neglected [5]. A complete exclusion of this radiation is not possible, however, it can be decreased by grinding the materials into fine powders, by diluting the samples with non absorbing standards and measuring the spectra relative to the same reference standards. Since the magnitude of the regular reflectance depends on the absorbancy of the sample, the extinctions of the reflectance spectra appear to be squeezed compared to the absorption spectra enhencing the weak transitions relative to the more intense peaks. This property which is usually considered as a shortcoming in reflectance spectroscopy, turns out to be favorable for localizing weaker transitions close to broad and stronger ones in the spectrum. Results concerning absorption coefficients and oscillator strengths are more difficult to be obtained and are of minor importance for the present purpose.

A Cary 17 spectrophotometer, equipped with a Varian model 1711 reflectance attachment has been used for recording the spectra. The materials were diluted one to five times by the white standard of analytical grade $BaSO_4$. In particular, with small dilutions only rather flat bands could be obtained which allow evaluation of peak maxima within only 100–300 cm^{-1}. The quality of the spectrum was improved by cooling the samples to about 90 K using nitrogen gas in an Oxford Instruments model CF 100 flow-cryostat. For these measurements a special sample holder and a vacuum jacket have been constructed which allowed the sample to be mounted as close as 1 mm in front of the entrance of the Ulbricht sphere. With this arrangement the reflected radiation enters into the Ulbricht sphere with a large spatial angle. However, since a heat radiation shield could not be mounted around the sample, a cooling down to liquid helium temperature was not possible with this equipment.

2.3. Computer programming

The calculations were carried out on a Telefunken computer model TR 445. The eigenvalues were obtained by diagonalizing the complete perturbation matrices using the Jacobi procedure. The iteration was terminated when the relation between off-diagonal and diagonal elements was less than 10^{-6}; by this the numerical accuracy for the theoretical eigenvalues (within the ligand field model) was better than 0.1 cm^{-1}. For calculating a complete level scheme computer time of about 100 sec was used.

3. Ligand field calculations

From the electron configurations $t_{2g}^{6-n}e_g^n$ $(n = 0, \ldots, 4)$ of octahedral d^6 complex compounds a large number of multiplets is obtained which are split by substantial amounts due to the spin-orbit coupling in higher transition elements (cf. Fig. 1). A reliable level scheme calculation must consider all $\binom{10}{4} = 210$ wave functions.

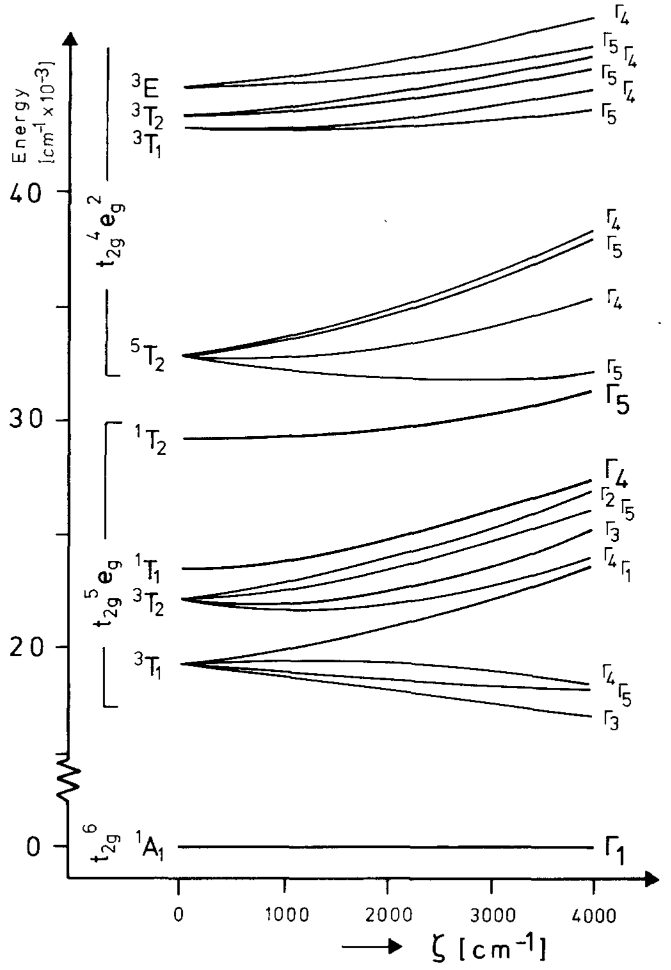

Fig. 1. Calculated energy level diagram showing term splittings due to spin-orbit coupling obtained with the parameter set $Dq = 2500$, $B = 400$ and $C = 2000\ cm^{-1}$ (ζ is the single electron spin-orbit coupling parameter)

The perturbation matrix elements of the d-electron repulsion and of the static cubic ligand field potential were given already by Tanabe and Sugano [14], the spin-orbit interaction matrices have been listed by Schroeder [15]. The energy levels calculated from the ligand field method depend on four model parameters (when the ground state energy is set equal to zero): the cubic ligand field *Dq*-, the Racah *B*- and *C*- and the spin-orbit coupling ζ-parameter. They are determined, within the semiempirical model, by comparison with the experiment. The number of parameters is actually small compared to the large number of energy states which are derived from all possible electron configurations, however, for a possible comparison between theory and experiment either an assignment of some of the states must be assumed or at least some indication on the size of the parameter values ought to be given. For the compounds presently investigated the parameters are known only very approximately since, in general, only assignments to spin-allowed transitions are sufficiently certain. In the case of K_2PtCl_6 also these assignments have been questioned recently [16] which makes any interpretation of Pt-spectra in general rather unreliable.

Therefore the general analysis was started with a qualitative energy level scheme which follows the main characteristics of the diagram given in Fig. 1. A first estimation of Dq can be appropriately obtained from the absorption maximum of the first singlet transition, an indication for B is given by the difference between the two singlet excited states (which are assigned to the largest peaks in the near ultraviolet); the relation C/B is obtained in the first approximation from the positions of the lowest singlet-triplet transitions and the splitting of the triplets is determined predominantely by the spin-orbit coupling constant ζ.

If sufficient experimental data is available the fitting of the calculated levels can be performed by an independent variation of parameters. Since the energy is not given by analytical expressions a large number of diagonalizations has to be carried out which would lead to an considerable amount of computer time. Therefore, a self consistent procedure has been used which contains only linear variations of energy expressions. With an estimated set of model parameters P_i^0 the energy level scheme $E_j^0 = f(P_i^0)$ and their derivatives $M_{ji}^0 = \Delta E_j^0 / \Delta P_i^0$ with respect to some assumed changes ΔP_i^0 are calculated. Comparing the theoretical eigenvalues $E_j^0 + \sum_i (P_i^1 - P_i^0) M_{ji}^0$ with the experimental E_j^e by a least square method, new parameters P_i^1 are calculated which lead to improved eigenvalues $E_j^1 = f(P_i^1)$. The variation is continued until no change of parameters P_i^n is obtained for a given variational limit. In general, the parameters converge to a final (optimal) set after only a few cycles if the spectrum is sufficiently high resolved (into about 5–6 bands) and if the starting parameters P_i^0 differ from the final parameter set by only 20–30%. By this procedure values for Dq and B were determined within small error limits. The parameters C and ζ more strongly depend on the actual position of triplet transitions in the spectrum, which due to the low intensity are in general less resolved; therefore the C- and ζ-parameters are subject to errors larger than those resulting for Dq and B.

Energy levels of $[Rh(SCN)_6]^{3-}$, $[Rh(dien)_2]^{3+}$ and $[Ir(NH_3)_6]^{3+}$, which have only poorly resolved spectra, could not be determined by the fitting procedure described above. Obviously, for some of these spectra, the number of band peaks measured is smaller than the number of the parameters to be determined. In this case only relative crude estimates of model parameters are to be expected. The calculation of these level schemes started from parameter sets derived from the spectrochemical and the nephelauxetic series [6] of the ligands followed by a parameter variation until the calculated transitions were in fair agreement with the band maxima of the spectra. The results obtained for these compounds are definitely of lower quality than those obtained by a best fit procedure, they are, however, of some significance as long as they obey the correct relations to other parameters predicted from the spectrochemical and nephelauxetic series.

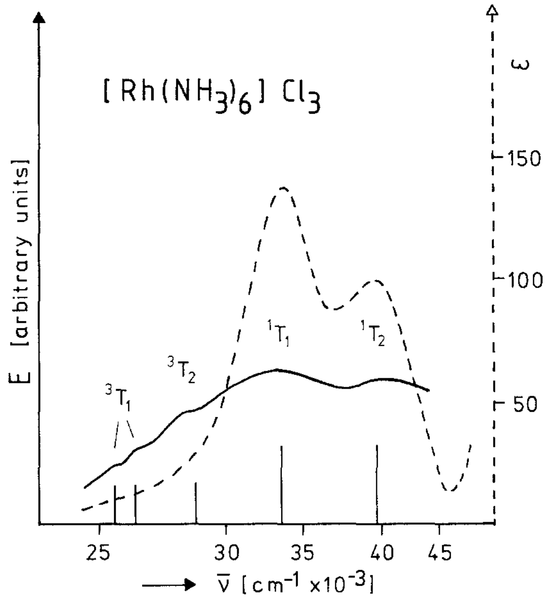

Fig. 2. The 90 K reflectance (——) and absorption (- -) spectrum in aqueous solution (Ref. [19]) of $[Rh(NH_3)_6]Cl_3$ and band assignments as obtained from ligand field results

4. Results and discussion

4.1. Rhodium complexes

In Fig. 2 the spectra of the hexammine complex are shown in absorption and remission. The two main peaks in remission are shifted to the red by a small amount and are broadened due to regular reflectance. They are assigned in the literature [6, 11] to singlet transitions $\Gamma_1(^1A_{1g}) \rightarrow \Gamma_4(^1T_{1g})$ and $\Gamma_5(^1T_{2g})$ which are not split by spin orbit coupling. Smaller absorptions can only be detected at the long wave length side of the reflectance spectrum, they are due to singlet-triplet transitions which gain oscillator strength due to spin-orbit interaction and by vibronic coupling [2, 9]. From the ligand field triplets $^3T_{1g}$ and $^3T_{2g}$ a total of eight spin-orbit levels is derived (cf. Fig. 1) from which only three can be detected in the hexammine spectrum. With the cyclic fitting procedure described in the last section, an energy level scheme is obtained which allows to attribute the two low energy absorptions to $^3T_{1g}$ and the shoulder near 27 800 cm^{-1} to $^3T_{2g}$. The actual assignment to spin-orbit levels is given in Table 1 which agrees with transition probability calculations [1] predicting larger intensities for $\Gamma_1 \rightarrow \Gamma_4$ and Γ_5 than for the transitions to other split levels.

The reflectance spectrum of $[Rh(dien)_2]Cl_3$ is similar to that of the hexammine complex but is less resolved. Ligand field results therefore are less accurate and the model parameters obtained for this compound are subject to larger errors compared to those for other compounds (cf. Table 2).

The band maxima of the first spin allowed transitions $\Gamma_4(^1T_1g)$ of Table 1 follow for a given central ion the spectrochemical series in which ligands are arranged

Table 1. Observed and calculated *d-d* transitions (wave numbers $cm^{-1} \times 10^{-3}$) and assignments obtained from present ligand field calculations

Compounds		$^3T_{1g}$			$^3T_{2g}$		$^1T_{1g}$	$^1T_{2g}$	$^5T_{2g}$	$^3T_{1g}$, $^3T_{2g}$, ^3E_g	CT^c
		Γ_3	Γ_5	Γ_4	Γ_4	Γ_5	Γ_4	Γ_5	Γ_4, Γ_5	Γ_4, Γ_5	
$K_3[RhCl_6]$	obs	15.4		16.0	17.9		20.0	24.8	28.5	34.0	38.5
	cal	15.4	15.5	16.1	18.1	19.4	19.7	24.8	26.6–28.1	34.7, 34.9	
$K_3[Rh(SCN)_6]$	obs			16.3	18.8		19.8	25.6	28.6		33.9
	cal	15.5	15.6	16.2	18.4	19.7	19.8	25.5	26.6–28.0	35.0–37.4	
$[Rh(NH_3)_6]Cl_3$	obs		25.6	26.3	27.8		32.3	39.0			
	cal	25.4	25.6	26.2	29.0	30.0	32.2	38.9	43.1–44.7	>57	
$[Rh\ dien_2]Cl_3^a$	obs		27.0				32.8	39.2			
	cal	26.6	26.7	27.4	30.0	31.0	32.9	39.3	46.1–47.7	>59	
$K_3[IrCl_6]$	obs	17.0	17.8	21.5	18.6	23.2	24.7	28.2	33.4, 36.3	40.2	
	cal	17.5	18.2	22.2	18.4	23.7	24.7	28.2	32.3–36.6	41.6, 42.2	
$A_3[Ir(SCN)_6]^b$	obs	16.2	16.6	20.8	17.2	22.2	25.0	28.2			32.8, 35.7
	cal	17.5	18.2	22.4	18.4	23.9	24.8	28.2	32.8–37.2	>41	
$[Ir(NH_3)_6]I_3$	obs		31.5	33.0			39.2				
	cal	30.9	31.6	32.2	36.0	37.7	39.2	44.2	57.3–61.6	>69	
$K_2[PtCl_6]$	obs	21.0	22.0	27.2	22.5	28.5	29.7	32.6			37.3
	cal	21.2	22.1	26.9	22.2	28.2	29.6	32.5	40.2–45.4	>51	

[a] dien = diethylentriamine

[b] A = tetra-n-butylammonium

[c] ligand to metal charge transfer transition

Table 2. Optimal ligand field parameter sets in cm^{-1} obtained from the calculation procedure described in the text

	Dq	B	C	ζ
$[RhCl_6]^{3-}$	1990	400	1400	1080
$[Rh(SCN)_6]^{3-a}$	2000	450	1400	1000
$[Rh(NH_3)_6]^{3+}$	3400	470	2850	1200
$[Rh(dien)_2]^{3+a}$	3450	450	2600	1200
$[IrCl_6]^{3-}$	2370	310	1620	2780
$[Ir(SCN)_6]^{3-}$	2350	305	1500	2880
$[Ir(NH_3)_6]^{3+a}$	3900	400	2200	3000
$[PtCl_6]^{2-}$	2840	260	1780	3400

[a] parameters not obtained by a best fit, they are subject to larger errors compared to the data given for the other compounds

according to increasing values of Dq:

$$SCN^- < Cl^- < NH_3 < dien.$$

This series also determines roughly the colour of the corresponding chromophor. For compounds with small parameter values of Dq also two electron ligand field transitions of the type $t_{2g}^6 \rightarrow t_{2g}^4 e_g^2$ can be expected to occur within the spectral range up to about 41 000 cm^{-1} where reflectance spectra can be properly recorded. These transitions are detected as distinct absorptions at 28 500 and near 34 000 cm^{-1} in the 90 K spectrum of K_3RhCl_6 (see Fig. 3). The higher energy absorption is observed as a shoulder at the long wave length flank of the charge transfer band Cl→Rh [17]. From the energy level scheme provided by the calculations these bands can be assigned for the first time to transitions into $^5T_{2g}$ and, respectively, into the higher triplet parent states $^3T_{1g}$, $^3T_{2g}$ for which rather

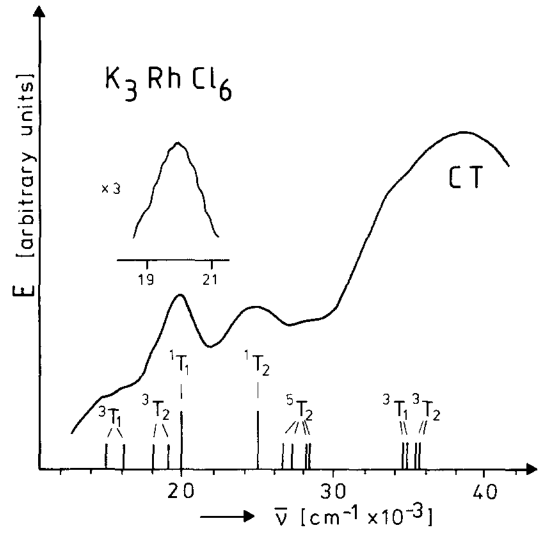

Fig. 3. Reflectance spectrum of K_3RhCl_6 at 90 K and ligand field energy levels as calculated from the parameter set of Table 2

low multiplet splittings are obtained (cf. Table 1). Due to the large spin-orbit coupling parameter ($\zeta = 1000\text{–}1200\,\text{cm}^{-1}$ for Rh(III) compounds), transitions belonging to spin quantum number changes of $\Delta S = 2$ are sufficiently allowed to be detected in low temperature reflectance spectra. For the low energy transitions a similar assignment can be made as proposed for the amine complexes.

Corresponding transitions are found also in the spectrum of $[\text{Rh(SCN)}_6]^{3-}$ although the spin-orbit components have not been resolved (see Table 1). The model parameters for this compound also listed in Table 2 are therefore of minor accuracy.

4.2. Iridium and platinum complexes

The spin-orbit coupling parameters ζ for iridium(III) and platinum(IV) compounds have been estimated larger than $2500\,\text{cm}^{-1}$ [15, 16]. This becomes apparent from the higher degree of multiplet splittings (cf. Fig. 1) and from the restrictions which are imposed on the spin selection rule. As a consequence the molar extinction coefficients for singlet-triplet transitions of iridium complexes are about three times larger than the corresponding rhodium compounds [18, 19]. Jørgensen [18] has assigned the weak bands at 16 300 and $17\,900\,\text{cm}^{-1}$ measured in the room temperature solution spectrum of IrCl_6^{3-} to transitions into ${}^3T_{1g}$ and ${}^3T_{2g}$ states, each of them split due to spin-orbit coupling in four component states. However, already Schroeder pointed out [15] that, for obtaining detailed assignments and reliable ligand field parameters, more resolved spectra must be available.

The 90 K reflectance spectrum of K_3IrCl_3 in Fig. 4 yields higher resolutions of spin-forbidden transitions showing additional peaks which are not present in the solution spectrum. In the low energy triplet region five peaks can be localized,

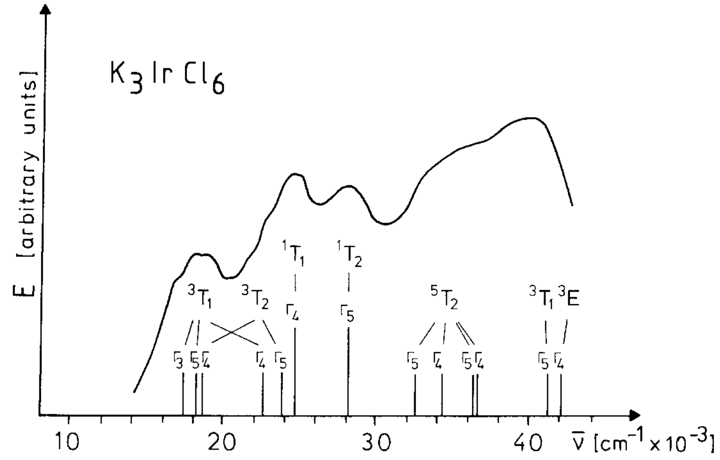

Fig. 4. Reflectance spectrum of K_3IrCl_6 at 90 K and energy levels as calculated from the parameter set of Table 2

one of them being the transition into $\Gamma_3(^3T_{1g})$ which according to our ligand field results is generally the lowest of the excited states and should give rise to only weak absorptions [1]. Comparing with the corresponding $RhCl_6^{3-}$ the degree of spin-orbit splitting of, e.g., the $^3T_{1g}$ state of $IrCl_6^{3-}$ (cf. Table 1) is about five times larger which, of course, favours the possibility of finding spin-orbit level components for heavier compounds. The large spin-orbit coupling also causes the exchange of interacting Γ_4 levels resulting from $^3T_1$ and $^3T_2$ in the energy scheme which is indicated by the eigenfunctions calculated from the ligand field perturbation. The ultraviolet spectrum of $IrCl_6^{3-}$ has two shoulders at about 33 400 and 36 300 cm^{-1} which are due to $^5T_{2g}$ spin-orbit level components. A ligand field calculation performed with the parameters of Table 2 yields states at 32 300 (Γ_5), 34 500 (Γ_4), 34 600 (Γ_3), 36 500 (Γ_5), 36 600 (Γ_4) and 36 600 cm^{-1} (Γ_1) which all result from $^5T_{2g}(t_{2g}^4e_g^2)$. Triplet states which arise from the same electron configuration are calculated to lie somewhat higher than 40 000 cm^{-1}. They may be identified with the maximum and 40 200 cm^{-1} close to the limit for recording reflectance spectra which is shifted to lower energy due to the strong increase in absorption expected from the charge transfer band at 48 500 cm^{-1} which is measured in solution [17].

For $Ir(SCN)_6^{3-}$ a spectrum is obtained showing band splittings similar to the chloro complex although the maxima are not as well resolved. The transition to the quintet states could not be observed due to superpositions by strong charge transfer absorptions at 32 800 and 35 700 cm^{-1} which occur at lower energy because of the smaller optical electronegativity of *S*-bonded thiocyanate ligands [20].

The *d-d* transitions of the iridiumhexaammino complex are located all in the ultraviolet and are poorly resolved due to absorption deficiencies resulting from scattered light in this region. Only one of the spin allowed transition is predicted in this region which is measured at 39 200 cm^{-1}, and from the spin-forbidden transitions only two peaks due to the first triplet are detected. The assignment proposed by the calculations is given in Table 1.

Although K_2PtCl_6 is apparently one of the most investigated platinum compounds, results concerning ligand field energy level diagrams are rather uncertain. The reason for this is that Pt(IV) complexes usually absorb at higher wave lengths, therefore, *d-d* transitions are for the most part covered by strong charge transfer bands [18, 21]. Since a comparison of model parameters for different Pt compounds hardly can be made, also approximate parameter values cannot be obtained. Only in the case of PtF_6^{2-} definite assignments for some of the transitions have been obtained [1]. For K_2PtCl_6 absorption peaks due to two-photon transitions have been assigned recently which would lead to a level scheme being at variance with earlier results [16].

In the 90 K reflectance spectrum of Fig. 5 a number of transitions are localized which have been unknown so far. Between 20 000 to 25 000 cm^{-1} three transitions due to triplet states can be distinguished and further in the ultraviolet four more *d-d*-bands due to triplet and singlet parent states are observed. The transition

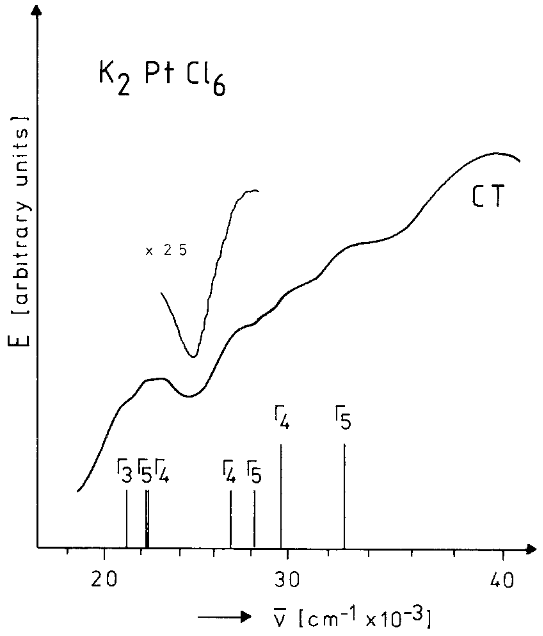

Fig. 5. Reflectance spectrum of K_2PtCl_6 at 90 K and spin-orbit energy levels as calculated from the parameter set of Table 2

into $\Gamma_5(^3T_{2g})$ which is assigned to the shoulder at 28 500 cm^{-1} gives rise to a relative strong peak in the two-photon spectrum [16]. For the singlet transitions, which are also expected in this spectral range, various possible assignments must be considered since no definite conclusions can be drawn from the reflectance spectrum concerning intensity relations. Therefore, ligand field calculations were used for obtaining an optimal fit of the experimental and theoretical energy levels considering all possible assignments. The conditions imposed on the set of parameter values to start with were $Dq > 2500$, $B < 400$ and $\zeta > 2500$ cm^{-1}. The cyclic adaptation procedure converged into a reasonable parameter set only for the assignment which is given in Table 1. The optimal parameters obtained from the calculations are listed in Table 2. The two singlet transitions are higher than 29 500 cm^{-1} which appropriately explains that these absorptions are covered in the solution spectrum by the strong charge transfer band. The relatively high absorptions for transitions into the Γ_4 and Γ_5 state resulting from the lower triplet states are explained by an intensity borrowing mechanism by virtue of spin-orbit coupling with singlet levels of the same symmetry lying very close in the energy level scheme. The calculated values for the model constants differ from an earlier estimate [16] in particular for the Racah parameters B and C. The spin-orbit coupling constant $\zeta = 3400$ cm^{-1} is slightly higher than that given in the literature ($\zeta = 3200$ cm^{-1} [16]), however, it is still lower than the corresponding value $\zeta = 3580$ cm^{-1} for PtF_6^{2-}[1] in accordance with the order predicted from the relativistic nephelauxetic effect for chloro compared to fluoro ligands [4].

At long wave lengths the transition into the lowest excited state $\Gamma_3(^3T_{1g})$ is also observed. An e_g progression found in the emission spectrum of K_2PtCl_6 [9] is an indication for a Jahn–Teller unstability of this state. This was also predicted from the PtF_6^{2-} luminescence spectrum which exhibits similar progressions for the pure compound spectrum and for materials doped in a host crystal as well [18]. In reflectance, the K_2PtCl_6 spectrum exhibits progressions only for some Γ_4 states; the vibrational structure of the lowest $\Gamma_3(^3T_{1g})$ state could not be resolved due to superpositions by transitions into other spin-orbit states which also arise from $^3T_{1g}$.

4.3. Vibrational structure

Some of the complex chloride spectra exhibit distinct vibrational structure. In the 90 K reflectance spectrum of K_3RhCl_6 a progression with $270 \pm 10\,cm^{-1}$ vibrational quanta has been found for the transition into $\Gamma_4(^1T_{1g})$ (cf. Fig. 3). Progressions are explained by vibronic coupling of electronic states to vibrational levels which gives rise to equilibrium changes or geometric distortions in the excited state compared to the ground state level. In the first order the forces acting on the nuclei of a molecule in the electronic state Γ along the coordinate Q_i are

$$F_i(\Gamma) = -\left\langle \Psi_\Gamma \left| \left(\frac{\delta V}{\delta Q_i}\right)_0 \right| \Psi_\Gamma \right\rangle$$

where V is the total potential energy operator of the system. This integral is finite if the symmetric direct product Γ^2 contains irreducible representations which are also found in the normal vibrational modes of the molecule. For octahedral complexes, Γ_3 states undergo symmetric changes of the nuclear framework by coupling with a_{1g} modes and distort by Jahn-Teller forces due to e_g active modes; in addition to these nuclear displacements, Γ_4 and Γ_5 states also distort by t_{2g} modes. Band analyses of octahedral complex compounds which were carried out so far identified only progressions in a_{1g} and Jahn-Teller e_g active modes [2, 8, 9, 22]; yet t_{2g} distorting modes have not been found to our knowledge.

Comparing the observed vibrational quanta obtained from the progressions in absorbance with corresponding Raman data one generally finds a reduction of vibrational quanta for corresponding modes in the excited electronic state relative to those of the ground state. For K_3RhCl_3 in aqueous solution Raman frequencies $\tilde{\nu} = 302$ and $280\,cm^{-1}$ are obtained for the $\tilde{\nu}_1(a_{1g})$ and $\tilde{\nu}_2(e_g)$ vibrational modes, respectively [23], which would compare with the $\tilde{\nu}^* = 270\,cm^{-1}$ mode derived from the reflectance spectrum yielding frequency factors $\beta = \tilde{\nu}^*/\tilde{\nu}$ of 0.89 or 0.96. Since these β-values are within the limits obtained for a_{1g} and e_g modes of other d^6 compounds [2, 24] an identification of the type of progression cannot be made on the basis of frequency changes. Therefore, we conclude that the excited $\Gamma_4(^1T_{1g})$ state can be symmetrically expanded and/or is subject to Jahn–Teller forces leading to tetragonal distortion induced by e_g vibrational modes (t_{2g} distortions would not give rise to this progression since their vibrational fundamental is expected lower than $270\,cm^{-1}$ [23]).

In the spectrum of K_2PtCl_6 two transitions $\Gamma_1(^1A_{1g}) \to \Gamma_4(^3T_{1g})$ and $\Gamma_4(^3T_{2g})$ are partially resolved showing vibrational progressions in 290 and 280 cm^{-1} ($\pm 10\ cm^{-1}$) quanta, respectively. With the Raman data $\tilde{\nu}_1(a_{1g}) = 343\ cm^{-1}$ and $\tilde{\nu}_2(e_g) = 319\ cm^{-1}$ [23] the frequency factors for the 290 cm^{-1} progression are $\beta_{a_{1g}} = 0.85$ and $\beta_{e_g} = 0.91$. Similar results can be evaluated from the PtF_6^{2-} spectrum which shows several progressions in absorption [1]. The progression in the Cs_2PtF_6 emission spectrum of the lowest excited state $\Gamma_3(^3T_{1g})$ was later explained by an e_g-Jahn–Teller active mode [8]. Since K_2PtCl_6 also emits out of this $\Gamma_3(^3T_{1g})$ state which is subject to a Jahn–Teller effect induced by an e_g mode [9] it is reasonable to assume that both the excited Γ_4 states originating from $^3T_{1g}$ and $^3T_{2g}$ undergo the same type of distortions. More reliable results on the vibronic coupling can, however, only be obtained if better resolved spectra would be available.

5. Conclusions

For determining excited states in the electronic energy level scheme measurements of low temperature reflectance spectra proves to be useful, in particular, when weak transitions are to be identified close to stronger ones. For the present purpose this technique is certainly superior to absorption spectra in solution and even to single crystal spectra if extinctions are so large that hardly any light can pass through the sample. An assignment of band peaks can be carried out using ligand field calculations and starting from parameter sets derived from the spectrochemical and nephelauxetic series which are varied within certain limits until the measured absorption peaks are fitted in an optimal way. Reflectance spectroscopy therefore is a convenient tool which should be considered as a supplement (not a replacement) to other spectroscopical methods for obtaining electronic and vibrational structures.

Acknowledgement. The authors are grateful to the Fonds der Chemischen Industrie, Frankfurt/Main, for financial support.

References

1. Patterson, H. H., DeBerry, W. J., Byrne, J. E., Hsu, M. T., LoMenzo, J. A.: Inorg. Chem. **16**, 1698 (1977)
2. Wilson, R. B., Solomon, E. I.: J. Am. Chem. Soc. **102**, 4085 (1980)
3. Komi, Y., Urushiyama, A.: Bull. Chem. Soc. Jpn. **53**, 980 (1980)
4. Sugano, S., Tanabe, Y., Kamimura, H.: Multiplets of Transition Metal Ions in Crystals. New York: Academic Press 1970
5. Kortüm, G.: Reflexionsspektroskopie. Berlin: Springer-Verlag 1969
6. Jørgensen, C. K.: Absorption Spectra and Chemical Bonding in Complexes. Oxford: Pergamon Press 1962
7. Mazur, U., Hipps, K. W.: J. Phys. Chem. **84**, 194 (1980)
8. Laurent, M. P., Patterson, H. H., Pike, W., Engstrom, H.: Inorg. Chem. **20**, 372 (1981)
9. Eyring, G., Schmidtke, H.-H.: Ber. Bunsenges. Phys. Chem. **85**, 597 (1981)
10. Jørgensen, S. M.: J. prakt. Chem. **44**, 48 (1891)

11. Schmidtke, H.-H.: Z. Phys. Chem. N. F. **38**, 170 (1963), **40**, 96 (1964)
12. Watt, G. W., Helvenston, E. P., Sharif, L. E.: J. Inorg. Nucl. Chem. **24**, 1067 (1962)
13. Schmidtke, H.-H.: Helv. Chim. Acta **50**, 1631 (1967)
14. Tanabe, Y., Sugano, S.: J. Phys. Soc. Jpn. **9**, 753 (1954)
15. Schroeder, K. A.: J. Chem. Phys. **37**, 2553 (1962)
16. Kozikowski, B. A., Keiderling, T. A.: Chem. Phys. Letters **86**, 463 (1982)
17. Jørgensen, C. K.: Mol. Phys. **2**, 309 (1959)
18. Jørgensen, C. K.: Acta Chem. Scand. **10,** 500, 518 (1956)
19. Schmidtke, H.-H.: J. Mol. Spectr. **11**, 483 (1963)
20. Schmidtke, H.-H.: Ber. Bunsenges. Phys. Chem. **71**, 1138 (1967)
21. Swihart, D. L., Mason, W. R.: Inorg. Chem. **9**, 1749 (1970)
22. Wernicke, R., Kupka, H., Ensslin, W., Schmidtke, H.-H.: Chem. Phys. **47**, 235 (1980)
23. Bosworth, Y. M., Clark, R. J. H.: J. Chem. Soc. Dalton 1749 (1974)
24. Urushiyama, A., Kupka, H., Degen, J., Schmidtke, H.-H.: Chem. Phys. **67**, 65 (1982)

Received June 22, 1983