

Vibrational Structure of a Spin-forbidden Band of Hexachlororheniate(IV)

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The absorption spectra of the complexes of elements in the second and third transition group can also be described by the crystal field theory, as will be shown later. These complexes are characterized by higher values of $(E_1 - E_2)$ than in the first transition group^{1,2}, as shown by Schmidt³ in the special case of trivalent molybdenum compared to trivalent chromium. Another system with three d-electrons is tetravalent rhenium, of which the hexachloro and hexabromo complexes, ReCl_6^{--} and ReBr_6^{--} , will be discussed here.

Maun and Davidson⁴ studied solutions of rhenium(IV) complexes and found two narrow, weak bands in the red wavelength region. These are undoubtedly due to transitions from the ground-state 4T_2 to the states 2T_3 , 2T_4 or 2T_5 of lower multiplicity, having the same strong crystal field electron configuration². They are found at nearly the same wave number, $\sim 14\,500\text{ cm}^{-1}$, as the similar bands of molybdenum(III)³ and chromium(III)⁵. The stronger bands, due to transitions to 4T_1 and 4T_2 , are probably represented in ReCl_6^{--} by the shoulder at $27\,000\text{ cm}^{-1}$ found⁶ at the very high "electron transfer" band in the ultraviolet. The K_2ReCl_6 was prepared according to Hurd and Reinders⁷ and measured in 10 cm cells on a Cary spectrophotometer, using a 0.02 M solution in 10 M HCl. One of the two bands in the red shows a considerable fine-structure of equidistant bands with a half width $\sim 80\text{ cm}^{-1}$. Fig. 1 shows the spectrum, and Table 1 the observed maxima of the first band group, giving the wave numbers ν_n and the molar extinction coefficients ϵ_n subtracted the constant background. The maxima are interpreted as a vibrational structure with a characteristic wave number $\nu_n = 150\text{ cm}^{-1}$, and values of Δn , the change in vibrational quantum number n , which are supported by the Boltzmann distribution of the levels at room temperature. If Gaussian analysis⁸ is applied to the bands, the maxima of $\Delta n = -1$ and 2 are displaced to $13\,880$

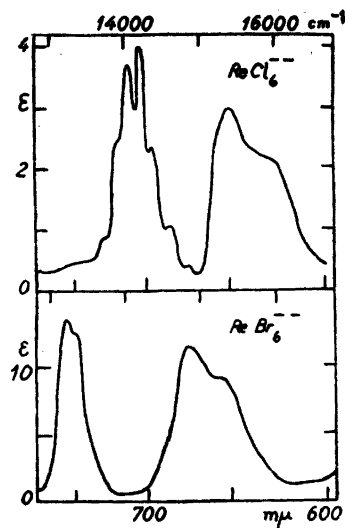


Fig. 1.

and $14\,350\text{ cm}^{-1}$, respectively, giving more regular wave number differences.

K_2ReBr_6 was prepared by boiling 0.5 g KReO_4 and 1 g KI with 20 ml 60 wt. % HBr for 30 minutes. The dark red crystals dissolved in 2 M HBr gave the spectrum shown in Fig. 1. The only trace of vibrational structure of the first band group is the distance 100 cm^{-1} between the two adjacent maxima. If the force constant discussed below is equal in ReBr_6^{--} and ReCl_6^{--} , this change of ν_c is exactly predicted from the mass of the bromide ion compared to the chloride ion. The two red band groups are displaced $\sim 800\text{ cm}^{-1}$ towards lower wave numbers. Besides this, ReBr_6^{--} gives a very complicated "electron

Table 1. The first band group of ReCl_6^{--} .

| ν_n in cm^{-1} | ϵ_n | Δn |
|-----------------------------|--------------|------------|
| 13 730 | 0.6 | -2 |
| 13 900 | 2.2 | -1 |
| 14 030 | 3.4 | 0 |
| 14 180 | 3.7 | 1 |
| 14 330 | 2.1 | 2 |
| 14 510 | 0.5 | 3 |
| 14 680 | 0.1 | 4 |

transfer" spectrum with shoulders and bands at 23 900, 26 400, 28 400, 30 800, 33 200 and 39 400 cm^{-1} , while the low shoulder at 26 900 cm^{-1} is probably due to crystal field transitions.

Schultz⁹ attempted to obtain force constants from Raman spectra and infra-red measurements, but ν_c of ReCl_6^{3-} seems to be the first vibrational wave number, obtained from the visible spectrum of an octahedral complex. The most remarkable feature is its low value compared to ν_c of the tetrahedral MnO_4^- and linear UO_2^{2+} , which are $\sim 750 \text{ cm}^{-1}$. The force constant k_1 is defined by $k_1 = 4\pi^2 m c^2 \nu_c^2$, m being the reduced mass of the oscillating ligand. In ReCl_6^{3-} k_1 is only $4.8 \cdot 10^4 \text{ erg/cm}^2$, corresponding to a maximal deviation x from the equilibrium position of the ligand = 0.079 Å, 0.137 Å and 0.177 Å, respectively, for $n = 0, 1$ and 2 of the harmonic oscillator. Thus, the potential hole of the ligand must have quite a flat bottom, while the absolute depth must be considerable (at least $50\,000 \text{ cm}^{-1}$). k_1 can only be relatively small, when the repulsing forces from the closed shells of Re^{+4} depend on a not very high power of the distance r from the nucleus, *i. e.* the bonding is distinctly electrostatic, while the complex is nevertheless robust⁴.

The empirical fact¹ that the halfwidths of the ordinary broad bands of the transition group complexes are roughly proportional to the change of their wave number as a function of the crystal field strength, has been explained by Orgel¹⁰ as an effect of the different equilibria positions of the ligands in the excited and the ground-state. Fig. 2 shows that simultaneous excitation of much higher vibrational states of the excited electronic state occurs when the ligand remains in the range of r , governed by the vibrations at room temperature ($kT = 210 \text{ cm}^{-1}$) in the electronic ground-state. Since the halfwidths are nearly as large towards lower as towards higher wave numbers, and since no absorption limit is observed at even very low wave numbers of a given band, the most probable transitions must go to highly excited vibrational states. But if ν_c hardly can be larger than 200 cm^{-1} , this type of excitation necessitates values of $\Delta n \sim 10$ and of $x \sim 0.4 \text{ Å}$, which seems improbable, even if somewhat lower values are possible, due to anharmonic parts of the potential curve. In the author's opinion, the broadening might also be connected with Heisenberg's uncertainty principle acting on the energy

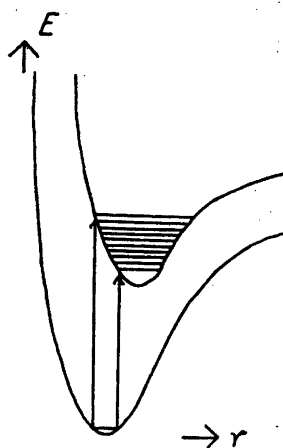


Fig. 2.

transfer from the excited state to the mechanical vibrations of the surrounding molecules, as pointed out in the case of uranyl nitrate by Stepanov¹¹. If the energy is propagated with the velocity of 10^8 cm/sec . (somewhat more than of ordinary sound), it takes 10^{-14} sec . for the distance 1 Å , corresponding to an uncertainty of the wavenumber $\Delta\nu = 3\,300 \text{ cm}^{-1}$ (because $\Delta\nu \cdot \Delta t \cdot c \sim 1$). In this theory the narrow bands (*e. g.* of chromium(III) in the ruby or of europium(III) and terbium(III) salts) have larger uncertainties in time than 10^{-13} sec ., corresponding to larger tendency of fluorescence. The explanation by Orgel¹⁰ can be extended by the uncertainty principle by assuming the lifetime of the excited electronic state to be only a half period or less of vibration. When the ligand collides with the solvent molecules $\sim 10^{-14} \text{ sec}$. after the excitation of the central ion, the energy is totally degraded to mechanical vibrations. This is only the case, when the equilibrium positions are different, corresponding to a different distribution of γ_s - and γ_a -electrons¹⁰. The difference between the equilibrium values of r needs only to be 2–5 %, which can be calculated by treating the crystal field perturbations as a part of the repulsing potential, *e. g.* proportional to r^{-5} .

Acknowledgments. I am very much indebted to Professor J. Bjerrum for his continued interest in the work, and to Dr. L. E. Orgel for the opportunity to see manuscripts previous

to the publication. Further, I thank Professor A. Tovborg Jensen for some grams of potassium perrhenate, and Miss Bodil Friis for assistance with the preparations.

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Received March 18, 1955.

Mixed Monolayers of Isodextropimaric and Normal Long Chain Fatty Acids

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In a previous study¹ it was found that the average area per molecule in fatty acid monolayers containing different amounts of isodextropimaric acid (IdP) was higher than that expected if the mixtures behaved ideally. The work described in this paper, which is a continuation of the earlier investigation, has yielded data for mixed monolayers with high ratios of IdP to fatty acids. The data will be compared with theoretical deductions based on an assumed structure for the mixed monolayers.

The variation of the average area per molecule measured at a surface pressure of 1.5 dynes per cm with the composition of the IdP-fatty acid monolayers is shown in Fig. 1. The experimental details have

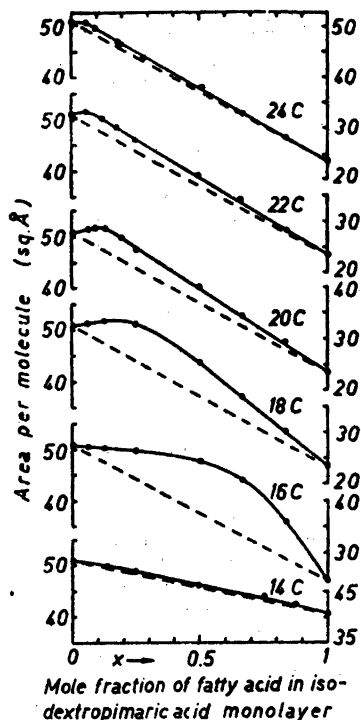


Fig. 1. Molecular areas of isodextropimaric acid monolayers containing normal fatty acids (C_{14} — C_{24}). Surface pressure, 1.5 dynes/cm. Substrate: dilute HCl (pH 3). 20° C.

been described in the earlier paper¹. Except for the mixtures containing myristic acid (Curve C 14), which are of the expanded type at room temperatures, positive deviations from the ideal behaviour ($A_{\text{mixt.}} = x_1 A_1 + x_2 A_2$, the dotted lines) are evident in the curves. The expansions are greatest for the layers containing palmitic acid (Curve C 16) and decrease as the chain length of the fatty acid increases. At the same time, the maximal expansion shifts to lower fatty acid contents.

Owing to the different dimensions of the molecules of the components, the hydrocarbon part of the mixed monolayer may be considered as being composed of two layers, an upper layer formed by the parts of the flexible fatty acid chains that project above the IdP-molecules and a lower densely packed layer comprising bulky inflexible IdP-molecules and the lower parts of the