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Far-Infrared Spectra and Vibrational Force Constants of the Ions $AuCl_4^-$, $AuBr_4^-$, and $PtCl_4^{2-}$

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The infrared spectra in the region 80–400 cm.$^{-1}$ of M_2PtCl_4 (M = K, Rb, Cs) and $MAuX_4$ (M = Rb, Cs; X = Cl, Br) have been measured. The two E_u vibrations were observed in all the spectra and the A_{2u} vibration was also observed in the spectra of the ions $PtCl_4^{2-}$ and $AuCl_4^-$. The force constants have been calculated by both general valence force field and Urey-Bradley force field methods.

Introduction

The far-infrared spectra of tetrahedral halo complexes have recently been studied by several authors and their general features are well understood.[1-3] The far-infrared spectra of square-planar tetrahalo complexes have been studied much less. Stammreich, *et al.*,[4] recently reported the Raman spectra of $AuCl_4^-$, $AuBr_4^-$, and $PtCl_4^{2-}$ in solution and Adams, *et al.*,[5] the far-infrared spectra of K_2PtCl_4 and $KAuBr_4 \cdot 2H_2O$. A complete vibrational assignment has not yet been achieved.

In view of the interest in this class of molecules we have studied the far-infrared spectra of the compounds M_2PtCl_4 (M = K, Rb, Cs), $MAuCl_4$, and $MAuBr_4$ (M = Rb, Cs) in order to obtain a criterion for the identification of lattice vibrations and in order to be able to base a force constant calculation on a complete vibrational assignment.

Experimental

The compounds examined were prepared by standard methods. The far-infrared spectra between 400 and 80 cm.$^{-1}$ were measured by means of a double-beam Perkin-Elmer Model 301 spectrograph. Nujol mulls and pressed polyethylene disks were employed; the spectra obtained were identical in both cases.

Results

Vibrational Assignment.—A square-planar molecule of the type MX_4 has D_{4h} symmetry and the nine normal modes of vibration are classified in this point group as follows ($A_{1g} + A_{2u} + B_{1g} + B_{1u} + B_{2g} + 2E_u$). Of these, only the E_u and A_{2u} modes will be infrared active in the isolated molecule. The selection rules applicable to the molecules arrayed in a crystal lattice, however, are determined by the molecular symmetry, the site symmetry, the factor group symmetry, and the correlation between them. Crystals of potassium tetrachloroplatinate(II) belong to the D_{4h}^1 space group; there is one $PtCl_4^{2-}$ ion per unit cell, at a site of D_{4h} symmetry. Therefore the selection rules governing the $PtCl_4^{2-}$ ion in the solid are the same as they would be for the free gaseous ion. We shall consider this most fortunate case first and interpret the spectra of the other compounds by correlation with the normal frequencies of the $PtCl_4^{2-}$ ion.

The far-infrared spectrum of K_2PtCl_4 exhibits four bands at 325, 193, 175, and 106 cm.$^{-1}$, whereas only three infrared-active modes are expected. The first three are affected very little by the replacement of the potassium ion by the heavier ions rubidium or cesium, while in the spectrum of Rb_2PtCl_4 the last band is found at 82 cm.$^{-1}$ and in the spectrum of Cs_2PtCl_4 it is below 80 cm.$^{-1}$. The mass-dependent shift of this band toward lower frequencies strongly indicates that it should be assigned to a lattice mode. The band at 325 cm.$^{-1}$ is undoubtedly the Pt–Cl E_u stretching mode.

Two deformation vibrations are expected to be active in the infrared, one species E_u and the other A_{2u}. Since the deformation in the plane likely has a higher frequency than that out of the plane, we assign the band at 193 cm.$^{-1}$ to the vibration of the E_u species and that at 175 cm.$^{-1}$ to the vibration of the A_{2u} species. Slightly lower frequencies are observed for these modes in Rb_2PtCl_4 and Cs_2PtCl_4, as shown in Table I.

In the spectra of the $AuCl_4^-$ and $AuBr_4^-$ ions (Table I) there is clear evidence of site symmetry splitting of the E_u fundamentals; ν_6 is split into two components in $CsAuCl_4$ and $RbAuBr_4$ and ν_7 is split in the spectra of $CsAuCl_4$, $RbAuCl_4$, and $CsAuBr_4$. The assignment for these ions follows directly from that of the $PtCl_4^{2-}$ ion and is shown in Table I. ν_2 (A_{2u}) for the $AuBr_4^-$ ion has not been detected; it probably lies below 80 cm.$^{-1}$.

Finally, a weak band has been found at 187 cm.$^{-1}$ in the spectrum of $CsAuBr_4$, which cannot be reasonably explained as a combination band. It is most probably the ν_5 (B_{2g}) infrared-inactive mode observed in the Raman spectrum at 196 cm.$^{-1}$. The 9 cm.$^{-1}$ difference between the Raman and infrared values is probably due to the fact that the measurements were made on different phases.

The assignments reported in Table I for the ions $PtCl_4^{2-}$ and $AuBr_4^-$ differ in some respects from those of Adams, *et al.*[5]

The frequencies of the cesium salts were used in the force constant calculations, as the interactions be-

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[1] R. J. H. Clark and T. M. Dunn, *J. Chem. Soc.*, 1198 (1963).

[2] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *ibid.*, 2189 (1963).

[3] A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).

[4] H. Stammreich and R. Forneris, *Spectrochim. Acta*, **16**, 363 (1960).

[5] A. M. Adams and H. A. Gebbie, *ibid.*, **19**, 925 (1963).

TABLE I

INFRARED ABSORPTION FREQUENCIES (CM.$^{-1}$) AND VIBRATIONAL ASSIGNMENT

$CsAuCl_4$	$RbAuCl_4$	$CsAuBr_4$	$RbAuBr_4$	Cs_2PtCl_4	Rb_2PtCl_4	K_2PtCl_4	Assignment
362 sh	358 vs	252 vs	255 vs	316 vs	320 vs	325 vs	ν_6 (E_u)
365 vs			250 vs				
		187 w					ν_5 (B_{2g})
179 vw	175 vw	108 sh	100 m	185 m	190 m	193 m	ν_7 (E_u)
168 vw	171 vw	100 m					
143 m	144 m			160 m	167 m	175 m	ν_2 (A_{2u})
				<80	82 s	106 m	Lattice vib.

tween neighboring ions are expected to be the weakest with the largest cation. Where a band is split the average frequency has been used in the calculations.

Force Constant Calculations.—Stammreich, *et al.*, recently reported[4] a force constant calculation based on the Raman frequencies for the square-planar ions $AuCl_4^-$, $AuBr_4^-$, and $PtCl_4^{2-}$. The potential function employed by Stammreich is derived from Maccoll's[6] force field assuming that $k_{\alpha\alpha} = k'_{\alpha\alpha} = 0$ and $k_{rr} = k'_{rr}$. We adopted the numerical values of k_r, k_α, and k_{rr} obtained by Stammreich to calculate the frequencies of the E_μ modes. The values obtained for ν_6 and ν_7 are 384 and 191 cm.$^{-1}$ for $AuCl_4^-$, 278 and 119 cm.$^{-1}$ for $AuBr_4^-$, and 372 and 183 cm.$^{-1}$ for $PtCl_4^{2-}$. The poor agreement with the observed frequencies shows that Stammreich's force field is inadequate to describe the in-plane vibrational modes of these ions and that further calculations are needed. We have therefore performed a new force constant calculation using both a valence force field and a Urey–Bradley force field to fit the five in-plane vibrational frequencies.

With a general valence force field the in-plane part of the potential energy of a square-planar system MX_4 is given by

$$2V = \Sigma f_r(\Delta r_i)^2 + \Sigma f_\alpha(r_0\Delta\alpha_{ij})^2 + 2\Sigma f_{rr}\Delta r_i\Delta r_j + 2\Sigma f'_{rr}\Delta r_i\Delta r_k + 2\Sigma f_{\alpha\alpha}(r_0\Delta\alpha_{ij})(r_0\Sigma\alpha_{jk}) + 2\Sigma f'_{\alpha\alpha}(r_0\Delta\alpha_{ij})(r_0\Delta\alpha_{kl}) + 2\Sigma f_{r\alpha}r_i(r_0\Delta\alpha_{ij}) + 2\Sigma f'_r\Delta r_i(r_0\Delta\alpha_{jk})$$

where r_i is the metal–halogen bond length with equilibrium value r_0, α_{ij} the angle between two adjacent bonds r_i and r_j, f_r and f_α the diagonal stretching and bending force constants, f_{rr} and f'_{rr} (or $f_{\alpha\alpha}$ and $f'_{\alpha\alpha}$) the interaction terms between adjacent or opposed bonds (or angles), and $f_{r\alpha}$ and $f'_{r\alpha}$ the interaction terms between a bond and an angle adjacent or opposed, respectively.

Since we have only five experimental frequencies some assumptions are necessary. Setting $f'_{r\alpha} = f_{\alpha\alpha} = f'_{\alpha\alpha} = 0$ leads to a set of complex force constants. We then set $f_{r\alpha} = f'_{r\alpha} = f'_{\alpha\alpha} = 0$; this assumption leads to two possible sets of force constants, only one of which is physically acceptable as shown in Table II. The definition of the bending force constant given in Table II is different from that of Maccoll; ours is defined as the XMX angle deformation force constant, whereas Maccoll's refers to the displacement of an MX bond from its equilibrium position.

TABLE II

VALENCE FORCE CONSTANTS[a] (MDYNES/Å.)

Ion	f_r	f_{rr}	f'_{rr}	f_α	$f_{\alpha\alpha}$
$AuCl_4^-$	2.10	0.08	0.22	0.25	0.05
$AuBr_4^-$	1.76	0.08	0.19	0.17	0.02
$PtCl_4^{2-}$	1.78	0.10	0.33	0.29	0.08

[a] f_r = stretching force constant of M–X bonds; f_{rr} = interaction force constant between two adjacent M–X bonds; f'_{rr} = interaction force constant between two opposite M–X bonds; f_α = bending force constants of X–M–X angles; $f_{\alpha\alpha}$ = interaction force constant between two adjacent X–M–X angles.

It is interesting to observe that the interaction term between two MX bonds is much larger when the two bonds make an angle of 180° than when they are at 90°. The assumption made by Stammreich and Forneris that $f_{rr} = f'_{rr}$ evidently appears to be inadequate.

The results of our calculations using a Urey–Bradley force field in which $F' = -0.1F$ are shown in Tables III and IV. The agreement between the observed and calculated frequencies is rather poor for $AuCl_4^-$ and $PtCl_4^{2-}$ and is acceptable only for $AuBr_4^-$. It is evident that the Urey–Bradley force field is a bad approximation for these ions since interactions between opposite bonds do not appear in the Urey–Bradley potential, whereas interactions of this kind are important as shown by the general valence force field results.

TABLE III

UREY–BRADLEY FORCE CONSTANTS[a] (MDYNES/Å.)

Ion	K	H	F
$AuCl_4^-$	2.021	0.087	0.110
$AuBr_4^-$	1.678	0.028	0.200
$PtCl_4^{2-}$	1.644	0.042	0.237

[a] K = stretching force constant of M–X bonds; H = bending force constant of K–M–X angles; F = repulsion force constant between X · · · X.

TABLE IV

OBSERVED AND CALCULATED UREY–BRADLEY FORCE FIELD FREQUENCIES (CM.$^{-1}$)

	$AuCl_4^-$		$AuBr_4^-$		$PtCl_4^{2-}$	
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.
ν_1 A_{1g}	347	339	212	210	335	318
ν_3 B_{1g}	171	186	102	109	164	184
ν_5 B_{2g}	324	311	196	187	304	281
ν_6 E_u	356	373	252	260	316	343
ν_7 E_u	173	147	100	92	185	144

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(6) A. Maccoll, *J. Proc. Roy. Soc. N.S. Wales*, **77**, 130 (1944).