

# A Study of Anionic Motions in Solid Rubidium and Cesium Tetrachloroaurates(III) by Measuring the Temperature Dependence of Chlorine Nuclear Quadrupolar Relaxation Times

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Z. Naturforsch. **44a**, 125–130 (1989); received December 10, 1988

The temperature dependences of  $^{35}\text{Cl}$  NQR frequencies and  $^{35}\text{Cl}$  nuclear quadrupolar relaxation times  $T_{1Q}$  and  $T_{2Q}$  were determined above 82 K for  $\text{Rb}[\text{AuCl}_4]$  and  $\text{Cs}[\text{AuCl}_4]$  up to ca. 340 and 320 K, respectively. Below these temperatures two  $^{35}\text{Cl}$  NQR frequencies were observed for each complex whereas no resonance could be detected above the respective temperatures. For both complexes,  $T_{1Q}$  observed below ca. 270 K was interpreted as mainly determined by the rotary lattice vibration around the pseudo- $C_4(C'_4)$  axis and each Cl-Au-Cl diagonal axis of the square planar complex anion, whereas  $T_{1Q}$  observed above ca. 270 K was definitely shown to be determined through the reorientation of the anions about their  $C'_4$  axis. The activation energies for the  $C'_4$  reorientation of the anions was evaluated to be 71 and 53  $\text{kJ mol}^{-1}$  for the rubidium and cesium salts, respectively. The anionic dynamics are discussed by assuming the motion of the anions within and out of the  $C_4$  potential wells at lower and higher temperatures, respectively.

## 1. Introduction

Previously, we investigated the temperature variation of the chlorine nuclear quadrupolar spin-lattice relaxation time  $T_{1Q}$  of pyridinium tetrachloroaurate(III),  $\text{pyH}[\text{AuCl}_4]$ , and found that the pseudohexad ( $C'_6$ ) reorientation of  $\text{pyH}^+$  ions about their  $C'_6$  axes and the pseudotetrad ( $C'_4$ ) reorientation of the complex anions about their  $C'_4$  axes play an important role for the determination of  $T_{1Q}$  in the temperature regions below ca. 350 K and above 360 K, respectively [1]. The activation energy for the  $C'_4$  anionic reorientation was evaluated as 67  $\text{kJ mol}^{-1}$ . For this complex, the chlorine quadrupolar relaxation resulting from lattice vibrations involving the complex anions was not detectable. The temperature dependence of chlorine  $T_{1Q}$  has also been observed for guanidinium tetrachloroaurate(III),  $\text{guH}[\text{AuCl}_4]$  [2]. In this complex, it was concluded that the  $C'_4$  reorientation and the rotary lattice vibration of the complex anions are responsible for the determination of the chlorine  $T_{1Q}$  in the high- and low-temperature regions, respectively.

ly. The same activation energy for the  $C'_4$  reorientation of the anions as that of  $\text{pyH}[\text{AuCl}_4]$  was accidentally obtained for this complex.

For the above complexes one can assume that the hindrance barrier to the  $C'_4$  reorientation of the complex anion arises mainly from N–H...Cl type H-bond formation between the cations and the complex anion. To definitely clarify the above point and also to investigate the ionic dynamics of the square planar  $[\text{AuCl}_4]^-$  anions in the crystal, the present study has been carried out for solid  $\text{Rb}[\text{AuCl}_4]$  and  $\text{Cs}[\text{AuCl}_4]$  by measuring the temperature dependence of  $^{35}\text{Cl}$  NQR frequencies and the chlorine  $T_{1Q}$  as well as the chlorine spin-spin relaxation time  $T_{2Q}$ .

## 2. Experimental

A homemade pulsed NQR spectrometer already described [3, 4] was employed for the observation of the spin-echo signals arising from  $^{35}\text{Cl}$  nuclei in the samples.  $T_{1Q}$  and  $T_{2Q}$  were measured by use of  $\pi/2-\tau-\pi/2-\tau_e-\pi$  and  $\pi/2-\tau-\pi$  pulse sequences, respectively, where the spacing time  $\tau$  was varied and  $\tau_e$  was set constant at ca. 150  $\mu\text{s}$  throughout the measurements. The echo amplitude decreased exponentially in the

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$T_{1Q}$  measurements. However, for  $T_{2Q}$  it evolved as a Gaussian-type function in a region of  $\tau < 1$  ms. For  $\tau > 1$  ms the decay was much slower than Gaussian-type. The values of  $T_{2Q}$  were estimated from the Gaussian-type decay signals by fitting their initial portion to the relation

$$M = M_0 \exp \{ -(2\tau/T_{2Q})^2 \}. \quad (1)$$

Here,  $M$  and  $M_0$  indicate the amplitude of echo signals for the spacing time  $\tau$  and  $\tau = 0$ , respectively. The sample temperature was controlled within  $\pm 0.5$  K by employing a temperature controller described elsewhere [3], and was determined by use of a copper – constantan thermocouple. The observed temperatures were estimated to be accurate within  $\pm 1$  K. Fourier transformed (FT) NQR spectra were calculated with a usual computation program [5] from 8192 accumulated echo signals at maximum.

The samples were prepared by adding rubidium or cesium chlorides to a hot hydrochloric acid solution of tetrachloroauric acid and slowly cooling the solution [6]. The yellow needle-shaped crystals obtained for both complexes were filtered off and dried in a desiccator. For the cesium salt, the crystallization water was completely removed by pumping at ca. 80 °C. To obtain good signal-to-noise ratios for the NQR spin-echo signals, the crystals thus obtained were annealed at 80 °C for 20 h. The samples were identified by observing the NQR signals of  $^{35}\text{Cl}$  nuclei at the frequencies reported [7].

### 3. Results

#### Chlorine NQR Frequencies

The temperature dependence of the  $^{35}\text{Cl}$  NQR frequencies determined from the spin-echo signals of  $\text{Rb}[\text{AuCl}_4]$  and  $\text{Cs}[\text{AuCl}_4]$  is shown in Fig. 1, and the values evaluated at various temperatures are given in Table 1. The resonance frequencies observed agree well with those reported by Sasane *et al.* [7].

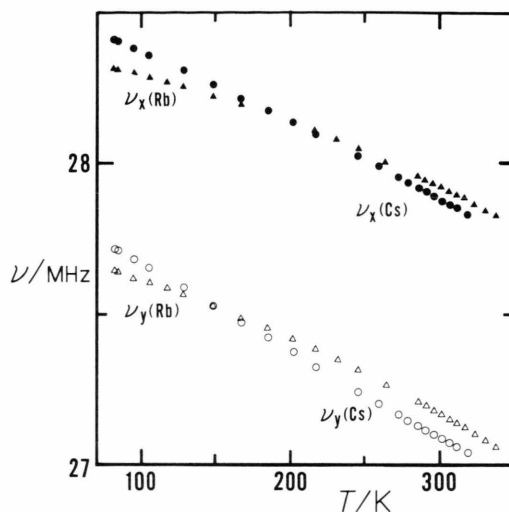


Fig. 1. Temperature dependences of the  $^{35}\text{Cl}$  NQR frequencies  $\nu_x(\text{Rb})$  ( $\blacktriangle$ ) and  $\nu_y(\text{Rb})$  ( $\triangle$ ) determined for  $\text{Rb}[\text{AuCl}_4]$ , and  $\nu_x(\text{Cs})$  ( $\bullet$ ) and  $\nu_y(\text{Cs})$  ( $\circ$ ) for  $\text{Cs}[\text{AuCl}_4]$ .

$\text{Rb}[\text{AuCl}_4]$				$\text{Cs}[\text{AuCl}_4]$			
$T/\text{K}$	$\nu/\text{MHz}$	$T_{1Q}/\text{ms}$	$T_{2Q}/\text{ms}^a$	$T/\text{K}$	$\nu/\text{MHz}$	$T_{1Q}/\text{ms}$	$T_{2Q}/\text{ms}^a$
82	28.316	670	1.7	82	28.411	265	—
	27.645	840	1.6		27.717	345	—
118	28.270	290	1.7	129	28.307	98	1.6
	27.587	360	1.6		27.590	114	1.6
129	28.255	250	—	186	28.175	43	1.6
	27.567	320	—		27.423	52	1.7
149	28.224	180	1.6	246	28.025	20	1.8
	27.528	230	1.7		27.244	23	1.7
246	28.049	46	—	273	27.955	7.2	1.5
	27.315	56	—		27.168	6.9	1.6
301	27.921	6.8	—	286	27.920	2.8	1.2
	27.169	6.6	—		27.133	3.0	1.3
306	27.908	4.1	1.4	296	27.894	1.6	0.95
	27.155	4.3	1.4		27.103	1.7	0.87
323	27.864	0.92	0.95	311	27.855	0.42	0.54
	27.104	0.94	0.97		27.063	0.50	0.52
330	27.844	0.57	0.66				
	27.082	0.54	0.61				

Table 1.  $^{35}\text{Cl}$  NQR frequencies  $\nu$ , spin-lattice relaxation times  $T_{1Q}$ , and spin-spin relaxation times  $T_{2Q}$  observed for  $\text{Rb}[\text{AuCl}_4]$  and  $\text{Cs}[\text{AuCl}_4]$  at several temperatures.

<sup>a</sup> Dashes indicate no measurements carried out.

Two resonance lines of the  $^{35}\text{Cl}$  nuclei were observed for each complex. Hereafter they are denoted as  $\nu_x(\text{Rb})$  and  $\nu_y(\text{Rb})$  for the high- and low-frequency lines of  $\text{Rb}[\text{AuCl}_4]$ , respectively, and analogously as  $\nu_x(\text{Cs})$  and  $\nu_y(\text{Cs})$  for the  $\text{Cs}[\text{AuCl}_4]$  lines. For both complexes the temperature dependence of the  $\nu_y$  lines was slightly steeper than that of the respective  $\nu_x$  lines. The temperature dependence of  $\nu_x(\text{Cs})$  and  $\nu_y(\text{Cs})$  was steeper than that of  $\nu_x(\text{Rb})$  and  $\nu_y(\text{Rb})$ . Above room temperature the echo signals of both complexes became gradually weak and faded out at ca. 340 and 320 K for both lines of  $\text{Rb}[\text{AuCl}_4]$  and  $\text{Cs}[\text{AuCl}_4]$ , respectively.

#### Chlorine $T_{1Q}$ and $T_{2Q}$

The temperature dependence of chlorine  $T_{1Q}$  and  $T_{2Q}$  for two resonance lines of both complexes observed between ca. 80 and 340 K are shown in Fig. 2, and the numerical values obtained at some temperatures are given in Table 1.

When the samples were warmed from 82 K to ca. 270 K, the  $^{35}\text{Cl}$   $T_{1Q}$  values of both complexes decreased gradually with increasing temperature and can be expressed by

$$T_{1Q} \propto T^{-n}. \quad (2)$$

The exponents  $n$  for the  $\nu_x(\text{Rb})$ ,  $\nu_y(\text{Rb})$ ,  $\nu_x(\text{Cs})$ , and  $\nu_y(\text{Cs})$  lines were 2.0, 2.3, 2.0, and 2.3 ( $\pm 0.2$ ), respectively.

When the temperature increased furthermore from ca. 270 K, the  $\nu_x$  and  $\nu_y$  lines of each complex gave almost the same  $T_{1Q}$  at a given temperature, and all the  $T_{1Q}$  decreased rapidly. The temperature dependence of  $T_{1Q}$  for the two lines of each complex above ca. 270 K can be expressed as

$$\log T_{1Q} \propto T^{-1}. \quad (3)$$

The values of  $^{35}\text{Cl}$   $T_{2Q}$  for all resonance lines studied were temperature independent between ca. 80 and 280 K, having the same value of 1.7 ms as indicated in Figure 2. Above ca. 280 K, the  $T_{2Q}$  values observed for the respective complexes decreased rapidly with increasing temperature, and the  $T_{1Q}$  and  $T_{2Q}$  values became almost the same at a given temperature above ca. 310 K.

#### FT NQR Spectra

Sasane *et al.* [7] reported that the resonance linewidth of  $\nu_y(\text{Cs})$  was broader than that of  $\nu_x(\text{Cs})$  and

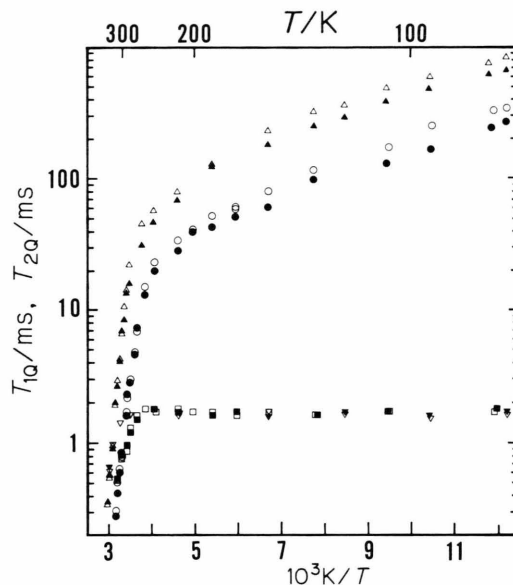


Fig. 2. The temperature dependences of nuclear quadrupole spin-lattice relaxation times  $T_{1Q}$  and spin-spin relaxation times  $T_{2Q}$  for the  $^{35}\text{Cl}$  NQR lines  $\nu_x(\text{Rb})$  and  $\nu_y(\text{Rb})$  of  $\text{Rb}[\text{AuCl}_4]$ , and  $\nu_x(\text{Cs})$  and  $\nu_y(\text{Cs})$  of  $\text{Cs}[\text{AuCl}_4]$ . The  $T_{1Q}$  values are indicated by  $\blacktriangle$ ,  $\triangle$ ,  $\bullet$ , and  $\circ$  for  $\nu_x(\text{Rb})$ ,  $\nu_y(\text{Rb})$ ,  $\nu_x(\text{Cs})$ , and  $\nu_y(\text{Cs})$ , respectively. The  $T_{2Q}$  values are indicated by  $\blacktriangledown$ ,  $\triangledown$ ,  $\blacksquare$ , and  $\square$  for the NQR lines in the same order.

both linewidths suddenly decreased with increasing temperature between 247 and 258 K for  $\nu_x(\text{Cs})$  and between 258 and 263 K for  $\nu_y(\text{Cs})$ . These experiments were performed with a superregenerative spectrometer, which is not a reliable means for the determination of NQR line shapes. Therefore we reinvestigated the line shape of the two  $^{35}\text{Cl}$  NQR lines of  $\text{Cs}[\text{AuCl}_4]$  at various temperatures by recording FT NQR spectra. The spectra obtained at several temperatures are shown in Figure 3. The linewidths for  $\nu_x(\text{Cs})$  and  $\nu_y(\text{Cs})$  recorded were almost the same and independent of temperature, in disagreement with the results of Sasane *et al.* previously reported [7]. This is presumably because they measured the linewidths with the sample including a small amount of water.

#### 4. Discussion

$\text{Rb}[\text{AuCl}_4]$  and  $\text{Cs}[\text{AuCl}_4]$  are known to be isomorphous at room temperature [8, 9], forming monoclinic crystals belonging to the space group  $I2/c$  with  $Z = 4$  [9]. The four complex anions in a unit cell are crystal-

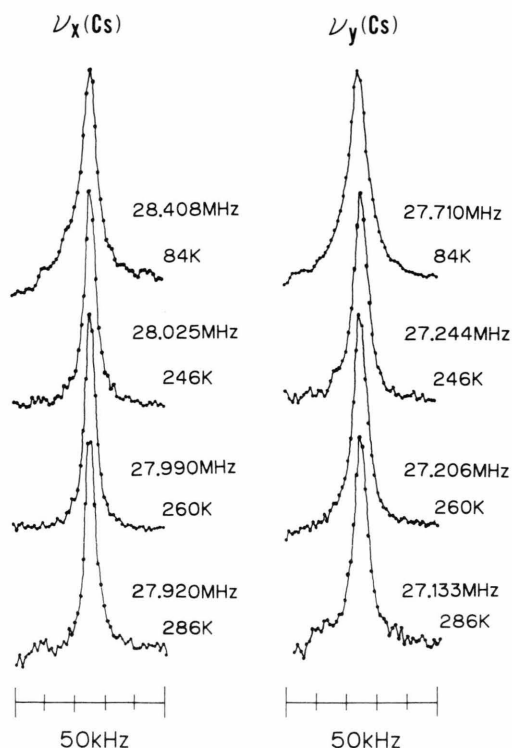


Fig. 3. Fourier transform NQR spectra for  $\nu_x(\text{Cs})$  and  $\nu_y(\text{Cs})$  lines at several temperatures.

lographically equivalent, and each anion forms a slightly deformed square involving two kinds of non-equivalent chlorines, the equivalent ones of which are located at trans positions. Accordingly,  $\nu_x$  and  $\nu_y$  can be attributed to be two kinds of chlorines in the  $[\text{AuCl}_4]^-$  anion. For both complexes  $\nu_x$  is higher than  $\nu_y$  by ca. 0.7 MHz. This may be too large to be attributable to the lattice effect. Therefore, the chlorines showing  $\nu_x$  can be considered to have a slightly shorter Au-Cl bond length than the others in the anion (by 0.01 Å for the rubidium salt [9]) [10].

For the present complexes,  $T_{2Q}$  is thought to be determined mainly by magnetic dipolar interactions between chlorine nuclei as in the case of  $\text{K}_2\text{PtCl}_6$  [11]. The  $T_{2Q}$  values for the chlorines exhibiting  $\nu_x(\text{Rb})$ ,  $\nu_y(\text{Rb})$ ,  $\nu_x(\text{Cs})$ , and  $\nu_y(\text{Cs})$  were almost the same at a given temperature in a temperature range studied. This means that the strength of dipolar interactions is approximately the same for both complexes, consisting with the assumption of pseudosquare-planar complex anions of nearly the same size. This is supported by the fact that both complexes give NQR frequencies very near to each other at a given temperature in the

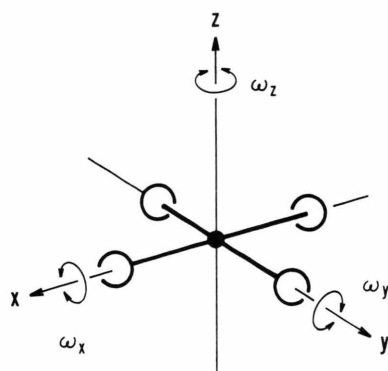


Fig. 4. The coordinate system for the  $[\text{AuCl}_4]^-$  anion used in the text. Solid and open circles indicate Au and Cl atoms, respectively.

whole temperature range where observation was made. In the following discussion we assume that the moments of inertia of the  $[\text{AuCl}_4]^-$  anions around the respective principal axes are equal to each other between both complexes.

#### $T_{1Q}$ in the High-Temperature Region

Above ca. 270 K, each complex gave the same  $T_{1Q}$  temperature dependence for the  $\nu_x$  and  $\nu_y$  lines and the exponential decrease of  $T_{1Q}$  with decreasing  $T^{-1}$  suggests that  $T_{1Q}$  of these complexes results from sudden but infrequent jumps of the spin quantization axis of the chlorine nuclei in the complex anions [12]. As the most probable candidate for this motion we assume a 90° reorientational jump of the pseudosquare-planar anion about its  $C'_4$  axis. Here, we employ the coordinate system given in Fig. 4 for the anion. The chlorines placed on the x- and y-axis are defined to give  $\nu_x$  and  $\nu_y$  lines, respectively.

According to the foregoing relaxation mechanism, the temperature dependence of  $T_{1Q}$  can be expressed [2] as

$$T_{1Q}(\nu_x) = T_{1Q}(\nu_y) = (2/3) \tau = (2/3) \tau_0 \exp(E_a/RT). \quad (4)$$

Here,  $\tau$  and  $E_a$  denote the correlation time and the activation energy for the present motion, respectively.  $\tau$  was assumed to be expressed by the Arrhenius relationship, where  $\tau_0$  indicates the correlation time at the limit of infinite temperature. Using (4),  $E_a$  can be evaluated from the gradient of the observed  $\log T_{1Q}$  vs.  $T^{-1}$  plots. The  $E_a$  values obtained for both complexes are listed in Table 2 together with other  $[\text{AuCl}_4]^-$  salts for comparison.

Table 2. The activation energy  $E_a$  for the  $90^\circ$  reorientational motion of  $[\text{AuCl}_4]^-$  anions.

Compound	$E_a/\text{kJ mol}^{-1}$	Ref.
guH[AuCl <sub>4</sub> ]	67	[2]
pyH[AuCl <sub>4</sub> ]	67	[1]
Cs[AuCl <sub>4</sub> ]	53	present work
Rb[AuCl <sub>4</sub> ]	71	present work
NH <sub>4</sub> [AuCl <sub>4</sub> ]	80	[13]

The  $E_a$  values for the cesium, rubidium, and ammonium tetrachloroaurates(III) [13] increase with decreasing ionic radii of the cations [14]. The guanidinium [2] and pyridinium [1] tetrachloroaurates(III) showed nearly the same  $E_a$  value as that of the rubidium salt, although these two cations can form N–H...Cl type H-bonds in the crystals. Generally speaking, ammonium ions also have a possibility to form N–H...Cl type H-bonds. However, the ammonium ion in NH<sub>4</sub>[AuCl<sub>4</sub>] is considered to be almost free from such interaction because the very low activation energy of  $4 \text{ kJ mol}^{-1}$  was estimated from the  $^1\text{H}$  NMR experiments for the cationic reorientation in NH<sub>4</sub>[AuCl<sub>4</sub>] crystals [15]. From the  $E_a$  data listed in Table 2 we can conclude that  $E_a$  for the motion of the anion in the present complexes is mainly determined by the packing scheme of the ions in the crystals, and N–H...Cl type H-bonding in the guanidinium and pyridinium salts does not give appreciable effect on  $E_a$ .

### $T_{1Q}$ in Low-Temperature Region

Below ca. 270 K the temperature dependence of  $T_{1Q}$  is approximately proportional to  $T^{-2}$ . This suggests that the rotary lattice vibration of the complex anions is responsible for the relaxation process [16]. When quadrupolar relaxation is governed by lattice vibrations involving the nuclei in question, the temperature dependence of  $T_{1Q}^{-1}$  for the nuclear spin  $I$  equal to  $3/2$  is given by the following equation at high temperatures under the harmonic oscillator approximation for the vibration [17, 18]:

$$T_{1Q}^{-1} = \sum_l (12 k^2 \omega_l^2 / \hbar I_l \tau_g) (T^2 / \omega_l^5) (1 + \gamma). \quad (5)$$

Here,  $\omega_l$ ,  $I_l$ , and  $\tau_g$  are the  $l$ -th librational angular frequency of the complex anion, the moment of inertia for the  $l$ -th librational axis, and the mean residence time of the anion in the ground state of the libration,

respectively. The NQR angular frequency is indicated by  $\omega_Q$ , and  $\gamma$  is equal to the ratio  $W_2/W_1$ , where  $W_1$  and  $W_2$  indicate the transition probabilities of the quadrupole interaction system with the selection rule  $\Delta m_l = \pm 1$  and  $\Delta m_l = \pm 2$ , respectively. In (5), a cylindrically symmetric electric field gradient is assumed for the chlorines of the anion.  $\tau_g$  and  $\gamma$  are assumed to be constant, independent of the librational modes.

Taking the librational oscillations about the  $x$ ,  $y$ , and  $z$  axes shown in Fig. 4 into account,  $T_{1Q}^{-1}$  for  $v_x$  and  $v_y$  can be written as

$$T_{1Q}^{-1}(v_x) \propto (v_x^2/I_z) [1 + (I_z/I_y)(\omega_z/\omega_y)^5] (T^2/\omega_z^5), \quad (6)$$

$$T_{1Q}^{-1}(v_y) \propto (v_y^2/I_x) [1 + (I_z/I_x)(\omega_z/\omega_x)^5] (T^2/\omega_z^5). \quad (7)$$

Accordingly, the ratio  $T_{1Q}^{-1}(v_x)/T_{1Q}^{-1}(v_y)$  at a given temperature becomes

$$T_{1Q}^{-1}(v_x)/T_{1Q}^{-1}(v_y) = (v_x/v_y)^2 \cdot \frac{[1 + (I_z/I_y)(\omega_z/\omega_y)^5]}{[1 + (I_z/I_x)(\omega_z/\omega_x)^5]}. \quad (8)$$

For both complexes,  $T_{1Q}$  was observed to be shorter for  $v_x$  than  $v_y$  at lower temperatures. For example, the experimentally determined value of  $T_{1Q}^{-1}(v_x)/T_{1Q}^{-1}(v_y)$ , for Rb[AuCl<sub>4</sub>] was 1.3 at 82 K. Since  $(v_x/v_y)^2 = 1.05$  at 82 K and  $I_x/I_y = 1.007$ , the value of which can be calculated by use of the atomic coordinates reported by Strähle and Bärnighausen [9], the difference observed between  $T_{1Q}(v_x)$  and  $T_{1Q}(v_y)$  should be attributed to the difference between the librational frequencies  $\omega_x$  and  $\omega_y$ .

The  $T_{1Q}^{-1}$  ratio of the  $v_x$  lines of Rb[AuCl<sub>4</sub>] and Cs[AuCl<sub>4</sub>] at a given temperature,  $T_{1Q}^{-1}(v_{xC})/T_{1Q}^{-1}(v_{xR})$ , can be written as

$$\begin{aligned} T_{1Q}^{-1}(v_{xC})/T_{1Q}^{-1}(v_{xR}) &= (v_{xC}/v_{xR})^2 \frac{I_{zR}[1 + (I_{zC}/I_{yC})(\omega_{zC}/\omega_{yC})^5]}{I_{zC}[1 + (I_{zR}/I_{yR})(\omega_{zR}/\omega_{yR})^5]} (\omega_{zR}/\omega_{zC})^5. \end{aligned} \quad (9)$$

Here, the subscripts C and R represent the physical quantities belonging to the Cs and Rb salts, respectively. Since  $I_l(\text{Cs}) \simeq I_l(\text{Rb})$  for  $l = x, y$ , and  $z$  discussed above, and also  $v_{xC} \simeq v_{xR}$ , the following equation can be derived provided the ratio of  $\omega_z/\omega_y$  is unchanged for both complexes:

$$(\omega_{zR}/\omega_{zC}) = [T_{1Q}^{-1}(v_{xC})/T_{1Q}^{-1}(v_{xR})]^{1/5}. \quad (10)$$

From the  $T_{1Q}$  values of Rb[AuCl<sub>4</sub>] and Cs[AuCl<sub>4</sub>] observed for the  $v_x$  lines at 82 K, the ratio of  $(\omega_{zR}/\omega_{zC})$  was obtained as 1.2 using (10). This means that the librational frequency of the anion in crystals about the  $C_4$  axis is larger for Rb[AuCl<sub>4</sub>] than for Cs[AuCl<sub>4</sub>].



The above results can be confirmed by applying a simple potential curve  $V$  approximated to have the  $C_4$  symmetry for the in-plane  $C_4$  reorientation of the anion. Here, we assume that  $V$  can be expressed as

$$V = (1/2) V_0 (1 - \cos 4\phi), \quad (11)$$

where  $V_0$  and  $\phi$  are the barrier height of the hindered potential and the angle of rotation, respectively. In the bottom of the above potential well we have

$$\omega_z = 4(V_0/2I_z)^{1/2} \quad (12)$$

for the librational frequency [19]. By assuming  $V_0 = E_a$ , and using equal  $I_z$  values of present com-

plexes,  $(\omega_{zR}/\omega_{zC})$  can be given as

$$(\omega_{zR}/\omega_{zC}) = (E_{aR}/E_{aC})^{1/2}. \quad (13)$$

From the  $E_a$  values determined above for Rb[AuCl<sub>4</sub>] and Cs[AuCl<sub>4</sub>], the value of 1.2 was obtained for  $(\omega_{zR}/\omega_{zC})$ . This value agrees very well with that evaluated from the analysis of the  $T_{1Q}$  data obtained at low temperatures by employing the lattice vibrational model.

The foregoing results for the activation energy and the librational frequency imply that the in-plane rotational motion of the complex anion in the cesium salt is more easily activated than that of in the rubidium salt.

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