The Vibrational Spectra and Crystallographic Properties of CsPF$_6$

A. M. HEYNS

Department of Chemistry, University of South Africa,
0001 Pretoria, South Africa

AND P. W. RICHTER AND J. B. CLARK

NPRL, CSIR, P.O. Box 395, 0001 Pretoria, South Africa

Indications are that CsPF$_6$(I) at ambient conditions is cubic with a possible space group of $Fm3m$-O$_h^5$. A slight distortion of the unit cell cannot, however, be ruled out. Assuming $Fm3m$ symmetry the Raman spectra of CsPF$_6$(I) are consistent with a disordered model in which the PF$_6^-$ ions are tilted away from the crystallographic axes. The phase transition which occurs below 90 K in CsPF$_6$ is reflected in the vibrational spectra and further significant changes occur below 60 K particularly in the Raman bands. It is not yet clear whether these changes represent the establishment of long-range order or whether a further phase of CsPF$_6$ exists below 60 K. A possible structure for CsPF$_6$ at very low temperatures is discussed.

Introduction

Cesium hexafluorophosphate CsPF$_6$ was reported to have a NaCl-type structure at room temperature (*1, 2*) but the exact space group to which this crystal belongs has not been established beyond any doubt. A primitive unit cell for CsPF$_6$(I) has been proposed by Bode and Clausen (*2*) but there is also no reason to believe that its crystal structure differs from that of the face-centered structure of NaPF$_6$(I) (*3*), KPF$_6$(I) (*4*), and possibly NH$_4$PF$_6$(I) (*5*). In KPF$_6$(I), CsPF$_6$(I), and RbPF$_6$(I) the sizes of the cations will cause the fluorine atoms to be offset from the lines connecting the heavy atoms (*6*), and evidence of tilted PF$_6^-$ groups has indeed been found in the single-crystal Raman spectra of KPF$_6$(I) (*4*). It has further been suggested that in view of the appre-

ciable expansion of the lattices in CsPF$_6$(I) and RbPF$_6$(I) over those of KPF$_6$(I) and NaPF$_6$(I) that the fluorine atoms in the former two salts will point to neighbouring PF$_6^-$ ions without appreciable repulsions between fluorine atoms in adjacent PF$_6^-$-ions (*6*).

Below 90 K, a phase transition occurs in CsPF$_6$ but the structure of the low-temperature phase (phase II) is not known (*7, 8*). It has been speculated that CsPF$_6$(II) might possibly have a trigonally distorted body-centered cubic structure (*8*).

A study of the vibrational and crystallographic properties of CsPF$_6$ is of interest for several reasons. These properties can be compared with the corresponding ones of NaPF$_6$, KPF$_6$, and NH$_4$PF$_6$ to see whether CsPF$_6$(I) has a structure corresponding to those of the other salts of

this series. The infrared and Raman spectra of $CsPF_6(II)$ can also provide information on the structure of this phase and more in particular as to whether the spectra can be interpreted in terms of one of the rhombohedral structures which are commonly found among related hexafluoro compounds. Furthermore, as the barrier to reorientational motions in the alkali hexafluorophosphates is generally regarded to decrease with increasing size of the cation (6), the effect of disorder on the vibrational spectra of $CsPF_6$ is also of importance.

Experimental

$CsPF_6$ was prepared by means of the reaction of equimolar quantities of HPF_6 (65% solution; K & K laboratories) and Cs_2CO_3 (Fluka AG, Switzerland). The product was recrystallized four times from distilled water and the fluorine contents of the samples were determined according to methods described by Palmer (9) and Vogel (10). The analyses of the $CsPF_6$ indicated a purity of 99.3% by total fluorine determination.

Details concerning the equipment used to record the infrared, far-infrared and Raman spectra have already been published elsewhere (3–5). For the low-temperature far-infrared spectra a RIIC variable-temperature unit, obtained from Beckman Instruments, has been used. Liquid nitrogen was used as the refrigerant in this cryostat and the I/II transition in $CsPF_6$, which lies below 90 K (7), could therefore not be studied in the far-infrared spectra; however, the mid-infrared and Raman spectra have been recorded down to temperatures of 17 K.

The spectral resolution in the infrared and far-infrared spectra was equal to 2 and 3.5 cm⁻¹ respectively and the positions of the Raman peaks are accurate within ±2 cm⁻¹.

X-Ray powder diffraction patterns were recorded on a Huber Guinier system using monochromatized $CuK\alpha_1$ radiation. Si was used as an internal calibrant and both film and counter techniques were employed.

Results

Crystallography

The X-ray powder diffraction pattern of $CsPF_6(I)$ is shown in Table I. The pattern could be satisfactorily indexed on the basis of a fcc unit cell with $a = 8.218$ Å. The Smith–Snyder figure of merit, F_N (11), is: $F_{22} = 40(0.022; 25)$. The indices appear to be all odd or all even and with $h00 = 2n$. According to the selection rules the possible space groups are there-

TABLE I

X-RAY POWDER DIFFRACTION PATTERN OF $CsPF_6(I)$
AT 25°C[a]

d_{obs} (Å)	d_{calc} (Å)	$2\Theta_{obs} - 2\Theta_{calc}$	hkl	I
4.743	4.744	0.007	111	5
4.113	4.109	−0.021	200	100
2.9051	2.9054	0.003	220	29
2.4787	2.4777	−0.016	311	29
2.3726	2.3722	−0.006	222	8
2.0549	2.0544	−0.012	400	3
1.8864	1.8853	−0.031	331	4
1.8381	1.8375	−0.016	420	9
1.6769	1.6774	0.019	422	5
1.5818	1.5815	−0.015	511	4
1.4519	1.4527	0.038	440	3
1.3885	1.3890	0.027	531	1
1.3690	1.3696	0.034	600	2
1.2991	1.2993	0.013	620	1
1.2386	1.2389	0.021	622	1
1.1506	1.1507	0.010	711	1
1.1401	1.1396	−0.051	640	1
1.0985	1.0981	−0.041	642	<1
1.0696	1.0698	0.027	731	<1
1.0271	1.0272	0.019	800	<1
0.9964	0.9965	0.021	820	<1
0.9687	0.9685	−0.040	660	<1

[a] $a = 8.218$ Å; $F_{22} = 40(0.022; 25)$; $CuK\alpha_1$.

fore $Fm3m$-O_h^5, $F432$-O^3, $F\bar{4}3m$-T_d^2, $Fm3$-T_h^3 and $F23$-T^2. Single-crystal studies are needed to determine the true symmetry.

Vibrational Spectra of $CsPF_6(I)$

The infrared and Raman spectra of $CsPF_6$ at various temperatures are shown in Figs. 1 and 2 and the frequencies and assignments of the bands are summarized in Tables II and III. With the exception of ν_6 which is of F_{2u} symmetry under O_h and therefore inactive in both the infrared and Raman spectra, all of the other fundamental modes, viz. ν_1–ν_5 of the PF_6^- groups have been observed. These spectra are also very similar to those of the PF_6^--ion in $NH_4PF_6(I)$, $KPF_6(I)$, and $NaPF_6(I)$ with the exception of frequency shifts which have been noted to occur in the symmetric and asymmetric P–F stretching modes in some of the salts (3–5). However, there are some indications

FIG. 2. The Raman spectra of $CsPF_6$ at (a) 295 K, (b) 60 K, and (c) 17 K.
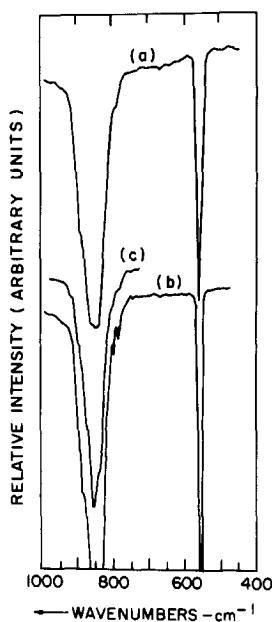

FIG. 1. The mid-infrared spectra of $CsPF_6$ at (a) 295 K, and (b) 17 K. The spectrum of a less concentrated pellet is shown in (c) at 17 K. The two components of ν_4 are so closely spaced that they are not clearly evident in this figure.
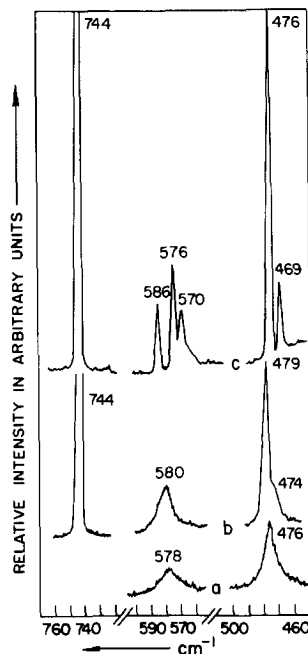
TABLE II

FREQUENCIES AND ASSIGNMENTS OF THE INFRARED BANDS OF $CsPF_6$

295 K (cm^{-1})	17 K (cm^{-1})	Assignment
~1410	~1410	$\nu_2 + \nu_3$
1260	~1255	?
~890 asym	890 sh	$\nu_2 + \nu_6$
—	882 sh	$\nu_2 + \nu_6$
—	873 sh	$\nu_4 + \nu_6$
~850 s	~848 s	ν_3
—	835 sh	ν_3
~790 sh	795 w	$\nu_5 + \nu_6$
—	783 w	$\nu_5 + \nu_6$
~773 sh	779 w	$\nu_5 + \nu_6$
743 vw	743 vw	ν_1
~665 vw	665 vw	?
—	575 sh	ν_2
559 s	560 s	ν_4
—	555 s	ν_4
—	310 vw^a	ν_6
—	~220^a	ν_{Rot}–PF_6^-?
~76 m	82 m^a	ν_T

^{a} These bands have been recorded at 90 K.

TABLE III

THE RAMAN SPECTRA OF POLYCRYSTALLINE AND SINGLE-CRYSTAL CsPF$_6$[a]

Polycrystalline samples						Single-crystal spectra (298 K)						
298 K			17 K			aa			ab			
cm^{-1}	RI	HW	cm^{-1}	RI	HW	cm^{-1}	RI	HW	cm^{-1}	RI	HW	Assignment
744	100	3	744	100	2	744	100	3	744	<1	—	ν_1
—	—	—	586	5	3	—	—	—	—	—	—	ν_2(LO)
578	5	15	576	8	3	~575	1	20	~577	3	12	ν_2(TO)
—	—	—	570	4	4, 5	—	—	—	—	—	—	ν_4(LO)
—	—	—	560–565	sh	—	—	—	—	—	—	—	ν_4(TO)
476	16	7	476	26	3	475	14	7	—	—	—	ν_5
—	—	—	469	6	3	—	—	—	472	1	12	ν_5

[a] RI, relative intensity; HW half-width in cm^{-1}.

in the spectra of polycrystalline samples that the symmetry of the crystal might be lower than the space group $Fm3m$ in which both the site- and factor-group symmetries are equal to O_h. This has also been the case in NH$_4$PF$_6$ (5) and KPF$_6$ (4) and it should be kept in mind that in all of these salts, the PF$_6^-$ ions are disordered and the space group $Fm3m$ can therefore be regarded as an average one obtained from a time-averaged technique such as X-ray diffraction studies. The apparent violations from O_h symmetry which are exemplified in the vibrational spectra of CsPF$_6$ are the following: $\nu_1(A_{1g})$ should be Raman active only, but in favorable cases a very weak feature (which is not evident in Fig. 1) is observed in the infrared spectra at 743 cm^{-1}. Real proof for a violation of O_h selection rules can, however, be found in the polarized Raman spectra of single crystals of CsPF$_6$(I) which are shown in Fig. 3. According to O_h selection rules, $\nu_5(F_{2g})$ should be observed in the polarization directions $uv(xy, yz, zx)$ but not in the ones corresponding to the diagonal polarizability elements $\alpha_{uu}(xx, yy, zz)$. However, it is evident from Fig. 3 that the most intense component of ν_5 is ob-

served at 475 cm^{-1} in the directions corresponding to the diagonal polarizability elements and that there is a frequency separation between the components observed in the directions corresponding to the diagonal and off-diagonal elements,
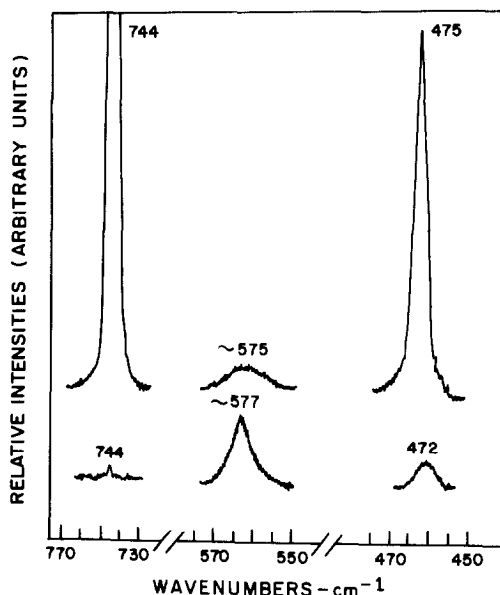

FIG. 3. The polarized Raman spectra of single crystals of CsPF$_6$ at ambient temperature in the polarization directions corresponding to the diagonal uu (top) and off-diagonal uv (bottom) polarizability elements.

respectively. In the spectra of polycrystalline samples at lower temperatures before the occurrence of any phase transitions, a low-frequency asymmetry of ν_5 can also be discerned, thus confirming the single-crystal results that two components of ν_5 are present. $\nu_2(E_g)$, on the other hand, should be seen in the Raman spectra in those directions corresponding to the diagonal polarizability elements. Fig. 3 shows that $\nu_2(E_g)$ occurs in the directions corresponding to both the diagonal and off-diagonal polarizability elements. The frequency separation between the latter two components might not be significant since the components observed in the uu directions are so broad that its frequency cannot be determined accurately within ± 3 cm^{-1}. $\nu_1(A_{1g})$ is observed in the uu directions only and the very weak feature in the uv polarization directions can possibly be due to a slight misalignment of the crystal in the laser beam.

The transformed tensors for the PF$_6^-$ ions which have been obtained by assuming that at any one stage during the measurement of the vibrational spectra *all* the P–F bonds are tilted away from the cubic axes (*4*) can, however, be used to explain the occurrence of the above components which have not been allowed according to O_h symmetry. The large Cs$^+$ ions will prevent a coincidence of the ionic and crystal axes (*6*) and this will cause deviations from octahedral symmetry. The real symmetry of the PF$_6^-$ ions in CsPF$_6$(I) will thus be lower than O_h and the polarized Raman spectra of single crystals of CsPF$_6$(I) provide concrete evidence that this is indeed so.

NMR results (*7*) have shown that the activation energy for the reorientational motions of the PF$_6^-$ ion in CsPF$_6$, E_a, is equal to 0.73 kcal/mole in the temperature range 90–300 K. These ions therefore have a great deal of reorientational freedom in CsPF$_6$(I) and can be considered as being more disordered than KPF$_6$(I) and NH$_4$PF$_6$(I). The vibrational spectra of CsPF$_6$(I) do not reflect this greater deal of disorder and the spectra of CsPF$_6$(I), KPF$_6$(I), and NH$_4$PF$_6$(I) are remarkably similar. The disorder in these crystals is expected to break the crystal translational symmetry and modes throughout the Brillouin zone can be activated. The far-infrared spectra of these compounds are therefore ill-defined and broad, thus reflecting the disorder of the PF$_6^-$ ions. Under $Fm3m$ symmetry the optical translational mode is of F_{1u} symmetry and is observed to occur at ~76 cm^{-1} in CsPF$_6$(I) but is, contrary to expectation, much more narrow (half-width = 30 cm^{-1}) than its counterparts in NH$_4$PF$_6$(I) ($HW \cong 100$ cm^{-1}) and KPF$_6$(I) ($HW \cong 70$ cm^{-1}).

Phase Transition and the Vibrational Spectra of CsPF$_6$(II)

If samples of CsPF$_6$ are cooled down the spectra do not change significantly down to 90 K with the exception of a sharpening of the bands and a low-frequency shoulder which develops on ν_5. Below 90 K, however, this shoulder develops into a well-defined satellite and ν_4 also shows a distinct splitting into two components but ν_2 is still observed in the Raman spectra as a single band. Below 60 K, ν_2 splits into three well-defined components as can be seen in Fig. 2 (possibly four if a weakly defined shoulder at 560–570 cm^{-1} is also taken into account). It is not clear whether a further transition occurs below 60 K, but since it has not been observed in the NMR measurements (*7*) that possibility seems unlikely. The intensities of the infrared bands such as the low-frequency component of ν_4 also reflect changes at this temperature, can be seen in Fig. 4. By anal-
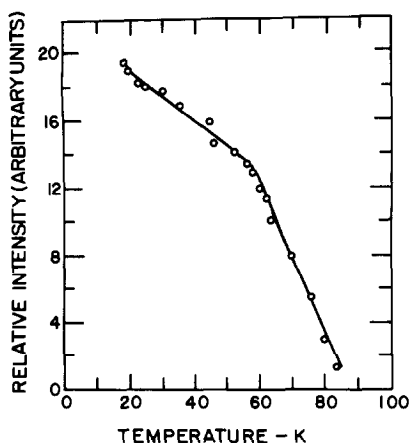
FIG. 4. The variation of the peak height of the lower frequency component of ν_4 with temperature.

ogy to KPF$_6$ (4), CsPF$_6$(II) may be expected to be related to a 8-coordinated CsCl-type structure and it is reasonable to expect it to be an ordered structure. No further details are available but if this is indeed so, then the I/II transition in CsPF$_6$ is one from a disordered NaCl-type structure to an ordered CsCl-type structure. The activation energies for the reorientational motions of the PF$_6^-$ ions in solid CsPF$_6$ were reported to show complex behavior below the phase transition temperature, being equal to 2.5 kcal/mole in the temperature range 73–88 K, 1.6 kcal/mole between 56 and 73 K and decreasing to 0.76 kcal/mole below 56 K (6). Changes in the slope of T_1 versus $1000/T$ have however been previously ascribed to paramagnetic impurities in samples of KSbF$_6$ (12) and KPF$_6$ (8) and these values of E_a for CsSbF$_6$ below 90 K might therefore not be significant.

In an order–disorder phase transition the establishment of long-range order might only be completed at temperatures well below that of the transition temperature (13). This might also be the case in CsPF$_6$(II) and the disorder still existing in the lattice will affect the vibrational bands or at least some of them in the sense that

they might be broad obscuring for example any longitudinal optic–transverse optic (LO–TO) splittings. This can then be used to explain the development of additional bands below 60 K in CsPF$_6$(II). On the other hand, the possibility that an additional phase exists in CsPF$_6$ can also not be excluded. KPF$_6$(II), for example, which is rhombohedral, exists only in a temperature interval of $\sim 15°$C at ambient pressures before it transforms into KPF$_6$(III) (4). The structure of the latter phase is not known. NH$_4$PF$_6$ undergoes a transition at ~ 190 K which is of the λ type associated with a change in the reorientational freedom of the PF$_6^-$ groups (5). The second transition at ~ 130 K is, however, associated with a corresponding change in the motions of the NH$_4^+$ ions and can therefore not be correlated with transitions in KPF$_6$ and CsPF$_6$.

The vibrational spectra of CsPF$_6$ between ~ 90 and 60 K can to a first approximation be interpreted in terms of both the space groups D_{3d}^5-$R\bar{3}m$ and C_{3i}^2-$R\bar{3}$ which are very common among rhombohedral $A^IB^VF_6$ compounds (14). Both of these models explain the facts that ν_3, ν_4, and ν_5 are split into two components, while ν_2 is observed as a single band. However, the fact that very weak features are observed at ~ 575 and 743 cm^{-1} in the infrared spectra, which correspond to the frequencies where ν_2 and ν_1 are observed in the Raman spectra, cannot be ignored, showing that the symmetry is in fact lower. Below 60 K, the splitting of ν_2 into at least three components is in total disagreement with these above-mentioned space groups and there is concrete evidence that the rule of mutual exclusion is no longer valid at these low temperatures. A comparison of the spectra of CsPF$_6$ below 60 K with those of NH$_4$PF$_6$(III) and KPF$_6$(III) shows remarkable similarities between both the number and frequencies of the components of ν_2,

but the number of components of ν_4 and ν_5 differs in the three cases. Assuming a rhombohedral structure for $CsPF_6(II)$ in which ν_1, ν_2, and ν_5 are activated in the infrared and ν_4 (and by implication also ν_3 and ν_6) becomes Raman active, the vibrational spectra of $CsPF_6(II)$ appear to be compatible with C_3 symmetry. The correlation between the O_h and C_3 point groups is as follows: $\nu_1(A_{1g}) \to A$; $\nu_2(E_g) \to E$; ν_3 and $\nu_4(F_{1u}) \to A + E$, $\nu_5(F_{2g}) \to A + E$, and $\nu_6(F_{2u}) \to A + E$. The A and E modes are both infrared and Raman active. This symmetry for the PF_6^- ions is possible in, for example, the space group $R3$-C_3^4. Accordingly the appearance of both ν_1 and ν_2 are explained in the infrared spectra and the splitting of ν_3, ν_4, and ν_5 into two components can be accounted for. However, ν_2 should be single and the two additional peaks which appear in this frequency range can possibly be attributed to the two components of ν_4 which are also Raman active. The frequencies at which these modes are observed in the Raman spectra do not coincide with those in the infrared spectra and can therefore not be due to activated components of ν_4. This means that the bands at 586 and 576 cm^{-1} must be due to components of ν_2, and this can only be so if the symmetry of the PF_6^- ions is lower than C_3 so that ν_2 is split and/or there are more than one molecule per primitive unit cell. Both of these effects must also show in the other modes such as ν_3, ν_4, and ν_5. The broadness of ν_3 prevents the determination of the number of its components accurately, but ν_5 in the Raman should reflect any splittings. As can be seen in Fig. 2, it is definitely split into only two components. If a space group of $R3$ is assumed for $CsSbF_6$ it must be remembered that the A and E modes are both infrared and Raman active and as a result of long-range electrostatic forces, these modes can be split into longitudinal optic (LO) and

transverse optic (TO) modes. Therefore, each mode can possibly be split into two components and the 578/588 cm^{-1} components of ν_2 can then represent TO and LO components, respectively. A possible assignment of modes on this basis is given in Table II. It is interesting to note that the vibrational spectra of $NH_4PF_6(III)$ and $KPF_6(III)$ can also be interpreted in terms of $R3$-C_3^4 if it is assumed that LO–TO splittings are observed in more bands than in $CsPF_6$. Further, Fermi resonance between symmetrically suited components of ν_2 and ν_4 can occur in this frequency range enhancing the intensities of very weak bands to such an extent that they are observed, thus explaining the occurrence of more components here than are observed in other frequency ranges. The LO scattering originates in long-range dipole–dipole interactions (13) and the interactions among disordered PF_6^- ions will have destructive interference and LO components will therefore be absent in disordered phases, or develop slowly during the establishment of long-range order. It is possible to say with the data which are presently available whether this is what is taking place between 90 and 60 K, or whether phase III develops below 60 K in $CsPF_6$. The lattice modes of a compound are normally very sensitive towards disorder which exists in the crystal but due to experimental limitations we could not record the far-infrared spectra of $CsPF_6$ at low temperatures. The far-infrared spectra of $CsPF_6$ were recorded at just below 90 K, but it is difficult to say whether the compound is in phase I or phase II. At this temperature a lattice mode is observed at 82 cm^{-1} and ν_6 appears at 310 cm^{-1}. A very broad absorption peak centered around 220 cm^{-1} could possibly represent rotational motions of the PF_6^- ions since features at this frequency have also been observed in $NH_4PF_6(III)$ and $NaPF_6(II)$ at lower temperatures (3, 5).

As in the case of NH$_4$PF$_6$ (5), KPF$_6$ (4), and NaPF$_6$ (3) the low-frequency Raman spectrum of CsPF$_6$ was observed to be featureless.

Conclusions

CsPF$_6$(I) is cubic and probably belongs to the space group $Fm3m$-O$_h^5$ as is also the case in the corresponding phases of NaPF$_6$, KPF$_6$, and NH$_4$PF$_6$ (3–5), but a slight distortion from cubic symmetry cannot be ruled out. The vibrational spectra of CsPF$_6$(I) exhibit weak features which are in disagreement with the O$_h$ symmetry predicted under $Fm3m$. These features can however be explained in terms of a disordered model in which the P–F bonds are tilted away from the crystallographic axes. In this respect the spectra of CsPF$_6$(I) closely resemble those of KPF$_6$(I) (4). With the presently available data the space group to which CsPF$_6$(I) belongs cannot be assigned unambiguously and it must be kept in mind that in the disordered CsPF$_6$(I), the space group $Fm3m$ might be an average one obtained from time-averaged methods such as X-ray powder diffraction studies and that the deviations from O$_h$ symmetry which have been indicated by the vibrational spectra, might probably point to a different space group. Single-crystal studies are thus necessary to determine the exact space group and to indicate if the unit cell is slightly distorted to lower symmetry. Step scan techniques are being planned to resolve any splitting of the peaks, if present.

The changes which have been observed in the vibrational spectra of CsPF$_6$ at 90 K are associated with the phase transition which has also been observed using different methods (7, 8). Further changes in the spectra occur at 60 K and possible explanations are discussed in the text. The vibrational spectra of CsPF$_6$ at very low temperatures can be interpreted in terms of a rhombohedral space group such as $R3$-C$_3^4$, provided that LO–TO splittings are resolved in a number of bands.

Acknowledgments

References

1. H. SEIFERT, Z. Krist. 76, 455 (1931).
2. H. BODE AND H. CLAUSEN, Z. Anorg. Allg. Chem. 265, 229 (1951).
3. A. M. HEYNS, C. W. F. T. PISTORIUS, P. W. RICHTER, AND J. B. CLARK, Spectrochim. Acta A 34, 279 (1978) and the correction note in Spectrochim. Acta A 35, 197 (1979).
4. A. M. HEYNS AND C. W. F. T. PISTORIUS, Spectrochim. Acta A 30, 99 (1974).
5. A. M. HEYNS AND G. J. VAN SCHALWYK, Spectrochim. Acta A 29, 1163 (1973).
6. G. R. MILLER AND H. S. GUTOWSKY, J. Chem. Phys. 39, 1983 (1963).
7. L. NIEMELÄ AND M. KOMU, Ann. Acad. Sci. Fenn. Ser. A 6, 403 (1973).
8. H. S. GUTOWSKY AND S. ALBERT, J. Chem. Phys. 58, 5446 (1973).
9. W. G. PALMER, in "Experimental Inorganic Chemistry," p. 306. Cambridge Univ. Press, Cambridge (1970).
10. A. I. VOGEL, "A Text-Book of Quantitative Inorganic Analysis," 3rd ed., p. 269. Longmans, London (1961).
11. G. S. SMITH AND R. L. SNYDER, J. Appl. Cryst. 12, 60 (1979).
12. A. M. HEYNS AND E. C. REYNHARDT, J. Phys. Chem. Solids, in press.
13. C. H. WANG AND R. B. WRIGHT, J. Chem. Phys. 58, 1411 (1973).
14. R. W. G. WYCKOFF, "Crystal Structures," Vol. 3. Interscience, New York (1965).