

Evidence for the Planar Structure of the Urea Molecule

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Crystal Structures of a Series of Rare Earth Phosphates

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August 25, 1948

THE crystal structures of the phosphates of trivalent lanthanum, cerium, praseodymium, and neodymium were determined by x-ray diffraction techniques in 1944 for the Manhattan Project. It was found that the crystals are dimorphic. One phase is monoclinic, isomorphous with the mineral, monazite; the other is a hexagonal structure of a new type, which easily converts to the monoclinic form at moderately high temperatures.

Hexagonal modification. There are three molecules of XPO_4 , where X may be La, Ce, or Nd, in the unit hexagonal cell. The cell constants and calculated densities for the isomorphous series are as shown in Table I.

The space group is $D_{3d}^4-C_{3i}21(D_3^6)$. The atomic positions, in fractions of the unit cell, are given for $CePO_4$ as a representative of the series as follows:

- Three Ce atoms in $x\ 0\ \frac{1}{2}$, $0\ x\ \frac{1}{2}$, $\bar{x}\ \bar{x}\ \frac{1}{2}$ where $x = \frac{1}{2}$.
- Three P atoms in $x\ \frac{1}{3}$, $0\ x\ \frac{2}{3}$, $\bar{x}\ \bar{x}\ 0$, where $x = \frac{1}{2}$.
- Two sixfold sets of oxygens in

$$xyz; \bar{y}x-y, \frac{1}{3}-z; y-x, \bar{x}, \frac{2}{3}+z;$$

$$yx\bar{z}; \bar{x}, y-x, \frac{1}{3}-z; x-y, \bar{y}, \frac{2}{3}-z,$$

where the parameter values are:

	x	y	z
O ₁	0.446	0.147	0.473
O ₂	0.554	0.853	0.473

In this structure, cerium is coordinated to either oxygens—four at 2.30Å and four at 2.66Å—in such a manner as to form open oxygen-lined channels along the hexagonal axis. The presence of zeolitic water in these channels [$XPO_4(0-0.5H_2O)$] is probably necessary to stabilize the structure.

Monoclinic modification. Four molecules of XPO_4 occupy the unit cell. Cell constants and densities for the isomorphous series are as shown in Table II. The space group is $C_{2h}^2-P2_1/n$. The atoms are all in fourfold general positions, namely, $\pm(xyz; \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z)$. The structural parameters, in fractions of the unit cell, are given in Table III for $CePO_4$ as a representative of the

TABLE I.

XPO_4	a_1 (Å)	a_2 (Å)	a_3/a_1	ρ g/cm ³
LaPO ₄	7.081±0.005	6.468±0.008	0.9134	4.122
CePO ₄	7.055±0.003	6.439±0.005	0.9127	4.193
NdPO ₄	6.98 ±0.01	6.34 ±0.02	0.9083	4.328

TABLE II.

XPO_4	a_1 (Å)	a_2 (Å)	a_3 (Å)	β	ρ g/cm ³
LaPO ₄	6.89±0.02	7.05±0.02	6.48±0.02	103° 34' ±15'	5.087
CePO ₄	6.76	7.00	6.44	103° 38'	5.234
PrPO ₄	6.75	6.94	6.40	103° 21'	5.344
NdPO ₄	6.71	6.92	6.36	103° 28'	5.500

TABLE III.

	x	y	z
Ce	0.292	0.156	0.083
P	0.292	0.156	0.581
O ₁	0.211	0.990	0.423
O ₂	0.374	0.323	0.464
O ₃	0.467	0.786	0.765
O ₄	0.116	0.235	0.680

series. The cerium atom is coordinated to eight oxygens—four at an average distance of 2.37Å—and four more at 2.66Å. Though the coordination distances are closely analogous to those in the hexagonal structure, the arrangement is such as to form a tightly packed structure. In consequence, there is an unusual difference in the densities of the two modifications of XPO_4 , the monoclinic being about 25 percent heavier than the hexagonal form.

A detailed account of these investigations will be published later.

Evidence for the Planar Structure of the Urea Molecule

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August 11, 1948

FROM x-ray data on crystals of urea¹ it is known that the heavy atoms, C, N, O, of each molecule lie in a plane and have symmetry C_{2v} , whereas the positions of the H atoms, too light to scatter x-rays, must be inferred. Though considerations of resonance² in the urea molecule, giving each of the two C—N linkages approximately 20 percent double-bond character, leads to favoring an entirely planar structure, the only published vibrational analysis³ has employed a model in which the H atoms lie in planes perpendicular to the plane of the remaining atoms. We believe that evidence from infra-red spectra obtained by directing plane-polarized radiation through oriented urea crystals provide support for the planar structure.

If the urea molecule possesses either of the configurations described above, the point-group for the molecule is C_{2v} . Furthermore, urea crystallizes in the tetragonal system with space-group $V_8^2(P4_2/m)$ and two molecules per unit cell;⁴ the molecules are at sites having symmetry C_{2v} . Halford's method⁴ is considered to yield valid selection rules for molecular crystals and, when applied to the data for urea, indicates that the molecule in the crystal should give rise to the same active frequencies as the free molecule. There should be 6 modes belonging to the totally symmetric representation (A_1) if the molecule is non-planar and 7 if planar. Since the crystal is uniaxial, there will be but two principal directions in which there will be a change of electric moment during a molecular vibration; modes belonging to A_1 will be polarized along the tetragonal axis, while the remaining active representations will have modes polarized in the plane perpendicular to this axis. We

should thus expect 6 or 7 fundamental modes polarized A_1 , depending on the configuration, but only if 7 are accounted for can the results be interpreted with any certainty.

Samples of oriented urea crystals were prepared by evaporation of urea from a methanol solution onto a AgCl plate. The evaporation was controlled by placing at one edge of the plate a heated transite rod; the crystals grew with the tetragonal axis parallel to the changing thermal gradient thus produced.

Assuming for the moment that urea is planar, representation A_1 will contain three groups of modes: two symmetrical H stretches; modes principally C—O stretch, symmetrical N—C—N bent and stretch; and two symmetrical H bends. The H stretch modes occur in a region (about 3200 cm^{-1}) where the resolving power of our instrument is inadequate, so that polarization data is poor. In the non-planar model only one of these modes should be active. We found two bands polarized A_1 at 1680 and 546 cm^{-1} , assignable to the C—O stretch and N—C—N bend, respectively. The N—C—N stretch has been found at 1010 cm^{-1} but is too weak to give good polarization data. Raman work,⁵ however, provides ample evidence for this assignment. These three modes would be polarized similarly in the non-planar structure. The most crucial data concerns the H bends, only one of which would be expected to be active in the non-planar model. We found two bands at 1160 and 1590 cm^{-1} polarized along the tetragonal axis and attributable to these modes. It is true that all first overtones, as well as certain combinations, will be polarized A_1 , but none of the frequencies observed by us or by other investigators would be expected to contribute to the spectrum at the frequencies listed above.

Our ability to account satisfactorily for 7 fundamental frequencies polarized A_1 leads us to choose the entirely planar structure for the urea molecule in the crystal.

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¹ R. W. G. Wyckoff, *Zeits. f. Krist.* **81**, 102 (1932); R. W. G. Wyckoff and R. B. Corey, *ibid.* **89**, 462 (1934).

² L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1939), p. 212f.

³ L. Kellner, *Proc. Roy. Soc.* **177A**, 546 (1941).

⁴ R. S. Halford, *J. Chem. Phys.* **14**, 8 (1946).

⁵ For example, J. W. Otvos and J. T. Edsall, *J. Chem. Phys.* **7**, 632 (1939).

Polarization of Raman Lines of *s*-Dichloroethane

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July 30, 1948

IN a recent paper Gwinn and Pitzer¹ use the *s*-dichloroethane frequency assignments of Wu² with the exception that a C_2 (staggered configuration) rather than a C_{2v} (eclipsed configuration) model is taken as one of the two forms. Ananthakrishnan's³ evaluations of the 123- cm^{-1} and 1206- cm^{-1} lines as depolarized are not consistent with this C_2 assignment, however. Other investigators⁴ have reported polarization on dichloroethane but only Anantha-

krishnan has evaluated the 123- cm^{-1} line and his work was qualitative. The C_2 configuration, in which the 123- cm^{-1} line is polarized, is similar to the C_{2v} configuration, in which the 123- cm^{-1} line would be depolarized, differing only in an internal rotation of 60°. It would not be expected, therefore, that the 123- cm^{-1} line, corresponding to the torsional vibration, would be strongly polarized. Since the 123- cm^{-1} line is somewhat obscured by the background from the exciting line, it is not surprising that the other investigators did not obtain polarization data, nor is it unlikely that a qualitative estimate of polarization, where the background intensity is high, might be in error if the polarization is not pronounced. The 1206 line is reported as depolarized by Ananthakrishnan and as polarized ($\rho=0.36$) by Cheng.³ In order to assign the polarization of these lines definitely, the writers have made a quantitative determination of the polarization.

The sample of dichloroethane obtained from Eastman Kodak Company was purified by washing with sulfuric acid, steam distilling, drying over MgSO_4 , and finally distilling into the Raman tube through a thirty-theoretical-plate fractionating column. A Steinheil GH type spectrograph with $f:10$ collimator and $f:3$ camera was used with a slit of 0.017 mm. The method used to obtain polarization was a combination of schemes either cited or described by Glockler and Baker.⁴ Illumination was furnished by two G.E. AH11 mercury arcs lying in a plane inclined 45 deg. to the vertical. Wratten 2A gelatin filters and baffles to eliminate light not perpendicular to the Raman tube were interposed between the arcs and the Raman tube. A quartz Wollaston prism with its axis inclined 45 deg. was placed between the collimator lens and the first prism of the spectrograph. Thus a single exposure produced two representations of the spectrum, one above the other and shifted slightly, in which the polarized lines appeared less intense in one representation than in the other. Differential reflection at the prism surfaces was eliminated by the device of inclining the plane of illumination and the Wollaston prism at an angle of 45 deg. Spectra were recorded on Eastman 103 H spectroscopic plates with exposure time varying from 6 to 24 hours. Intensity calibrations were placed on each plate by means of a rotating stepped sector disk, and intensity traces of plates were made with a microphotometer of our own design. Wave number assignments were taken from the work of Ananthakrishnan.³ A graph was obtained by plotting the photometer reading of the intensity calibration at the frequency of the particular line against the intensity of the light that produced the calibration. Line intensities were

TABLE I.

cm^{-1}	ρ	cm^{-1}	ρ	cm^{-1}	ρ
123	0.63	880	0.88	1302	0.45
263	0.31	940	0.26	1429	0.82
302	0.40	989	P^*	1440	D^*
411	0.81	1052	0.47	2844	P^*
654	0.18	1144	D^*	2872	P^*
675	D^*	1206	0.65	2956	0.23
754	0.23	1262	D^*	3002	D^*

* This line was too weak for quantitative evaluation of ρ . P (polarized) or D (depolarized) represents a qualitative estimate.