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Infrared Absorption Spectra of Phosphine

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The 10μ absorption region of PH_3 has been resolved into three bands, a pair with centers at 1121 cm^{-1} and 992 cm^{-1} in which the line intervals are approximately 11 cm^{-1}, and a single band at 990 cm^{-1} with line intervals of approximately 8.5 cm^{-1}. The 4.3μ band has intervals of approximately 8.5 cm^{-1} and its center is at 2327 cm^{-1}. All apparently have zero branches, as do the two higher frequency bands at 3428 cm^{-1} and 4541 cm^{-1}. No absorption was observed between 16μ and 22μ. The two parallel type bands may be identified by comparison with the pure rotation spectrum observed by Randall and Wright. They are the ones at 990 cm^{-1} and 2327 cm^{-1}. The doubling observed in the corresponding bands of NH_3 does not appear here; hence the phosphorus atom cannot pass readily through the plane determined by the three hydrogen atoms. The perpendicular type bands have intense central maxima, and do not show an intensification of every third line as in NH_3. This indicates that PH_3 behaves like a spherical top. The moment of inertia about the axis of symmetry and the interatomic distances cannot be determined precisely until information is available concerning the coupling of rotation and vibration.

THIS study of the infrared bands of phosphine was undertaken not only for the information which it might yield regarding PH_3 but also in the hope that it might throw some further light upon the problem of ammonia. It is quite certain that the form of the NH_3 molecule is a low pyramid with the three hydrogen atoms located at the corners of its equilateral triangular base, thus constituting one of the simplest axially symmetrical systems. The spectrum is extensive and fairly well known, but its correlation with the intramolecular motions is not yet complete. Should PH_3 prove to be similar mechanically, then the points of correspondence and of difference in the two spectra might assist in the problem of interpretation for both.

The spectrum of phosphine has been mapped very accurately and completely by Robertson and Fox,[1] but with a resolution not quite adequate to show conclusively the character of the different bands. The most striking feature reported by them is a pair of intense bands near 10μ with zero branches separated by about 130 wave numbers. There is a temptation to correlate this group at once with the well-known double band of NH_3 at 10μ where the splitting results from the two minima in the potential energy function on opposite sides of the base plane. This would suggest that the corresponding minima for PH_3 must be separated by a very low potential barrier, since the apparent splitting is large, and hence that the phosphorus atom lies very near to the plane of the hydrogen atoms. A more intimate study of these bands however shows that this conclusion is not justified, and that the correspondence with the NH_3 band is entirely superficial.

EXPERIMENTAL

A supply of PH_3 was generated by dropping 50 percent KOH solution upon crystals of phosphonium iodide contained in a flask which had been initially evacuated. The evolving gas was passed through P_2O_5 and CaOH, and then frozen in a trap immersed in liquid air. A first fraction was discarded. After a sufficient amount had collected the generating flask was cut off and part of the phosphine vaporized into a storage reservoir with a mercury manometer. The remainder was also discarded. In withdrawing a sample for use a sufficient quantity was always frozen out in the trap, and then allowed to vaporize to the desired pressure in the previously evacuated absorption cell. Then, after the stopcocks on the cell had been closed, the gas remaining in the connecting tubes was frozen once more and returned from the trap to the reservoir. With this procedure very little trouble was experienced as long as the initial vacua were sufficiently good.

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[1] Robertson and Fox, Proc. Roy. Soc. **A120**, 161 (1928).

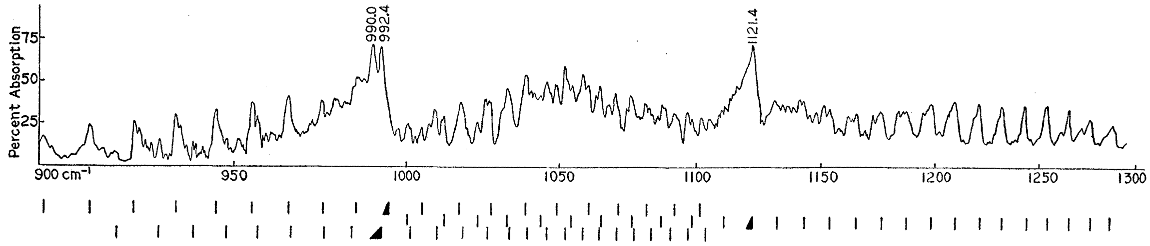

FIG. 1. The 10μ bands of PH_3.

A trace of air is instantly indicated by a bright flame which leaves a solid deposit upon the cell windows and greatly reduces their transmission. Two absorption cells were used, one 11 cm long with windows of NaCl, and one 2.5 cm long with KBr windows. Two spectrometers were also available, one being completely enclosed so that CO_2 could be excluded from the optical path. Unfortunately this one had a less effective optical system and gave only moderate resolution.

The structure observed in the 10μ region is shown in Fig. 1, the curve representing absorption of 11 cm of gas at about 30 cm pressure. The second order of a 1200 line grating was used. It is clear that the pattern does not consist simply of a pair of parallel type bands. The two strong maxima at 992 cm^{-1} and 1121 cm^{-1} suggest zero branches, but the former is accompanied by a close neighbor at 990 cm^{-1}. Upon a reduction of the gas pressure to 2 cm all the weaker portions of the structure vanish, but these three peaks persist with approximately equal intensities. On both high and low frequency sides of the region lesser absorption maxima occur at almost equally spaced intervals. They do not have the appearance of simple rotation lines, however. Near the center many poorly resolved maxima are seen. An attempt has been made to assign all of the strong lines to three band series, although this may not be entirely convincing. The bands are indicated diagrammatically below the curves. The two associated with the centers at 992 cm^{-1} and 1121 cm^{-1} have approximately equal spacing of about 11 cm^{-1}, while the intervals in the third band are only about 8.5 cm^{-1}, showing that it must be of quite a different character. The positions of these lines and their wave-number differences are given in Table I. It would seem as if the irregularities are rather greater than would have been expected even when account is taken of the effects of overlapping of the three bands, and of upper stage components due to absorption by excited molecules.

TABLE I. *The 10μ bands.*

Line No.	ν	$\Delta\nu$	ν	$\Delta\nu$	ν	$\Delta\nu$
−8	919.5	9.6	913.0	10.5	1030.8	11.5
−7	929.1	10.2	923.5	10.5	1042.4	10.5
−6	939.3	8.9	934.0	10.8	1052.8	11.6
−5	948.2	8.2	944.8	10.2	1064.4	11.4
−4	956.4	9.2	955.0	9.7	1075.8	11.2
−3	965.6	8.9	964.7	9.6	1087.0	10.9
−2	974.5	15.5	974.3	18.1	1097.9	10.6
−1					1109.5	11.9
0	990.0		992.4		1121.4	
+1	1000.7	10.7	1005.0	12.6	1130.5	10.1
+2	1009.1	8.5	1015.8	10.8	1142.2	11.7
+3	1017.6	8.5	1026.5	10.7	1153.3	11.1
+4	1025.3	7.7	1036.9	10.4	1164.2	10.9
+5	1032.4	7.1	1048.6	11.7	1175.2	11.0
+6	1038.9	6.5	1060.0	11.4	1186.7	11.5
+7	1045.6	6.7	1070.0	10.0	1198.1	11.4
+8	1051.6	6.0	1080.2	10.4	1209.0	10.9
+9	1058.0	6.4	1090.8	10.6	1220.3	11.3
+10	1064.4	6.4	1101.3	10.5	1231.4	11.1

The question must be raised whether or not these three bands are all fundamentals. In a symmetrical molecule the harmonic of a perpendicular type band is double, and consists of one perpendicular and one parallel component, slightly separated. This suggests the situation at 990 and 992 cm^{-1}. We have taken observations through the region from 16μ to 22μ with the short cell and found no positive evidence of absorption, although a band of the required intensity could hardly have escaped detection. Dr. Wright has also been kind enough to make a search near 20μ with the large grating, using reststrahlen for isolating the region and his results are also negative. The absence of low frequency bands leaves no alternative to the assignment of three fundamental frequencies at 990, 992 and 1121 cm^{-1}.

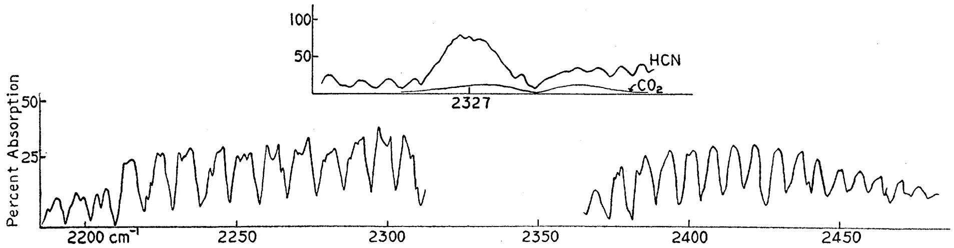

FIG. 2. The band at 4.3μ.

A second region of intense absorption is found at 4.3μ. Robertson and Fox have correlated this with the 3μ band (ν_1) of NH_3. The middle portion of this band is almost completely cut out by the very strong atmospheric CO_2 absorption, but the two wings are shown in the lower curve of Fig. 2 as mapped with a 4800 line grating and a slit including about one wave number. The upper curve of Fig. 2 shows the same band as measured with the enclosed spectrometer containing air almost free of CO_2. The background curve taken with the absorption cell removed shows only a slight indication of the CO_2 doublet. The center of the rather broad zero branch lies at 2327 cm^{-1} and the spacing of the rotation lines is about 8.5 cm^{-1}. The structure suggests a parallel type band as expected, with some complications perhaps from upper stage transitions. The line positions and intervals are shown in Table II.

Two weaker bands have been observed with low resolution, one at 2.9μ (3428 cm^{-1}) and the other at 2.2μ (4541 cm^{-1}). The contours look much alike and both show intense zero branches.

TABLE II. *The 4μ band.*

Line No.	ν	$\Delta\nu$	Line No.	ν	$\Delta\nu$
0	2327		−2	2307	
+5	2370		−3	2298	9
+6	2377	7	−4	2290	8
+7	2386	9	−5	2281	9
+8	2394	8	−6	2272	9
+9	2401	7	−7	2262	10
+10	2408	7	−8	2253	9
+11	2415	7	−9	2244	9
+12	2422	7	−10	2233	11
+13	2430	8	−11	2224	9
+14	2437	7	−12	2215	9
+15	2443	6			
+16	2450	7			

DISCUSSION

If it be assumed that the PH_3 molecule has the form of a symmetrical pyramid, there should be two fundamental bands of the perpendicular type and two of the parallel type, the former with many zero branches, and the latter with one or at most two. The line spacing must be the same for both parallel type bands, and the same as that of the pure rotation spectrum. It seems reasonable to interpret the band at 2327 cm^{-1} as ν_1, the higher frequency parallel vibration; ν_3 must then be the band at 990 cm^{-1}. This assignment is confirmed by the observations of Randall and Wright[2] upon the pure rotation spectrum, which were made while this study was in progress upon a sample of our gas. They found an average interval of 8.7 cm^{-1} between four successive lines, and no indication of the doubling which is characteristic of NH_3. It is necessary to conclude that the bands at 992 and 1121 cm^{-1} must represent the independent perpendicular vibrations ν_2 and ν_4. The higher frequency bands seem to involve combinations of ν_1 with ν_4, neither of the other frequencies appearing as differences.

The spacing in the parallel bands provides a measure of the moment of inertia about an axis normal to the symmetry axis which is in good agreement with the value 6.22×10^{-40} computed by Randall and Wright. The absence of observable doubling in these bands, and in the pure rotation lines, shows that the pyramid cannot be extremely low as at first supposed. A precise determination of the height of the pyramid, and of the moment of inertia with respect to the axis of symmetry, will be possible only when more in-

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[2] Randall and Wright, Phys. Rev. **44**, 391 (1933).

formation is available with regard to the coupling between rotation and the perpendicular vibrations.

Of the six bands which have been observed, every one appears to have an intense zero branch. None shows the form usually characteristic of a perpendicular band attributable to an axially symmetrical molecule, and there is no indication of an accentuation of intensity in every third line, such as appears in perpendicular bands of NH_3 and the methyl halides, indicative of the equilateral triangular arrangement of the hydrogen atoms. These facts may be harmonized by supposing that PH_3 behaves like a *spherical* top, i.e., as if its three moments of inertia were all equal. This would result in a superposition of the various components of any perpendicular band, effectively masking variations in their relative intensities, and producing a single sharp central maximum. If rigid coupling between rotation and vibration be assumed, so that the apparent equality of moments of inertia becomes real, then the molecular dimensions could be computed at once. The distances between hydrogen atoms would be 1.9×10^{-8} cm, from the phosphorus atom to any hydrogen atom 1.5×10^{-8} cm, and the height of the pyramid would be 1.0×10^{-8} cm. While these values are not unreasonable it should be emphasized that the apparent moment of inertia with respect to the figure axis may be appreciably different from the actual one, and that these dimensions cannot be considered as final. The difference of spacing in the parallel and perpendicular type bands is an obvious indication that vibration and rotation are not rigidly coupled.

Raman spectra, if available, might be expected to contribute important information regarding PH_3.