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function of the quotient

$$(\gamma_1 p_1{}^0 - \gamma_2 p_2{}^0)/x_3 \qquad (12)$$

in which both numerator and denominator approach zero. Any reasonable representation of activity coefficients shows that the numerator can be developed with respect to $x_2 - x_{2az}$ and x_3. The slope of the distillation lines again turns out to be a continuous function of the ratio $(x_2 - x_{2az})/x_3$.

It may be concluded that, contrary to Schreinemakers assertion, the distillation lines in the vicinity of corner points and azeotropic points are *not* tangent to the boundary lines.

The careful measurements of Reinders and de Minjer[2a] fully confirm this conclusion although these authors accepted[2b] Schreinemakers' theorem and, not quite successfully, attempted[2c] to represent their results in accord with Schreinemakers.

The Microwave Spectra and Molecular Structure of Phosphorus and Arsenic Trichloride*

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(Received May 25, 1950)

The pure rotational spectra of PCl₃ and AsCl₃ have been observed in the microwave region, and the observed fine structure has been partially explained. The distance P—Cl is 2.043±0.003A and the angle Cl—P—Cl is 100° 6'±20'. The distance As—Cl is 2.161±0.004A and the angle Cl—As—Cl is 98° 25'±30'.

THE pure rotational spectra of phosphorus and arsenic trichloride have been observed in the microwave region with all possible combinations of the chlorine isotopes. The results are listed in Tables IA, B and C.

Because J is large (4—6) and a number of different K values occur, the quadrupole interactions of the three chlorine nuclei split each transition into several hundred lines, even after selection rules and the degeneracies due to the symmetry of the molecule are taken into account. The case of AsCl₃ is further complicated by the quadrupole interaction of the arsenic nucleus. These lines were not resolved, although the lines appeared broader than those of the majority of molecules which have been investigated by microwave spectroscopy. The main AsCl₃ line, for example, was about 20 megacycles wide at about 0.05 mm pressure, and showed a double peak at reduced pressures and Stark voltages.

From the frequencies of the $J=4-5$ transition of PCl₃³⁵ and PCl₃³⁷, and the $J=5-6$ transitions of AsCl₃³⁵ and AsCl₃³⁷, the bond angles and internuclear distances were calculated† (method I of Table II), and are compared with other determinations in Table II. Using these parameters the expected spectrum of PCl₂³⁵Cl³⁷ was calculated and compared with the observed spectrum (Fig. 2). Agreement was satisfactory, and it was decided to calculate the two structural parameters of PCl₃ from the frequency of the PCl₃³⁵ line and the separation between the two lines of PCl₂³⁵Cl³⁷ corre-

sponding to $K=1$ in the limiting (oblate) symmetric rotor (method II of Table II). Since zero-point vibrations enter in a different way into the calculation of molecular structure by the two above methods, the difference between the results obtained (see Table II) probably indicate roughly the magnitude of errors due to zero-point vibrations. Method II, using an asymmetric isotopic species, should be particularly helpful in eliminating uncertainties due to zero-point vibrations in symmetric tops containing three hydrogens and is being applied in this laboratory to CH₃Cl.

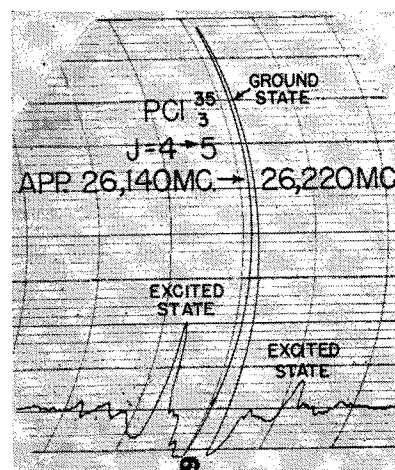The angle Cl—As—Cl is found to be slightly smaller than the angle Cl—P—Cl in keeping with the tendency

Fig. 1. PCl₃³⁵, $J=4-5$ at dry ice temperature.

* Work supported jointly by the Signal Corps and the ONR.
† Thanks are due to Mr. Henry Friedman for most of the computations.

TABLE IA. Microwave absorption lines of phosphorus trichloride.

Molecule	Transition	Frequency (megacycles/sec.)
PCl_3^{35}	$J=4\to5$, ground state	26,171[a]
	$J=4\to5$ excited vibrational states	$\begin{cases}26,190\\26,152\\26,210\end{cases}$
$PCl_2^{35}Cl^{37}$	$J=4\to5$	
	$4_{31}-5_{41}$	25,552[a]
	$4_{22}-5_{32}$	25,649
	$4_{13}-5_{23}$	25,716
	$\left.\begin{array}{l}4_{04}-5_{14}\\4_{14}-5_{24}\\4_{23}-5_{33}\end{array}\right\}$	25,725
	$4_{32}-5_{42}$	25,748
	$4_{41}-5_{51}$	25,971[a]

Several more weak lines were observed, attributable to excited vibrational states.

| $PCl^{35}Cl_2^{37}$ | $J=4\to5$ | 25,306 |
| PCl_3^{37} | $J=4\to5$ | 24,875[a] |

[a] These frequencies are subject to an error of ±1 mc. All others are only correct to within 10 Mc.

TABLE IB. Microwave absorption lines of arsenic trichloride.

Molecule	Transition	Frequency
$AsCl_3^{35}$	$J=4\to5$, ground state	21,472
	$J=4\to5$, excited vibrational state	21,426
	$J=5\to6$ ground state	25,767[a]
	$J=5\to6$ excited vibrational states	$\begin{cases}25,724\\25,675\end{cases}$
$AsCl_2^{35}Cl^{37}$	$J=5\to6$	25,308
		25,354
		25,381
		25,393
		25,411

Several more weak lines were observed, attributable to excited vibrational states.

$AsCl^{35}Cl_2^{37}$	$J=5\to6$	24,932
		24,973
$AsCl_3^{37}$	$J=5\to6$	24,536[a]

[a] These frequencies are subject to an error of ±2 mc. All others are only correct to within 10 Mc.

TABLE IC. Rotational constants of PCl_3 and $AsCl_3$.

PCl_3^{35}	PCl_3^{37}
$B_0=2617.1\pm0.1$	2487.5 ± 0.2
$AsCl_3^{35}$	$AsCl_3^{37}$
$B_0=2147.2\pm0.2$	2044.7 ± 0.3

TABLE II.

	Internuclear distance $M-X$ in Angstroms	Bond angle $X-M-X$
PCl_3		
Method I	2.044 ± 0.003	$99°\ 56'\pm20'$
Method II	2.041 ± 0.003	$100°\ 17'\pm20'$
Swingle[a]	$2.03\ \pm0.02$	$100°\ 30'\pm90'$
Pauling and Brockway[b]	$2.00\ \pm0.02$	$101°\pm2°$
Brockway and Wall[c]	$2.02\ \pm0.02$	$100°\pm2°$
Wierl[d]	$2.04\ \pm0.06$	$102°$
Sum of covalent radii	2.09	
$AsCl_3$		
Method I	2.161 ± 0.004	$98°\ 25'\pm30'$
Swingle[a]	$2.17\ \pm0.02$	$99°\pm2°$
Pauling and Brockway[b]	$2.16\ \pm0.03$	$103°\pm3°$
Brockway and Wall[c]	$2.18\ \pm0.03$	$101°\pm40'$
Sum of covalent radii	2.20	

[a] S. M. Swingle, quoted by P. W. Allen and L. E. Sutton, Acta Crystallographica 3, pt. 1, 46 (1950).
[b] L. Pauling and L. O. Brockway, J. Am. Chem. Soc. 57, 2684 (1935).
[c] L. O. Brockway and F. T. Wall, J. Am. Chem. Soc. 56, 2373 (1934).
[d] R. Wierl, Ann. d. Physik 8, 521 (1931).

noted by Pauling[1] for heavier elements to have smaller bond angles. Previous measurements on these molecules had reversed the relative size of these angles, but there is reasonable agreement with the electron diffraction measurements on the whole. The P—Cl distance is found to be somewhat longer than the previously accepted value, indicating less drastic shortening of the bond by double bond and ionic character, but it is still shortened relatively more than the As—Cl bond. It is to be expected that the double bond character would shorten the P—Cl bond relatively more than the As—Cl bond,[2] as was observed but ionic character would produce more shortening of the As—Cl bond.

Both PCl_3 and $AsCl_3$ have several normal vibrational

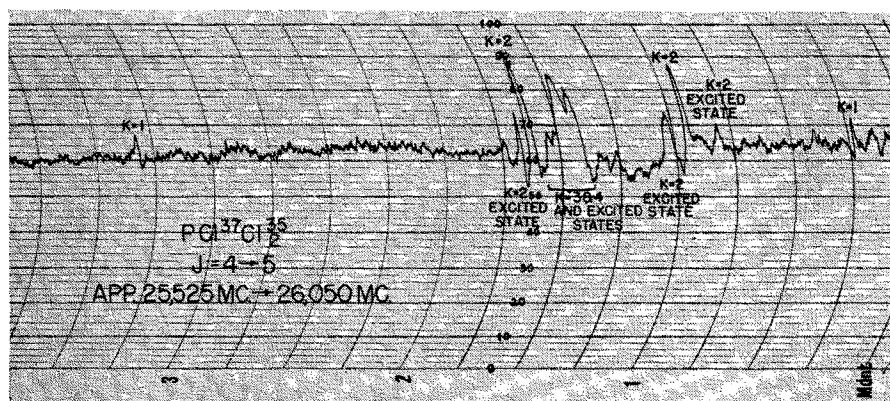FIG. 2. $PCl_2^{35}Cl^{37}$, $J=4-5$ at dry ice temperature.

[1] L. Pauling, The Nature of the Chemical Bond (Cornell University Press, Ithaca, New York, 1940), p. 80.
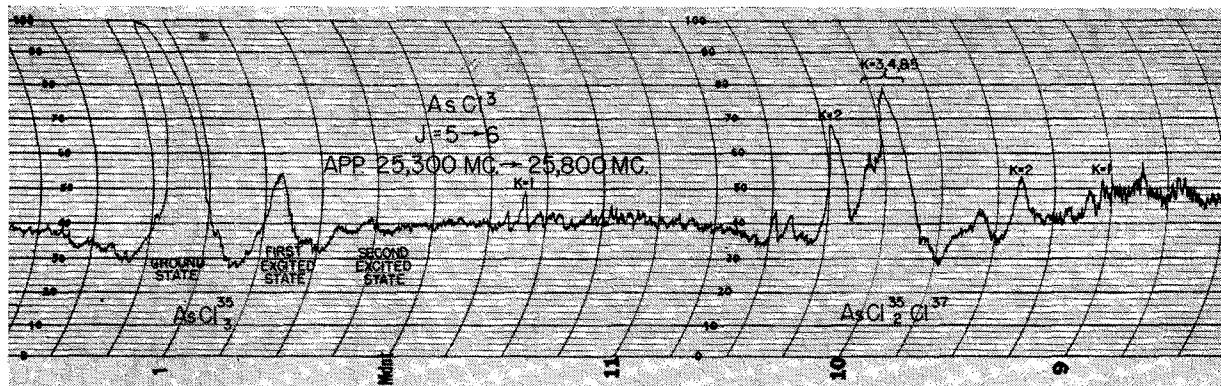[2] See reference 1, p. 235.

FIG. 3. AsCl$_3^{35}$ and ClsCl$_2^{35}$Cl^{37}, $J=5-6$ at room temperature.

modes of frequency sufficiently low to make observable lines due to the excited states. Several of these were measured as listed in Tables IA and B. These were shown not to be hyperfine structure in PCl$_3$ by the effect of temperature changes on their relative intensity. This was also supported by the frequency spacing and relative intensity in the two cases where more than one excited state of the same vibration was observed. The remaining expected vibrational states apparently have such a small vibration-rotation interaction that they were observed as part of the rather broad ground state line. From the relative intensities at room and at dry ice temperature, the two lines of higher frequency than the ground state line of PCl$_3$ (see Fig. 1) are tentatively assigned to the vibration of frequency ω_4,[3] and the single one of lower frequency than the ground state line to ω_2. The observed excited states in AsCl$_3$ (Fig. 3) are assigned to ω_2. These assignments are not completely satisfactory because the observed intensity ratios indicate somewhat higher vibrational frequencies in all three cases.

[3] Following the nomenclature of G. Herzberg, *Molecular Spectra and Molecular Structure, II. Infrared and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945), p. 164.