Physics. -- *On the Crystal Structure of Methane.* II. By H. H. MOOY. Communication N°. 216*a* from the Physical Laboratory at Leiden). (Communicated by Prof. W. H. KEESOM).

(Communicated at the meeting of May 29, 1931.)

§ 1. *Introduction.* In a former communication [1]) we stated that solid methane has a cubic close-packed structure, side of the elementary cube at 20.5° K. 5.89 A.U.

We have now made an attempt to determine the spacegroup of this structure and the distance C-H in the methane molecule.

If we consider the four carbon atoms in the elementary cube to be crystallographically identical, and if we make the same assumption regarding the sixteen hydrogen atoms, then the only possible space-groups are T^2 and T_d^2 [2]). In both groups the coordinates of the carbon atoms are: 000, $\frac{1}{2}\frac{1}{2}0$, $\frac{1}{2}0\frac{1}{2}$, $0\frac{1}{2}\frac{1}{2}$ and those of the hydrogen atoms uuu, $u\bar{u}\bar{u}$, $\bar{u}u\bar{u}$, $\bar{u}\bar{u}u$, (fz).

For the methane molecule a tetrahedral as well as a pyramidal model has been proposed [3]).

It is remarkable that (with the assumption of crystallographical identity) the tetrahedral structure follows directly from the geometrical structure theory.

We may mention here that TELLER and TISZA [4]) recently solved the difficulty that the different moments of inertia of the methane molecule, resulting from the infra-red band analysis of methane [5]), could not be explained with the tetrahedral model on a quantum-mechanical basis [6]).

The values of ν coincide, except for planes $(pq0)$ and (pqr), for which the values are $\nu = 12$ and $\nu = 24$ respectively in the case of T^2 and $\nu = 24$, and $\nu = 48$ respectively in the case of T_d^2.

§ 2. *Experiments and calculations.* With the films described previously [1]) we were not sure about the intensities of the reflexions (220) and (400), as the corresponding lines coincided with lines from the copper rod. Therefore we made two exposures at 20.5° K where methane was solidified

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[1]) These Proceedings **34**, 550, 1931. Comm. Leiden N°. 213*d*.

[2]) Cf. Tables of MARK-ROSBAUD.

[3]) For a survey of the reasons in favour of the pyramidal model see V. HENRI, Chem. Rev. **4**, 189, 1927; for those in favour of the tetrahedral model G. GLOCKLER, J. Amer. Chem. Soc. **48**, 2021, 1926. Further literature references concerning this question: K. LONSDALE, Phil. Mag. **6**, 433, 1928, and J. K. MORSE, Proc. Nat. Acad. Sc. **14**, 166, 1928

[4]) E. TELLER und L. TISZA, Phys. Zs. **32**, 219, 1931.

[5]) J. P. COOLEY, Astrophys. Journ. **42**. 73, 1925.

[6]) W. ELERT, Zs. f. Ph. **51**, 6, 1928.

Intensities for various parameter values.

$h\,k\,l$	Q	ν	Intensity calculated, relative to (111) reflexion					Intensity observed
			$u=0$	$u=0.08$	$u=0.09$	$u=0.10$	$u=0.13$	
111	34.8	8	150	150	150	150	150	150
200	26.5	6	86	75^5	72	67^5	46^5	70
220	12.0	12	78	52^5	49^5	47	50	50
311	8.2	24	106	55^5	50	45^5	43	50
222	6.7	8	29	19^5	20	21^5	27	18
400	5.1	6	16^5	4	3	2	1	4
331	4.2	24	54^5	28	31	36	58^5	30
420	3.8	12 or 24	24^5 or 49	8.4 or 16^8	8.5 or 17	9 or 18	17 or 34	25
422	3.1	24	40	19^5	21	22	26	25
333 } 511 }	2.9	8	50	15	14^5	15	27	20
	2.9	24						
440	2.8	12	18	11	15	20	32	14
531	2.7	24 or 48	35 or 70	17 or 34	20 or 40	26 or 52	36 or 72	35
600 } 442 }	2.7	6	44	22^5	25	26	30	20
	2.7	24						

upon a silver rod. The thickness of the layer was 0.4^5 mm, both films were very clear and showed intense lines (about 1000 mA minutes, 26 kV). We used them to make a more differentiated estimation of the relative intensities.

The intensities to be expected theoretically were calculated with the usual formula:

$$I_h \sim \frac{1+\cos^2 2\vartheta}{\sin^2\vartheta\cos\vartheta} \cdot \nu_h \cdot \left|S_h\right|^2 = Q(\vartheta)_h \cdot \nu_h \cdot \left|S_h\right|^2$$

They have been evaluated for the values of u: 0, 0.08, 0.09, 0.10, 0.13.

§ 3. *Results.* Comparison of the observed intensities with the calculated ones shows that a rather satisfying agreement is obtained for values of u

of about 0.1. The value 0.09 seems to be the best, but an accurate determination of this parameter is impossible from our data for the following reasons. In the intensity formula mentioned above several factors have been omitted (DEBIJE-WALLER etc.), partly because they are not known exactly. It is generally assumed that they would give a very gradual change of the intensity as a function of the glancing angle. As regards the influence of the absorption in the sample we believe (under special circumstances) the assumption just mentioned not to be valid.

The value $u = 0.09$ corresponds to a distance C-H : 0.09 A.U., whereas from the moment of inertia $5.66.10^{-40}$ given by the infra-red band analysis follows C-H = 1.13 A.U. This suggests that the distance C-H is a bit smaller in the crystal phase than it is in the gas phase [1]).

In view of the observed intensities of the reflexions (420) and (531) one may conclude that the space-group of the structure is T_d^2.

I want to express my gratitude to Prof. Dr. W. H. KEESOM for the opportunity to carry out these investigations and for his continued interest during their course.

With pleasure I thank cand. phil. J. W. L. KÖHLER for his valuable help with the intensity calculations.

[1]) From the vapour pressure curve may be deduced C-H = 1,00 A. U ; see K. F. HERZFELD, Hdb. d. Physik 22, p. 479.