REDETERMINATION OF THE DEPOLARISATION OF LIGHT SCATTERING IN GASES AND VAPOURS.

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1. *Introduction.*

IN a previous communication to these *Proceedings*,[1] the author has discussed at length the question of the dependence of the observed value of the depolarisation on the finite convergence of the incident beam, when, as is usual in dealing with gases and vapours of small depolarisation, a condensing lens is employed to concentrate the light on the scattering medium. In view of the conclusion arrived at theoretically, and confirmed experimentally that *the depolarisation of the transversely scattered light measured at the focus is definitely higher than the genuine value,* the magnitude of the deviation depending in a perfectly determinate way on the convergence of the incident beam, it appeared to be highly important to take up a systematic redetermination of the depolarisation in the case of a number of gases and vapours because of the uncertainty that attaches to the values reported by previous experimenters who have partially or totally ignored the correction for the convergence of the incident beam. The present paper contains the results of the experimental study of more than a dozen gases and vapours. The values of the depolarisation show in many cases not only a definite departure from those reported by previous workers, but present certain new and interesting features which will be discussed in the course of the paper.

2. *Experimental Technique.*

By far the greater portion of the experimental study of the depolarisation of gases and vapours is due to the pioneer work of Lord Rayleigh in England, of Cabannes and his co-workers in France, and of Prof. Raman and his students at Calcutta. A critical review of the experimental technique of the different workers is given in Cabannes' book.[2] While Lord Rayleigh and Prof. Raman have employed metallic crosses of large capacity painted black inside, with suitable diaphragms to protect against parasitic light, Cabannes and his co-workers have mostly used smaller crosses made of glass

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[1] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1935, 2, 133.

[2] J. Cabannes, *La Diffusion Moleculaire de la Lumiere*, 1929.

with no diaphragms inside, and painted black externally. Although each technique has its own advantages, experience has shown the present author that the best arrangement is one in which the advantages of both the above modes of experimentation are sought to be combined. Towards this end, a cross in pyrex glass of over a litre in capacity was made with the following approximate dimensions. The tube taken was 4 cms. in diameter, and three of the four arms were about 20 cms. in length. The fourth arm opposite the observation side was much longer and was drawn out and bent up in the shape of a horn to the end of which was attached a pyrex stopcock for admission of gas into the cross. Although the use of diaphragms may not be very important when the photographic method is adopted for depolarisation measurements, accurate visual photometry is practically impossible unless the utmost precautions are taken to avoid parasitic light from entering within the field of observation. Suitable diaphragms of oxidised brass were therefore put in inside the cross. These diaphragms were made out of short lengths of thin brass tube one of the ends being closed by a thin brass plate having a central hole of ½ inch diameter. The surfaces of the diaphragms were rendered black by immersing them in an ammoniacal solution of copper carbonate. They were then rolled in thin asbestos paper and introduced into the arms of the cross. After fixing the positions of the diaphragms within the cross by a preliminary experiment, the open ends of the three arms were closed by fusing on flat pyrex plates (previously examined between crossed nicols for strain) in the way recommended by Martin.[3] The whole cross excepting the end windows was painted dull black externally. The complete eschewal of all traces of paint from within the cross ensured perfect freedom from contamination of the gases and vapours studied.

The cross was mounted on a stool provided with levelling screws and spirit level, and observations were made within a dark cabin into which sunlight was reflected by a single mirror Foucault heliostat. A Dallmeyer photographic lens of adjustable aperture, and focal length 1 foot fixed to the wall of the cabin served to concentrate the sunlight at the centre of the cross. The whole arrangement was such as to give an exceedingly nice background against which even the faintest tracks could be seen with but little difficulty.

All the gases were taken directly from commercial cylinders supplied by the Ohio Chemical and Manufacturing Co., and were guaranteed a high degree of purity. The scheme of the experimental arrangement is shown diagrammatically in the figure. The gases were admitted into the cross at atmospheric pressure through a tube of anhydrous P_2O_5 and a long plug

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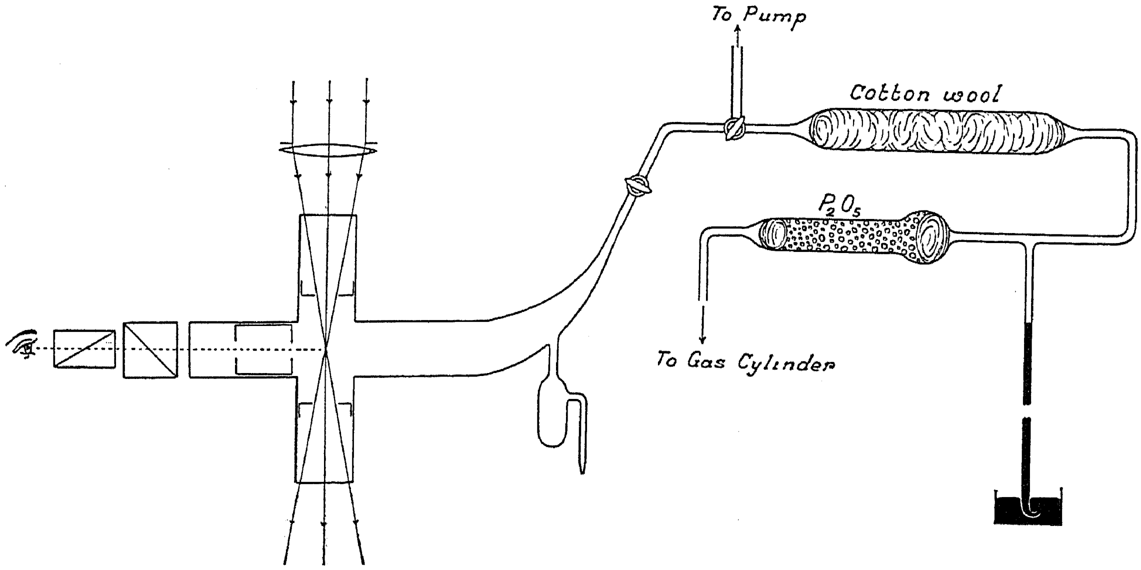
[3] W. H. Martin and S. Lehrman, *Jour. Phys. Chem.*, 1922, 26, 76.



of compressed cotton wool after evacuating the whole system by means of a Cenco Hyvac Pump. Rubber connections were avoided as far as possible to minimise leaks, and special care was taken to see that the system was perfectly leak-tight before commencing the experiments. Estimates of depolarisation were made visually by the usual Cornu method.

In the case of CCl_4, the technique adopted was slightly different. Extra-pure CCl_4, guaranteed to be free from CS_2, was refluxed with freshly distilled mercury for several hours and finally distilled at constant boiling point. A small quantity of the liquid was introduced into the bulb attached to the longer arm of the cross by means of the side tube and the latter was then sealed off. The CCl_4 was frozen in liquid air, and the cross was exhausted to the highest vacuum. The stopcock was then closed, and the liquid air bath removed. As the CCl_4 rises up to the room temperature, the vapour pressure is quite appreciable to give a scattering of sufficient intensity to make accurate measurements.

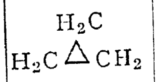
3. *Adjustments and Sources of Error.*

The accurate estimation of small depolarisation values with which one is confronted in the case of the majority of gases and vapours necessitates the utmost precautions to safeguard against various sources of error which tend to vitiate the observations. Unpolarised light diffused by the background is highly detrimental in the case of visual photometry as has been already pointed out. The error arising from this source is got rid of by the use of suitable diaphragms, and by viewing the two images of the track seen through the double image prism against the same background. Horizontality of the axis of the incident beam is very important, and is secured by setting the cross horizontal with the spirit level. Normality of the direction of observation to the axis of the incident track is easily secured when the container is cross-shaped. The principal section of the double image prism is set vertical by viewing an illuminated plumb line, and rotating the prism about a horizontal axis till the two images are entirely superposed.

The effect of the finite convergence of the incident beam is to enhance the value of the depolarisation, and the correction to be applied to the observed value under this head is given by $\theta^2/2$, where θ is the semi-angle of convergence. It may be remarked that the experimental results of Dr. I. Ramakrishna Rao[4] and the later work of Parthasarathy[5] require correction in this direction.

4. *Results.*

The table below gives the experimental results after being corrected for the convergence of the incident beam. An aperture of F/5·6 was employed in all cases and the correction required for the observed value can be easily seen to be 0·4%.

Gas		% Purity	Depolarisation
Methane	CH_4	96·5	0·34%
Ethane	C_2H_6	90	0·50%
Propane	C_3H_8	99·9	0·66%
N. Butane	C_4H_{10}	99	0·85%
Isobutane	C_4H_{10}	99	0·46%
Cyclopropane	 H_2C $H_2C \triangle CH_2$	99·5	0·52%
Propylene	C_3H_6	99·5	2·91%
Methyl Chloride	CH_3Cl	99·5	1·95%
Ethyl Chloride	C_2H_5Cl	99·5	1·49%
Carbon Tetrachloride	CCl_4	..	0·15%
Dimethyl Ether	$CH_3·O·CH_3$	99·95	1·20%
Argon	A	86	0·42%
Hydrogen Sulphide	H_2S	99·73	0·30%
Nitrous Oxide	N_2O	98	12·95%

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[4] I. R. Rao, *Ind. Jour. Phys.*, 1927, 2, 61.

[5] S. Parthasarathy, *Ind. Jour. Phys.*, 1932, 7, 139.

5. *Discussion of Results.*

As has been already remarked, the results of the author are, in many cases, entirely at variance with those of previous experimenters.

Methane.—We shall commence with methane, the leading member of the paraffin series. The first outstanding result of the investigation is that the genuine depolarisation factor of methane is considerably lower than what it has been till now assumed to be. While Cabannes gave the value 1·5% and Parthasarathy 1·12%, the actual value appears to be of the order of 0·3%. Considering the fact that the residual impurities in methane are most probably some of the higher hydrocarbons whose depolarisation factors are quite small, the observed depolarisation of methane seems to be quite genuine. Thus, for instance, if we assume that the 3·5% impurity is all ethane whose intensity of scattering is roughly thrice as great as that of methane, the observed depolarisation of methane will be affected only in the second place of decimals. It is not improbable that the source of this depolarisation is to be sought for in the existence of depolarised Raman scattering. The Raman Spectrum of methane shows an intense line at 2915 cm.$^{-1}$ corresponding to the total symmetric vibration of the molecule, which according to the observations of Bhagavantam[6] is depolarised to the extent of 8%, but possesses no rotational fine structure. On the other hand, the intense band at 3022 cm.$^{-1}$ is highly depolarised to the extent of 80%, and shows equispaced rotation lines on either side of it. Stuart[7] seems to be of opinion that this strongly depolarised vibration band would be responsible for a spurious depolarisation of the Rayleigh radiation to the extent of 0·1 to 0·5%, when one is working with white light as is usual in depolarisation measurements. Thus, in the present case where sunlight was employed, the photographic lens used for focussing the beam transmits the far violet end of the spectrum, say up to 3000 Å U. and the corresponding vibration scattering would fall well within the region of greatest visibility. If this view be correct, and a filter be employed which cuts off the entire violet and blue regions of the spectrum on the incident side, and another which cuts off the entire region beyond the green and yellow be employed on the observation side, we should expect the depolarisation of methane not to differ from zero. All these considerations lend strong support to the view that the Rayleigh scattering in the case of methane is completely polarised. This conclusion is in perfect accord with the observation of Bhagavantam,[8]

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[6] S. Bhagavantam, *Nature,* 1932, **129**, 830.

[7] H. A. Stuart, *Molekulstruktur,* 1934, p. 192.

[8] S. Bhagavantam, *Nature,* 1932, **130**, 740.

later confirmed by Lewis and Houston,[9] that even prolonged exposures extending over a week fail to bring out any rotation wings for the Rayleigh line in the case of methane. The assumption of the anisotropy of the carbon atom thus appears to be definitely uncalled for to explain the depolarisation of methane. In this connection, a redetermination of the depolarisation factor of the total symmetric vibration line would be of great interest, since, as has been remarked by Stuart,[10] Bhagavantam's value appears to be too high.

Higher homologues.—The second important outcome of the experimental work is the fact that as we pass from methane to the higher homologues, the depolarisation shows a steady increase from 0·34% in the case of methane to 0·85% in the case of normal butane. Cabannes, however, arrived at the conclusion that the depolarisation does not change appreciably from one member to another, but the conclusion of the author is supported by the observations of Parthasarathy.[11] It thus appears that anisotropy is not wholly unconnected with the geometric form of the molecule. That this is so is again shown by the fact that while normal butane has a depolarisation of 0·85%, for isobutane the depolarisation drops down to 0·46%, in conformity with the greater symmetry of the molecule.

Other hydrocarbons.—Cyclopropane, whose depolarisation does not appear to have been measured by any of the previous workers, shows a very small value, which is not surprising in view of the known low depolarisation of Cyclohexane. Propylene shows a high depolarisation, as would be expected on account of the double bond.

Methyl and Ethyl chlorides.—Methyl chloride is definitely more anisotropic than ethyl chloride, contrary to the observations of Cabannes. The large increase in the value of the depolarisation which results from the substitution of one atom of hydrogen in methane by an atom of chlorine is very significant. While this observation is in qualitative agreement with the results of Parthasarathy, it is in total disagreement with those of Cabannes who finds very little change between the depolarisation factors of methane and methyl chloride.

Carbon tetrachloride.—The depolarisation of the tetrahedral molecules has remained for a long time a puzzling and unintelligible problem. For CCl_4, the depolarisation in the vapour state was estimated to be 0·77% by Cabannes, 0·5% by Ramakrishna Rao and 0·62% by Parthasarathy. Stuart[12] finds these values to be wholly incompatible with

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[9] M. Lewis and W. V. Houston, *Phys. Rev.*, 1933, 44, 903.

[10] H. A. Stuart, *loc. cit.*, p. 329.

[11] S. Parthasarathy, *loc. cit.*

[12] H. A. Stuart, *loc. cit.*, p. 193.

his measurements of the Kerr-constant of CCl_4 from which he concludes that the departure of the molecule from spherical symmetry is imperceptibly small, and would not be responsible for a depolarisation of the vapour exceeding 0·15%. The author's result stands in good agreement with this value. It should, however, be pointed out that the experimental value itself gives only an upper limit for the depolarisation, since in the actual measurements, all possible sources of error only tend to enhance the genuine value, and also because, here, one is well-nigh at the limit of accuracy in depolarisation measurements. As Stuart[13] has pointed out, the investigation of the fine structure of the Rayleigh line, as well as that of the total symmetric vibration Raman line in the case of CCl_4 vapour, would be of extreme interest in this connection.

It might on first consideration seem conceivable that a small anisotropy would be caused in the case of CCl_4 by the presence in one and the same molecule of chlorine isotopes of different masses (35 and 37). However, on account of the physical similarity of isotopes with nearly equal masses, the magnitude of this anisotropy would appear to be vanishingly small.

Argon.—The case of argon demands special explanation. In the first place, it will be noticed that the sample employed is very impure. The most probable impurity appears to be nitrogen and if it be assumed that the 14% impurity is all nitrogen, it follows from simple calculation that the depolarisation of argon is not sensibly different from zero, as the depolarisation of nitrogen is about 3%, and the relative scattering powers of argon and nitrogen are not very different.

The reality or otherwise of the depolarisation of the rare gases has been an unsettled issue. Experimentally, Cabannes appears to have found a small depolarisation of 0·5% for argon, krypton and xenon, while for neon the upper limit is given as 1%. The case of helium is again very uncertain, the upper limit for its depolarisation being given as 6·5% by Lord Rayleigh and as 3% by Parthasarathy. From the theoretical standpoint these values are difficult to comprehend. The ground state of the atoms of the rare gases is the ^1S state, and theory indicates that the scattered radiation corresponding to such terms should be linearly polarised. Placzek[14] has therefore expressed himself as very sceptical of the reality of these depolarisation values. The author's experimental results indicate that the finite depolarisations reported by earlier workers are not trustworthy. However, this conclusion is only tentative, and the author hopes, before long, to take up

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[13] H. A. Stuart, *loc. cit.*, p. 194.

[14] G. Placzek, *Quanten Mechanik der Materie und Strahlung*, Teil II, Leipzig, 1934, p. 259.

the purification of argon, and a direct experimental test of the anisotropy of this gas, as well as of other rare gases, particularly helium.

Hydrogen sulphide.—H_2S shows an extremely small depolarisation (0·3%) the reality of which however is quite definite. Of the previous workers, Ramanathan estimated the depolarisation as 1% and Parthasarathy as 0·93%. The depolarisations for other hydride molecules such as HCl, HBr, NH_3, etc., as estimated by Parthasarathy are also of the same order of magnitude. In view of the author's low value for H_2S, it would seem that the other values would also be similarly low. These very low values are not difficult to understand, since, as Stuart[15] remarks, "die Hydridmoleküle HCl, H_2O, H_2S und NH_3, die wir als Pseudoedelgase mit mehreren unpolarisierbaren H-Kernen in einer geminsamen Elektronenwolke auffassen können, trotzdem sie elektrisch unsymmetrisch sind, d.h. ein elektrisches Moment besitzen, einen sehr hohen optischen Symmetriegrad haben".

In conclusion, the author wishes to record his grateful indebtedness to Professor Sir C. V. Raman for valuable guidance and suggestions in the course of the present work.

6. *Summary.*

It is pointed out that the existing depolarisation data of gases and vapours are gravely defective, and a redetermination of the values has been made with improved experimental technique. The results obtained are strikingly different from those of previous workers, and afford at the same time a natural explanation of many of the existing anomalies. The genuine depolarisation of methane appears to be only of the order of 0·3% which is in all probability to be attributed to the highly depolarised vibration Raman lines. The depolarisation shows a steady increase as one goes to the higher members of the homologous series, but the values in all cases are much smaller than they were hitherto assumed to be. Cyclopropane shows a very small depolarisation in conformity with the known small depolarisation of cyclohexane, while propylene shows a high value as would be expected from the presence of the double bond in it. Methyl chloride is more anisotropic than ethyl chloride, and the depolarisation factor of the former is much higher than that of methane. Carbon tetrachloride shows an extremely small depolarisation of 0·15% which is discussed in detail. It is tentatively concluded that the depolarisation of argon is nil. The depolarisation of H_2S is only 0·3%. An explanation is offered for the low depolarisation of the hydride molecules in general.

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[15] H. A. Stuart, *loc. cit.*, p. 190.