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## Raman Spectra of Compounds in the Gaseous and Liquid States\*

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An apparatus for exciting the Raman spectra of gases and liquids at temperatures up to 300°C is described. For phosphorus trichloride, methyl chloride, methyl bromide, methyl alcohol, methylene chloride, methylene bromide, chloroform, and carbon tetrachloride, the Raman spectra of the gas and the liquid at the same temperature have been photographed in juxtaposition with a liquid-prism spectrograph of speed  $f : 2.9$  and linear dispersion 27Å/mm at 4400Å. The Raman spectra of gaseous *n*-pentane, *n*-hexane, and deuterium oxide have been photographed with 2537Å excitation. The change in the Raman frequencies with the state of aggregation is different for different vibrations and varies greatly from compound to compound. In the absence of an adequate theory for this phenomenon, a search has been made for empirical regularities. The perpendicular bands of the symmetrical-top molecules are much less diffuse in the liquid than in the gas, showing that the intermolecular forces are effective in quenching the rotation of the molecules in the liquid. The other bands are about equally sharp in gas and liquid.

### INTRODUCTION

LESS than one-half percent of the papers published on the Raman effect have reported observations on substances in the gaseous state. This is to be regretted, since the present theory of Raman spectra is strictly applicable only to free molecules. While data on compounds in the gaseous state are more difficult to obtain than data for liquids, they are of greater value. For some purposes, e.g., for testing Placzek and Teller's theory of the rotational structure of

Raman bands,<sup>1</sup> data for the gaseous state are absolutely essential. In the present paper an apparatus for observing the Raman spectra of compounds in the gaseous and liquid states is described, and results are given for several compounds.

### EXPERIMENTAL

The apparatus devised is shown schematically in Fig. 1. A Raman tube of the type used for vapors is shown in position, and a Raman tube for liquids is shown to the right of the figure. The tubes were mounted vertically in such a way that they could be interchanged without disturbing the alignment with the spectrograph. Each tube had a plane window at the upper end and a light trap at the bottom, and the necessary provisions

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† Present address: Magnolia Petroleum Company, Dallas, Texas. The present paper is based largely upon a thesis presented by Newton E. Ward to the faculty of the Graduate School of the University of Oklahoma in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

<sup>1</sup> G. Placzek and E. Teller, *Zeits. f. Physik* **81**, 209 (1933); E. Teller, *Hand- und Jahrbuch der Chemischen Physik*, Vol. 9, II.

were made for preventing light from reaching the ends of the tubes. The effective length of the vapor tubes was 18 cm. The Raman tubes used for liquids were somewhat shorter and were constructed in such a manner that the surface of the liquid was above the plane window through which the scattered light was observed.

The Raman tubes were surrounded by a double-walled Pyrex tube and were heated to the desired temperature by hot air circulated by a centrifugal pump, the air entering at the top to keep the window free from condensed vapor. To reduce the temperature drop along the Raman tube, the space between the walls of the furnace tube was evacuated to below  $10^{-4}$  mm of mercury. The top of the furnace tube was closed with a plane glass window held in place by a closely fitting brass cap. The temperatures of the air entering and leaving the furnace tube were read on the thermometers  $T_1$  and  $T_2$ . From these temperatures it was possible, after securing the requisite data, to compute the temperatures at the ends of the Raman tube. The apparatus is

suitable for temperatures up to  $300^\circ\text{C}$  and can be used also for very low temperatures.

A Pyrex filter jacket surrounded the furnace tube. The filter was a solution of 100 g of *p*-nitrotoluene and 0.10 g of rhodamine 5 GDN Extra<sup>†</sup> in one liter of ethyl alcohol, as suggested by Edsall and Wilson.<sup>2</sup> In a thickness of 5 mm this filter transmits about 70 percent of the 4358Å line but only a trace of 4047Å. The filter decomposed slowly under the action of the light and had to be renewed every 15 or 20 hours.

Six symmetrically arranged mercury lamps surrounded by a six-section elliptical reflector of polished aluminum provided the irradiation. The lamps were made of Pyrex and had tungsten spiral anodes. The Raman spectra were photographed with a liquid-prism spectrograph built by the senior writer. When a camera lens of speed  $f:2.9$  is used this instrument has a linear dispersion of 27Å/mm at 4400Å.

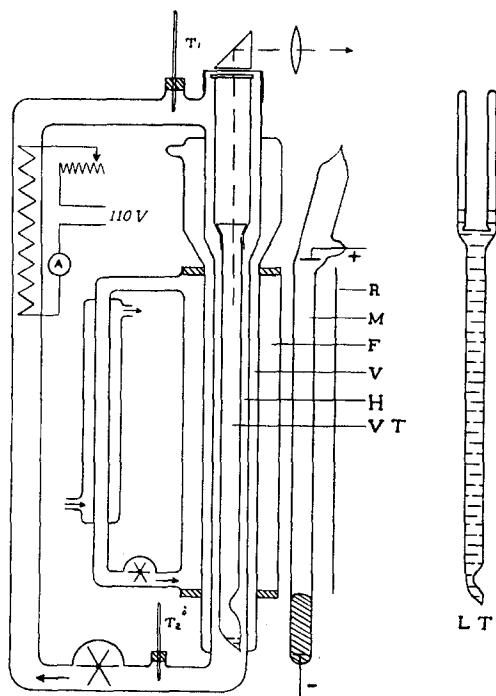
In most cases the Raman spectra of the vapor and of the liquid at the same temperature and pressure were photographed in juxtaposition through slightly overlapping holes in a Hartmann diaphragm. In this way any difference in frequency or intensity distribution between the two spectra is readily observed. The slit width was usually 0.05 mm. Agfa Super Plenachrome Press cut films were used. The exposure time ranged from 12 to 36 hours for the vapors and from 5 to 30 minutes for the liquids. Except for methyl chloride and methylene chloride, which were of a grade used for refrigeration, the purest commercially obtainable chemicals were used. With the exception of the volatile methyl chloride, which was placed directly into the Raman tube, all materials were redistilled before being distilled into the Raman tube under vacuum.

## RESULTS

Results of varying degree of completeness have been obtained for phosphorus trichloride, methyl chloride, methyl bromide, methylene chloride, methylene bromide, chloroform, carbon tetrachloride, methyl alcohol, *n*-pentane, *n*-hexane, and deuterium oxide. Figure 2 shows a repro-

FIG. 1. Apparatus for observing the Raman spectra of vapors and liquids excited by Hg 4358Å.

VT—Raman tube for vapors; H—hot air space; V—vacuum jacket; F—filter jacket; M—mercury lamp; R—reflector;  $T_1$ ,  $T_2$ —thermometers; LT—Raman tube for liquids.



<sup>†</sup> This dye was presented to us by E. I. du Pont de Nemours and Company.

<sup>2</sup> J. T. Edsall and E. B. Wilson, *J. Chem. Phys.* **6**, 124 (1938).

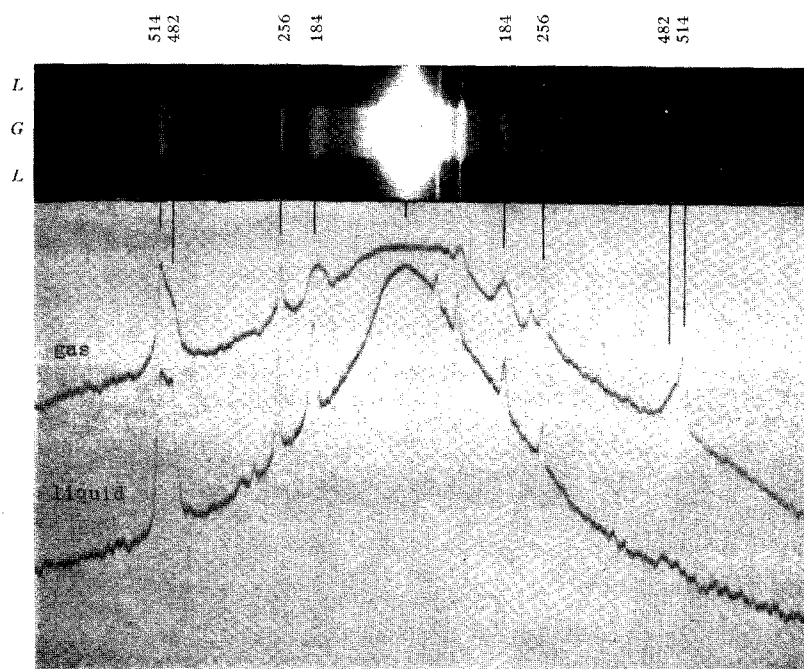


FIG. 2. Raman spectra of gaseous and liquid phosphorus trichloride.

duction of one of the films obtained with phosphorus trichloride together with microphotometer records of the spectra of the gas and the liquid. In Table I are listed the data obtained for the majority of the compounds studied. The pressure of the saturated vapor is given in the second column. In the third column are listed the differences  $\Delta\nu$  between the frequencies of the Raman bands of the compound in the gaseous and liquid states. These frequency differences were determined directly from the distance between the adjacent Raman bands for gas and liquid and should be more accurate than values obtained by taking differences between frequencies for the gas and the liquid, measured separately. In the sixth column are given the Raman frequencies  $\nu_l$  observed for the compound in the liquid state at a temperature roughly equal to the average temperature of the vapor during its exposure and at a pressure a little higher than that listed in column 2. Only such Raman bands are included in column 6 which were observed also for the vapor. Each value of  $\Delta\nu$  and  $\nu_l$  is the average of several independent measurements, all exposures and both Stokesian and anti-Stokesian bands having been considered. The Raman fre-

quencies  $\nu_g$  for the compound in the gaseous state, obtained by adding  $\Delta\nu$  to  $\nu_l$ , are listed in the fourth column. In columns 5 and 7 are given the visually estimated intensities of the Raman bands for the liquid and the gas as obtained from the most satisfactory exposure. The diffuse character of certain bands is indicated by the symbols *d* or *vd* (very diffuse).

Although four exposures were made with carbon tetrachloride vapor, no entirely satisfactory Raman spectrum was obtained. The Raman bands appeared with less intensity than expected and were partly masked by a continuous background. Within the experimental error  $\Delta\nu$  was zero for all the bands. The two bands at 760 and 790  $\text{cm}^{-1}$  were broadened to appear as a single diffuse band extending from about 740 to 810  $\text{cm}^{-1}$ . In liquid carbon tetrachloride at the same temperature (140°C) these bands were barely resolved. No difference in the intensity distribution for gas and liquid could be observed for the other bands.

The work with *n*-pentane, *n*-hexane, and deuterium oxide was done with 2537Å excitation, two Hanovia Sc-2537 lamps being used for irradiation and a medium-sized quartz spectro-

TABLE I. Raman bands of compounds in the gaseous and liquid states.

Compound	Pressure	$\Delta\nu$	$\nu_g$	$I_g$	$\nu_l$	$I_l$
PCl <sub>3</sub>	5.8 atmos.	-4 cm <sup>-1</sup>	184 cm <sup>-1</sup>	8vd	188 cm <sup>-1</sup>	5d
		-2	256	10	258	5
		0	482	3d	482	3d
		3	514	10	511	4
CH <sub>3</sub> Cl	6.5	14	726	10	712	5
		10	2968	7	2958	7
CH <sub>3</sub> Br	3.2	10	610	10	600	5
		14	2973	5	2959	5
CHCl <sub>3</sub>	4.0	0	261	2d	261	10
		-3	363	3	366	10
		4	672	4	668	10
		0	760	1vd	760	6d
		0	1217	1	1217	2
		11	3030	1	3019	6
CH <sub>3</sub> OH	3.2	0	1032	2d	1032	4d
		9	2945	4d	2836	10d
		10	2955	4d	2945	10d
CH <sub>2</sub> Cl <sub>2</sub>	3.2	-3	281	5	284	5
		12	712	10	700	10
		12	3002	5	2990	7
CH <sub>2</sub> Br <sub>2</sub>	3.5	-3	169	10	172	8
		6	584	10	578	10
		0	640	0d	640	1d
		12	1402	0	1390	2
		18	3008	1	2990	5

graph for photographing the spectra. The frequencies and intensities of the Raman bands obtained in the first exposure of *n*-pentane vapor at 5 atmos. and 124°C are given in Table II, columns 1 and 2. In the third and fourth columns are listed the corresponding data for liquid *n*-pentane at room temperature as given in Landolt-Börnstein, *Physikalisch-chemische Tabellen*. In addition to the Raman bands listed there appeared in the light scattered by the vapor several bands which are evidently due to fluorescence of a product formed by photochemical decomposition of *n*-pentane. The wavelengths and intensities of these bands are given in the last two columns of Table II. In a second exposure with the same Raman tube only the two Raman bands at 2890 and 2940 cm<sup>-1</sup> appeared, a thin greenish-yellow deposit, which absorbed the 2537Å strongly, having formed on the walls of the Raman tube. It may be of interest to mention that the Raman tube did not contain any mercury vapor. Normal hexane vapor, at 150°C and 5 atmos., also decomposed rapidly when illuminated by the Sc-2537 mercury lamps. Only two very diffuse Raman bands, at 2887 and 2947 cm<sup>-1</sup>, were observed. Six exposures were made with deuterium oxide, but only the previously reported Raman band at 2666 cm<sup>-1</sup> was observed.<sup>3</sup> The material fluoresced strongly even after prolonged treatment with potassium permanganate.

<sup>3</sup> Cf. D. H. Rank, K. D. Larsen, and E. R. Bordner, J. Chem. Phys. 2, 464 (1934).

## DISCUSSION OF RESULTS

### (1) Completeness and Accuracy

All the fundamental Raman bands of phosphorus trichloride and chloroform were observed in the gaseous state. With the vapors of the other compounds, the observed Raman spectra were incomplete. Although a few additional Raman bands could undoubtedly have been observed with longer exposure times, especially for methylene chloride and methylene bromide, it would hardly have been possible to observe as complete Raman spectra for the vapors as for the compounds in the liquid state. This is mainly due to the fact that the Rayleigh scattering is more intense in the gas than in the liquid. Not only do the Rayleigh lines broaden more with long exposure, but more light is scattered in the prisms and lenses, thus increasing the fogging of the film.

The observed differences  $\Delta\nu$  between the Raman frequencies for the gaseous and liquid states should be accurate to 1 cm<sup>-1</sup> or better; in fact, only in one case did the values of  $\Delta\nu$  as determined from Stokesian and anti-Stokesian bands differ by more than this amount. On the other hand, because of the inaccuracy in the observed Raman frequencies for the liquids, the frequencies  $\nu_g = \nu_l + \Delta\nu$  for the gaseous state have inaccuracies ranging from  $\pm 1$  cm<sup>-1</sup> for sharp bands to  $\pm 5$  cm<sup>-1</sup> for very diffuse bands, the average inaccuracy being  $\pm 1.5$  cm<sup>-1</sup>. Somewhat more accurate values for the  $\nu_g$ 's can be obtained by adding the observed  $\Delta\nu$ 's to values for  $\nu_l$ .

TABLE II. Raman bands of gaseous and liquid *n*-pentane. Fluorescence band of decomposition product.

$\nu_g$	$I_g$	$\nu_l$	$I_l$	Fluorescence Bands $\lambda$	$I$
401 cm <sup>-1</sup>	1	400	2d	2657.0Å	1
850	1vd	838	5	2668.5	10
		865	4	2674.7	3
1073	0	1073	5d	2679.6	6
1142	0	1140	3	2686.0	4
				2691.5	5
1309	1	1300	5	2698.5	3
1455	2vd	1438	6d	2704.3	4
		1463	6d	2709.8	3
				2716.0	1
2890	4vd	2873	12	2744.9	4
		2906	8		
		2936	10d		
2940	10vd	2962	8		

TABLE III. Depression of vibration frequencies in liquid state.

Com- pound	$\Delta\nu$ in $\text{cm}^{-1}$									Dipole moment $\times 10^{18}$
CH <sub>4</sub>	$\Delta\nu_1$ (5)		$\Delta\nu_3$ (0)		$\Delta\nu_2$		$\Delta\nu_4$			0
CCl <sub>4</sub>	0		0		0		0			0
CH <sub>3</sub> Cl	$\Delta\nu_1 \parallel$ 10	$\Delta\nu_2 \perp$ (9)	$\Delta\nu_3 \parallel$ 14	$\Delta\nu_4 \perp$ (11)	$\Delta\nu_5 \parallel$ (-2)	$\Delta\nu_6 \perp$ (7)				1.86
CH <sub>3</sub> Br	14	—	10	—	—	—	—	—	—	1.45
CH <sub>3</sub> OH	9, 10	—	—	—	0	—	—	—	—	1.68
CHCl <sub>3</sub>	4	0	11	0	-3	0				1.05
CH <sub>2</sub> Cl <sub>2</sub>	$\Delta\nu_1(s)$ 12	$\Delta\nu_1(a)$ —	$\Delta\nu_2(a)$ —	$\Delta\nu_2(s)$ 12	$\Delta\delta$ —	$\Delta\delta_1(s)$ -3	$\Delta\delta_2(s)$ —	$\Delta\delta_1(a)$ —	$\Delta\delta_2(a)$ —	1.51
CH <sub>2</sub> Br <sub>2</sub>	6	0	—	18	12	-3	—	—	—	1.40

obtained with a spectrograph of greater linear dispersion.

There are few previous results with which to compare the present data. The single Raman frequency  $523 \text{ cm}^{-1}$  found by Braune and Engelbrecht<sup>4</sup> for gaseous  $\text{PCl}_3$  is evidently not accurate. The Raman frequencies  $726$  and  $2968 \text{ cm}^{-1}$  for gaseous  $\text{CH}_3\text{Cl}$  and  $610$  and  $2973 \text{ cm}^{-1}$  for gaseous  $\text{CH}_3\text{Br}$  are, on the whole, in excellent agreement with the frequencies  $732$  and  $2967 \text{ cm}^{-1}$ ,  $610$  and  $2973 \text{ cm}^{-1}$ , respectively, found by Bennett and Meyer<sup>5</sup> and Barker and Plyler<sup>6</sup> in the infra-red spectra of these vapors. The Raman frequencies  $1032$ ,  $2845$ , and  $2955 \text{ cm}^{-1}$  for  $\text{CH}_3\text{OH}$  vapor agree fairly well with the values  $1035$ ,  $2842$ , and  $2850 \text{ cm}^{-1}$  reported by Kastler.<sup>7</sup> The infra-red absorption spectrum of gaseous methyl alcohol has been investigated by Borden and Barker<sup>8</sup> who found, in part, the frequencies  $1034.18$ ,  $2845$ , and  $2978 \text{ cm}^{-1}$ . The first two of these agree well with the Raman frequencies obtained by Kastler and by the present writers. The frequency  $2978 \text{ cm}^{-1}$  belongs to another band than  $2957 \text{ cm}^{-1}$ .

## (2) Changes in Raman Frequencies with State of Aggregation

No complete theory exists at present for the effect of intermolecular forces upon molecular

vibration frequencies. Breit and Salant<sup>9</sup> have pointed out that there should be three distinct effects: (1) a coupling of the molecules produced by the electric moments induced by the incident radiation field (Lorentz-Lorenz effect), (2) an effect of quantum-mechanical exchange forces between neighboring molecules upon the molecular force constants, and (3) a purely electrostatic effect. Breit and Salant evaluated the Lorentz-Lorenz effect but found that it accounts for only two percent of the frequency difference between gaseous and liquid hydrogen chloride. Cremer and Polanyi<sup>10</sup> found that the exchange effect could explain only ten percent of the frequency change observed for hydrogen chloride. Buchheim<sup>11</sup> estimated the effect of a uniform electric field upon molecular vibrations. Assuming that the large variable fields existing in the immediate neighborhood of molecules will have essentially the same effect as a constant, uniform field, he concluded that in the case of dipole substances the vibration frequencies should be shifted by an amount roughly of the observed order of magnitude and that the Raman bands should suffer a broadening depending upon the concentration of the scattering substance but not upon the temperature. Buchheim could not predict the direction of the shift. His formulas indicate that  $\Delta\nu$  may have different signs for different vibrations. Kastler,<sup>7</sup> on the other hand, has given arguments which indicate that  $\Delta\nu$  should usually be positive.

<sup>4</sup> H. Braune and G. Engelbrecht, *Zeits. f. physik. Chemie* **B19**, 303 (1932).

<sup>5</sup> W. H. Bennett and C. F. Meyer, *Phys. Rev.* **32**, 888 (1928).

<sup>6</sup> E. F. Barker and E. K. Plyler, *J. Chem. Phys.* **3**, 367 (1935).

<sup>7</sup> A. Kastler, *Comptes rendus* **194**, 858 (1932).

<sup>8</sup> A. Borden and E. F. Barker, *J. Chem. Phys.* **6**, 553 (1938).

<sup>9</sup> G. Breit and E. O. Salant, *Phys. Rev.* **36**, 871 (1930).

<sup>10</sup> E. Cremer and M. Polanyi, *Bodenstein-Festband of Zeits. f. physik. Chemie* (1930), p. 77.

<sup>11</sup> W. Buchheim, *Physik. Zeits.* **36**, 694 (1935).

Most of the observed vibration frequencies are greater for the gas than for the liquid, i.e.,  $\Delta\nu$  is predominantly positive. In the absence of an adequate theory, one may search for empirical regularities in the values of  $\Delta\nu$  for different vibrational states and for a possible correlation with the dipole moment of the molecule.

For phosphorus trichloride  $\Delta\nu$  is positive for one of the totally symmetrical vibrations and negative for the other. For one of the degenerate vibrations  $\Delta\nu$  is zero and for the other it is negative. However, all the observed values are rather small, indicating that the molecular interaction is small. This is undoubtedly connected with the fact that the dipole moment is rather small ( $0.61 \times 10^{-18}$  for  $\text{PCl}_3$  dissolved in  $\text{CCl}_4$ ).<sup>12</sup> The values of  $\Delta\nu$  found for the methyl halides are listed in Table III, the symbols designating the various vibrations being those used by Wu.<sup>13</sup> Since methyl alcohol has approximately the same symmetry as  $\text{CH}_3\text{Cl}$ , the data for  $\text{CH}_3\text{OH}$  are included in the table. In order to make the table as complete as possible, two values for methane, obtained by subtracting the Raman frequencies for liquid methane from those for gaseous methane at room temperature,<sup>14</sup> and some values for methyl chloride, obtained by subtracting Raman frequencies for the liquid<sup>15</sup> from infra-red frequencies of the gas,<sup>5</sup> have been added, in parentheses. The dipole moments of the molecules are listed in the last column.

It is seen that  $\Delta\nu$  varies from molecule to molecule and has widely different values for different vibrations. For  $\text{CH}_4$  and  $\text{CCl}_4$ , which have no dipole moments, the  $\Delta\nu$ 's vanish or, at least, are very small. In the case of chloroform, which has a fairly small dipole moment, the average value of the  $\Delta\nu$ 's is rather low. For the remaining molecules the shifts are larger, but it is not possible to trace any simple dependence of  $\Delta\nu$  upon the dipole moment. In fact, whereas  $\Delta\nu_3$  is greater for  $\text{CH}_3\text{Cl}$  than for  $\text{CH}_3\text{Br}$ , which has the lower dipole moment, the opposite is true about  $\Delta\nu_1$ . Some regularity in the values of  $\Delta\nu$  for different types of vibration is indicated by Table

III. For the molecules of symmetry  $C_{3v}$  the totally-symmetrical energy levels  $1\nu_1$  and  $1\nu_3$  are greatly depressed relative to the ground level in the liquid, and the same is true about the corresponding levels  $1\nu_1(s)$  and  $1\nu_2(s)$  for the molecules of symmetry  $C_{2v}$ . On the other hand, the  $1\nu_3$  level lies higher in the liquid than in the gas for the two compounds for which data are obtained. For the methyl derivatives the  $1\nu_1$  state is strongly perturbed by the  $2\nu_4$  state.<sup>16</sup> However, only for methyl alcohol could both of the levels,  $(1\nu_1, 2\nu_4)$ , be observed in the Raman spectrum of the gas. As might be expected, they are about equally depressed in the liquid. In the case of chloroform, the shift is zero for all three degenerate vibrations. However, that seems not to be the case for methyl chloride. For both  $\text{CH}_2\text{Cl}_2$  and  $\text{CH}_2\text{Br}_2$   $\Delta\delta_1(s) = -3 \text{ cm}^{-1}$ . On the other hand,  $\Delta\nu_1(s)$  is greater for the chloride, while  $\Delta\nu_2(s)$  is greater for the bromide.

Since no exposures were made of liquid *n*-pentane, less accurate values of the  $\Delta\nu$ 's have been obtained for this compound. However, a comparison of the observed frequency values for gaseous *n*-pentane at  $125^\circ$  with the frequencies reported for the liquid at room temperature shows that the values of  $\Delta\nu$  are very small. This may be expected from the fact that the dipole moment is zero. The incomplete data for *n*-hexane permit no definite conclusions regarding the  $\Delta\nu$ 's. For deuterium oxide  $\Delta\nu$  has the very large value  $150 \text{ cm}^{-1}$ , and, as in the case of ordinary water, the Raman band is extremely diffuse. These phenomena are undoubtedly connected with the formation of hydrogen bonds.

### (3) Intensity Distribution. Quenching of Molecular Rotation in the Liquid State

When the visually estimated intensities of the Raman bands for the gas are compared with those for the liquid, the low frequency bands appear enhanced in the gas. However, this effect is probably an illusion caused by the continuous background which decreases in intensity with increasing distance from the Rayleigh line.

The two Raman bands observed for methyl chloride are slightly wider in the liquid than in

<sup>12</sup> E. Bergmann and L. Engel, *Zeits. f. physik. Chemie* **B13**, 232 (1931).

<sup>13</sup> Ta-You Wu, *Vibrational Spectra and Structure of Polyatomic Molecules* (Kun-Ming, China, 1939).

<sup>14</sup> Cf. Landolt-Börnstein, *Physikalisch-chemische Tabellen*.

<sup>15</sup> J. Wagner, *Zeits. f. physik. Chemie* **B40**, 36 (1938).

<sup>16</sup> A. Adel and E. F. Barker, *J. Chem. Phys.* **2**, 627 (1934).

the gas, in agreement with Buchheim's theoretical prediction<sup>11</sup> and with the findings of other observers.<sup>17</sup> For the other compounds investigated, such an effect could not be verified with certainty.

A striking result of the present investigation is the finding that the bands of phosphorus trichloride and chloroform corresponding to degenerate vibrations are much broader in the gas than in the liquid. The broadening of the  $184\text{ cm}^{-1}$  band of  $\text{PCl}_3$  in the gaseous state is clearly shown in Fig. 2. The other perpendicular band  $482\text{ cm}^{-1}$  is also seen to be broadened. However, the diffuse character of this band in the gas is somewhat obscured by its proximity to the band at  $514\text{ cm}^{-1}$  and perhaps also by the presence of an overtone  $2\nu_3 \cong 512\text{ cm}^{-1}$ . The bands  $256$  and  $514\text{ cm}^{-1}$ , which correspond to parallel, non-degenerate vibrations, seem to be as sharp in the gas as in the liquid.

In the case of chloroform, the perpendicular bands  $261$  and  $760\text{ cm}^{-1}$  are definitely broader in the gas than in the liquid. The third perpendicular band  $1217\text{ cm}^{-1}$  is so weak that its diffuse character in the gas could not be ascertained. The three parallel bands of chloroform, on the other hand, are about as sharp in the gas as in the liquid. For methyl chloride, methyl bromide, and methyl alcohol, only parallel bands were observed, and no bands were observed to be broadened in the gaseous state. No broadening was found for methylene chloride and methylene bromide which have only nondegenerate vibrations.

<sup>17</sup> Cf. K. W. F. Kohlrausch, *Der Smekal-Raman Effekt, Ergänzungsband* (Springer, 1938), Chapter V.

The fact that some Raman bands are much narrower in the liquid than in the gaseous state shows that the intermolecular forces in the liquid are effective in quenching the rotation of molecules. Although Bhagavantam<sup>18</sup> has reported that the  $2611\text{ cm}^{-1}$  band of hydrogen sulfide is more diffuse in the gas than in the liquid, and Kirby-Smith and Bonner<sup>19</sup> that the perpendicular band,  $1460\text{ cm}^{-1}$ , of gaseous methylamine is very diffuse, this quenching effect seems not to have been clearly recognized by previous workers on infra-red and Raman spectra.

The quenching is most readily observed for bands with strong rotational branches, such as the perpendicular bands of symmetrical-top-molecules. The diffuse character of such Raman bands, even in the liquid state, has been used, in the absence of polarization data, to differentiate them from parallel bands.<sup>20</sup> Our results indicate that this can be done with far greater safety when observations of the Raman spectrum for the gaseous state are available.

No accurate intensity measurements were made in the present work. However, Mr. D. K. Coles, in collaboration with the senior author, has recently made quantitative determinations of the intensity distribution in certain Raman bands of cyclopropane. These measurements not only throw further light on the quenching of the molecular rotation in liquids but furnish the first experimental test of Placzek and Teller's theory<sup>1</sup> for the rotational structure of Raman bands.

<sup>18</sup> S. Bhagavantam, *Nature* **126**, 502 (1930).

<sup>19</sup> J. S. Kirby-Smith and L. G. Bonner, *J. Chem. Phys.* **7**, 880 (1939).

<sup>20</sup> Cf. A. Langseth and E. Walles, *Zeits. f. physik. Chemie* **B27**, 214 (1934).