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have been made by Wagner,[6] and the present ones are in good agreement with his work, and in all cases extend his conclusions. Attempts have been made to deduce complete schematic assignments for the ethyl chloride molecule by Linnett[12] and Pitzer.[13] Our present results differ somewhat from the results of these authors in the assignment of non-observed frequencies.

[12] J. W. Linnett, Trans. Faraday Soc. **36**, 527 (1940).
[13] J. Gordon and W. F. Giauque, J. Am. Chem. Soc. **70**, 1506 (1948).

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Raman Spectra of Polycrystalline Hydrocarbons at Low Temperatures. Rotational Isomerism. II*

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Making use of the low pressure, water-cooled Hg arcs as the source of nearly monochromatic radiation, a simple method was developed for the investigation of the Raman spectra of polycrystalline solids. The method was applied to the study of the first four normal paraffins. The Raman spectra of the solids between 600–1500 cm^{-1} are compared with those in the liquid phase. All these spectra undergo a marked simplification on solidification due to the disappearance of all but one of the rotational isomers. This process is shown to be discontinuous at the melting point.

IN the first paper[1] of this series we have calculated the energy difference of the rotational isomers of *n*-butane by measuring the relative intensity of "line pairs" as a function of temperature in the liquid range. Numerous considerations make it desirable to extend the investigation of the spectra of rotational isomers to the solid phase.

During the war work was done in Japan** on the Raman spectra of some hydrocarbons in the solid phase. These Japanese workers have reported that certain lines in the spectra disappear in the solid phase. In the light of this work and our observed behavior of line intensity ratios as a function temperature,[1] it would seem to be of importance to investigate whether the intensity ratio of "line pairs" varies continuously or not when one proceeds from the liquid to the solid phase.

It is relatively easy to obtain the Raman spectra of solids if they can be prepared as homogeneous glasses or single crystals. The preparation of solid hydrocarbons in an optically homogeneous state can and has been accomplished by a number of investigators. However, preparation of such solid samples will require practically a special investigation for production of satisfactory solids for each molecule studied.

Crystal powder methods of obtaining Raman spectra have been brought to a state of more or less perfection by Kohlrausch[2] and his coworkers. More recently Cabannes[3] and his col-

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[1] G. J. Szasz, N. Sheppard, and D. H. Rank, J. Chem. Phys. **16**, 704 (1948).
** T. Shimanouchi and S. Midzushima, J. Chem. Soc. (Japan) **63**, 1215 (1942); Chem. Abs. **41**, 3332 (1947); Sci. Pap. Inst. Phys. Chem. Research (Tokyo) **40**, 467 (1943), Chem. Abs. **41**, 6089 (1947); M. Takeda, J. Chem. Soc. Japan **62**, 896 (1941); Chem. Abs. **41**, 5390 (1947); H. Okazaki, J. Chem. Soc. Japan **63**, 1136 (1942); Chem. Abs. **41**, 3740 (1947). Unfortunately, the complete papers have been inaccessible to us so far.
[2] K. W. F. Kohlrausch, *Ramanspektren* (Akad. Verlag., Leipzig, 1943), p. 49.
[3] J. Cabannes, R. Lennuier, and M. Harraud, Comptes Rendus **223**, 301 (1946).

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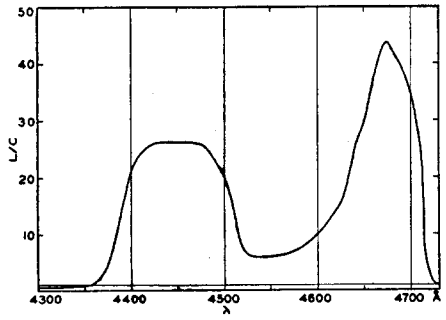

FIG. 1. Plot of the relative weakening of continuum compared to the exciting line *vs.* wave-length.

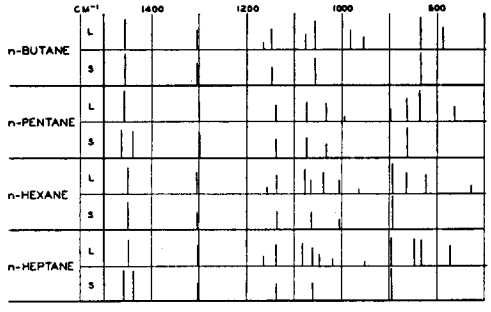

FIG. 3. Schematic representation of the Raman spectra of *n*-paraffins in the liquid (*L*) and solid (*S*) phases.

laborators have developed a crystal powder method which is elegant in principle. The method of Kohlrausch is very complicated both in arrangement of the optical system and in adjustment thereof. Cabannes' method makes use of a monochromator to illuminate the sample and the spectra produced are very feeble. Neither of the two methods of obtaining crystal powder spectra mentioned above seem to lend themselves easily to work at low temperatures.

The problem of obtaining Raman spectra of crystal powders essentially resolves itself to producing the excitation by means of sufficiently monochromatic light. The crystal powder will diffusely reflect a much greater percentage of the incident light than will be scattered by the individual molecules. The relative intensity of the continuum in a spectrum compared to the intensity of an ideal monochromatic line will vary inversely as the true resolving power of the spectrograph. In the case of Raman spectra, however, it is not possible to greatly weaken the continuum relative to the Raman line by simply increasing the resolving power of the spectrograph, since the Raman lines in general have considerable breadth.

A great deal of the work recorded in the literature on Raman spectra has been done, making use of relatively high pressure mercury arcs as light sources. It has been shown[4] that in the low pressure Hg arc the continuous spectrum is only about $\frac{1}{10}$ as strong as in the moderately high pressure sources. In addition it is possible to reduce the continuous spectrum on the long wave side of λ4358 very materially by means of a praseodymium ammonium nitrate filter. Figure 1 shows a plot of L/C as a function of wave-length for the praseodymium filter which we have used in this work. L is the fractional part of incident light of wave-length λ4358 transmitted by the filter and C is the transmission of the filter for wave-length λ. This curve shows the relative weakening of the continuum compared to the exciting line. From inspection of Fig. 1 it can be seen that the relative intensity of the continuous spectrum of the Hg arc can be reduced by more than an order of magnitude over most of the region from λ4400 to λ4700A by means of this filter.

A schematic diagram of the apparatus we have used to obtain the Raman spectra of polycrystalline hydrocarbons at low temperatures is shown in Fig. 2. The sample tube S is placed in the Dewar flask which is painted black, except for entrance windows for the incident light marked W in the figure. The light scattered and diffusely reflected from the polycrystalline solid passes out through the aperture D and is reflected into the

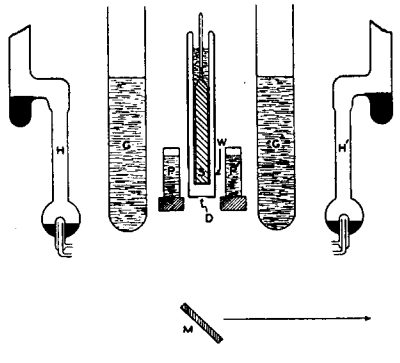

FIG. 2. The experimental arrangement used to obtain Raman spectra of polycrystalline solids.

[4] D. H. Rank and J. S. McCartney, J. Opt. Soc. Am. **38**, 279 (1948).

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spectrograph by means of the mirror M. H and H' are low pressure water-cooled Hg arcs similar to those described previously.[5] G and G' are cylindrical lenses containing sodium nitrite solution to suppress the short wave part of the Hg spectrum and P and P' are cells which hold the praseodymium ammonium nitrate filter solution. The thickness of the cells was 12 mm and they contained a solution of 50 percent by weight of crude praseodymium ammonium nitrate in water. (Specific gravity *ca.* 1.50.) The crude salt was obtained from the Lindsay Light and Chemical Company, West Chicago, Illinois.

The spectrograph employed in this work was a 3-prism glass instrument equipped with an f:3.5 objective lens. The dispersion of the instrument was about 30A per mm at λ4500. The objective produces very sharply defined images which allows the slit width to be kept to a minimum value consistent with the natural breadth of the Raman lines. In order to avoid halation as much as possible, the plates were backed with Eastman "opaque." The λ4358 line was prevented from falling on the plate by being absorbed by means of a diaphragm placed in front of the plate. Even though the direct image of this line could not fall on the plate the intensity of this line is so great that light of this wave-length produces an ill-defined image in the neighborhood of the line position as the result of scattering in the various parts of the spectrograph. For this reason it was not possible to observe any lines in the solid spectra when the frequency shift was less than 600 cm^{-1}.

By filling the Dewar shown in Fig. 2 with liquid air, the sample could be frozen into a polycrystalline mass and the spectrum photographed in the manner described above. Suitable plates of the crystal powder spectra could be obtained in four to five hours' exposures. It was possible to obtain spectra of the liquid hydrocarbons at low temperatures with this apparatus by cooling the sample to the desired temperature with cold dry air as described in our previous paper.[1]

The n-paraffins used were obtained from the Petroleum Refining Laboratory of this college (n-butane, n-pentane, and n-hexane) and from the Phillips Petroleum Company (n-heptane).

The spectra of the liquid and solid hydrocarbons are schematically represented in Fig. 3. There are several features apparent in these spectra which are of particular interest. In general, the lines are considerably sharper at the low temperatures. The much simplified spectra of the solid normal paraffins investigated seem to consist of lines which arise from a single rotational isomer. On comparing results obtained from photoelectric intensity measurements of line pairs as a function of temperature with the qualitative intensities obtained from the solid spectra, it is apparent that the intensity changes of the line pairs are discontinuous when going from the liquid to the solid state.

There are several obvious improvements which can be made in the crystal powder technique which we have described in this paper. However, the incorporation of these improvements will make the method considerably more complex. Since it is possible to secure usable solid spectra in the simple manner described in this paper, it was thought worth while to describe our method in sufficient detail so as to clearly bring out the advantages and limitations of this technique.

A detailed discussion of the quantitative results obtained on the liquid and solid spectra of some normal and branched hydrocarbons will be given in two subsequent papers.

We thank Dr. M. R. Fenske, Director of the Petroleum Refining Laboratory in this college and the Phillips Petroleum Company (Bartlesville, Oklahoma) for supplying the hydrocarbons used. The figures were prepared by Mr. E. Shull.

[5] D. H. Rank, N. Sheppard, and G. J. Szasz, J. Chem. Phys. 16, 698 (1948).

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