Rotational Isomers of *n*-Pentane

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The *n*-pentane molecule has three possible rotational isomers, TT (trans-trans), TG (trans-gauche) and GG(gauche-gauche). It was reported by Mizushima *et al.*[1] and Sheppard *et al.*[2] that in the solid state only the TT form exists and in the liquid state the TT and TG forms coexists. Theoretical considerations[1,3,4] forecast the stability of the GG form. However, no experimental evidence has been reported as yet. We have recently measured the far infrared spectra of *n*-pentane in the liquid and solid states and succeeded in finding a band due to the GG form.

In Fig. 1 the spectra in the region 500—100 cm^{-1} are shown. The solid state spectrum shows only the

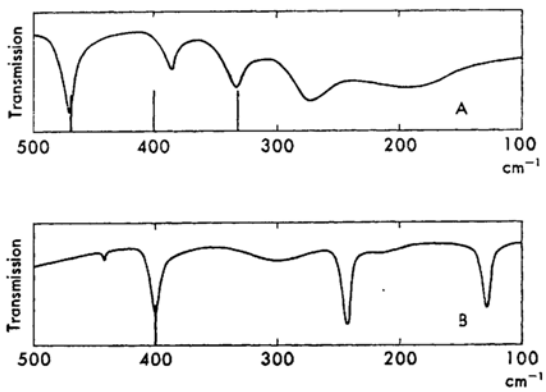

Fig. 1. Infrared spectra of *n*-pentane.
Curve A: liquid at room temperature, thickness 4 mm.
Curve B: solid at liquid nitrogen temperature.
The spectra were measured by a Hitachi FIS-1 spectrometer.
The vertical lines show the frequencies of Raman lines.

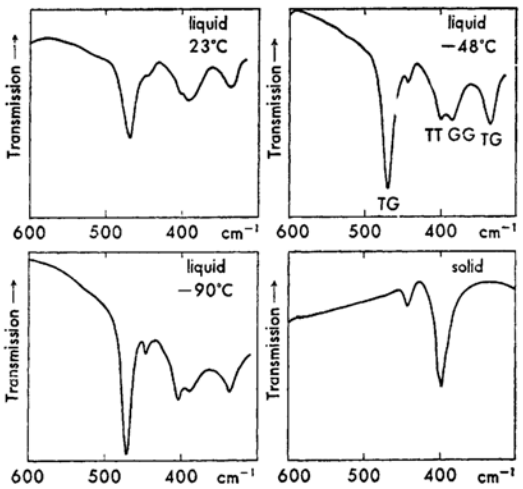

Fig. 2. Infrared spectra of *n*-pentane at various temperatures.
The measurements were made by a Hitachi EPI-L spectrometer.

1) T. Shimanouchi and S. Mizushima, *Sci. Papers Inst. Phys. Chem. Research*, **40**, 467 (1943); S. Mizushima and H. Okazaki, *J. Am. Chem. Soc.*, **71**, 3411 (1949); S. Mizushima, "Structure of Molecule and Internal Rotation," Academic Press Inc., N. Y. (1954).
2) N. Sheppard and G. J. Szasz *J. Chem. Phys.*, **17**, 86 (1949).
3) A. Abe, R. L. Jernigen and P. J. Flory, *J. Am. Chem. Soc.*, **88**, 631 (1966).
4) R. A. Scott and H. A. Scherraga, *J. Chem. Phys.*, **44**, 3054 (1966).

TABLE 1. OBSERVED AND CALCULATED FREQUENCIES OF *n*-PENTANE IN cm^{-1}

Observed				Calculated		
Liquid IR	Liquid Raman	Solid IR	Solid Raman	TT form	TG form	GG form
470	467				456	
444*		444*		416		439
400	400	400	399	392		
386						395
334	333				350	
276		246		223	283	321
		131		221	250	318
				184	215	249
				121	130	153
				112	101	104

* This band is weak and the frequency somewhat deviates from what calculated for the TT form. This band may be ascribed to the impurity band.

bands of the TT form. In the liquid state new bands appear. The details of the spectra in the region 600—300 cm^{-1} are shown in Fig. 2. In the liquid state at −90°C the bands at 470, 386 and 334 cm^{-1} appear in addition to the 400 cm^{-1} band of the TT form. The 470 and 334 cm^{-1} bands are assigned to the TG form, since they are in agreement with the frequencies of the TG form calculated from the force constants of propane (see Table 1).[5] The TG form does not have any calculated frequencies near 386 cm^{-1}. The intensity of the 386 cm^{-1} band increases far more largely than the 470 and 334 cm^{-1} bands at higher temperatures as shown in Fig. 2 Furthermore, the observed frequency, 386 cm^{-1}, corresponds very well to the value, 395 cm^{-1}, calculated for the GG form. Accordingly, this band is assigned to the GG form. The intensity increase in the absorption of the 386 cm^{-1} GG band at higher temperature shows that the GG form is less stable than the TG form. The energy difference between the two forms could not be accurately obtained, since the 386 cm^{-1} band has a shoulder due to the TT band at 400 cm^{-1}. All the observed bands shown in Fig. 2 are assigned to the TT, TG, and GG forms as shown in Table 1. The bands due to the GG′ form could not be found.

After this work was finished Snyder[6] proved existence of the GG form from the CH_2 wagging vibrations. The conclusion is in agreement with ours.

5) A. Tomonaga and T. Shimanouchi, to be published.

6) R. G. Snyder, private communication.