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The Infra-Red Absorption Spectra of Propane-D-1 and Propane-D-2*

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The infra-red absorption spectra of the isomeric mono-deutero propanes have been observed. A difference in the position of the primary and secondary C-C stretching frequencies is reported. This difference places the secondary C-D frequency $45\text{ cm}^{-1} \pm 5\text{ cm}^{-1}$ lower than the corresponding primary C-D vibration.

INTRODUCTION

AN investigation of the infra-red absorption spectra of propane-D-1 and propane-D-2 was undertaken in an attempt to determine the precise position of the vibrational frequencies of the isolated primary and secondary carbon-deuterium bonds. Interest in these frequencies was based mainly on the need for an analytical method for the determination of the distribution of deuterium in isotopically substituted hydrocarbons.¹

MATERIALS AND EXPERIMENTAL

The isomeric propane-D-1 and propane-D-2 were prepared in 0.05-mole batches by decomposing normal and isopropyl magnesium bromide with 99.8 percent heavy water. This decomposition was carried out in a vacuum line and initial batches of the gas of the order of 15-20 cc were discarded to minimize any light hydrogen impurity. The propane formed was separated from any contaminating Grignard solvent, which in

this case was iso amyl ether, by distillation from dry-ice to liquid-air traps. The infra-red spectra were obtained from 2-15 μ with a Baird Associates, NaCl prism, recording spectrophotometer. The gas cell used was a 5-cm long and spectra in the case of propane-D-2 were taken at pressures of 50, 125, and 200 mm. Tank propane and propane-D-1 were measured at pressures of 50, 125, 200, and 400 mm.

DISCUSSION OF RESULTS

The infra-red absorption spectrum of propane has been investigated by Bartholome² and under high resolution by Wu and Barker.³ The assignment of frequencies presented in Table I is from Herzberg⁴ and is essentially that of Wu and Barker with a slight revision due to Pitzer.⁵ In addition in Table I our own experimentally observed frequencies for propane are reported. These are in good agreement with the values presented in A.P.I. Research Project 44 serial No. 99.⁶ The spectra of propane, propane-D-1 and propane-D-2 are presented in Figs. 1, 2, and 3, and the tabulation of the frequencies of the deuterium compounds in Table II.

The 3.4 μ band is due to 4 or 5 unresolved carbon-hydrogen stretching frequencies. The values obtained

TABLE I. Propane.*

Assignment	Infra-Red (Herzberg)	Infra-Red (Observed)
$\gamma_{20}-\gamma_{14}(B_2)$	720 (M) Q	
$\gamma_{26}(b_2)$	748 (S) Q	748 (S) Q
	864 (W) Q	
$\gamma_8\text{C}-\text{C}(a_1)$	870 (W)	870 (W)
$\gamma_{21}\text{C}-\text{C}(b_1)$	922 (M)	912 (M) Q
	925 (M) Q	
$\gamma_{20}(b_1)$	1053 (M) Q	1060 (M) Q
$\gamma_7(a_1)\gamma_{19}(b_1)$	1152 (M)	1152 (M)
$\gamma_{25}(b_2)$	1179 (M) Q	1172 (M) Q
$\gamma_{20}+\gamma_{14}(B_2)$	1338 (M) Q	1338 (M) Q
$\gamma_6\text{CH}_3(a_1)$	1370 (M)	1380 (M)
$\gamma_{18}\text{CH}_3(b_1)$	1375 (S)	1390 (S)
$\gamma_{17}\text{CH}_3(b_1)$	1465 (S) Q	
$\gamma_4\text{CH}_2(a_1)$	1468 (S)	1468 (γ S)
$\gamma_{24}\text{CH}_3(b_2)$	1470 (γ S) Q	
$\gamma_8+\gamma_{21}(B_1)$	1730 (W)	1730 (W)
$\gamma_{20}+\gamma_{21}(A_1)$	1936 (W)	1936 (W)
$\gamma_6+\gamma_{18}(B_1)$	(2640)	2640 (γ W)
$\gamma_{16}\text{CH}(b_1)$	2885 (M) Q	
$\gamma_2\text{CH}(a_1)$	2960 (M)	2980
$\gamma_{15}\text{CH}(b_1)\gamma_{23}\text{CH}(b_2)$	2968 (S) Q	
$\gamma_{22}\text{CH}(b_2)$	2980 (M)	
	3190 W	3120 W
		3300 W

* All frequencies in Tables I and II are in units of cm^{-1} .

* Work presented has been carried out under the auspices of the AEC.

¹ Turkevich, Friedman, Wrightson, and Solomon, J. Am. Chem. Soc. **70**, 2638 (1948).

TABLE II. Monodeutero propanes.

Propane-D-1	Propane-D-2
702 (W)	667 (W)
744 (W)	
870 (W) ?	
912 (S) Q	912 (S) Q
992 (W)	992 (W)
1050 (M) Q	
1140 (W)	1150 (M)
	1230 (W)
1290 (M) Q	
1335 (M)	1325 (W)
1350 (M)	
1370 (M) Q	
	1390 (M) Q
1407 (M) Q	
1470 (γ S)	1470 (γ S)
1650 (W)	1650 W
2164	2125
2980 (γ S)	2970 (γ S)

² E. Bartholome, Zeits. f. physik. Chemie **B23**, 152 (1933).

³ V. L. Wu and E. F. Barker, J. Chem. Phys. **9**, 487 (1941).

⁴ G. Herzberg, *Infra-Red and Raman Spectra* (D. Van Nostrand Company, Inc., New York, 1945).

⁵ K. S. Pitzer, J. Chem. Phys. **12**, 310 (1944).

⁶ A.P.I. Report 44 (National Bureau of Standards, Washington, D. C., 1945).

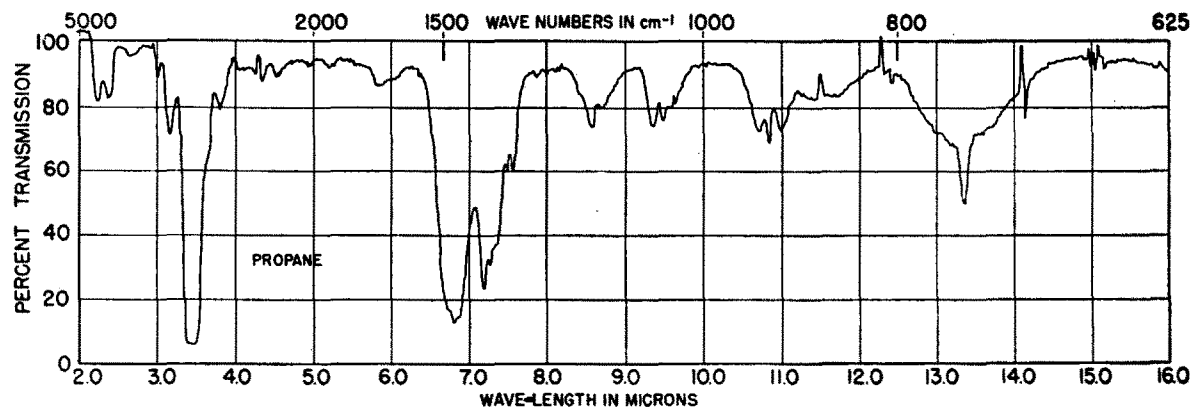


FIG. 1.

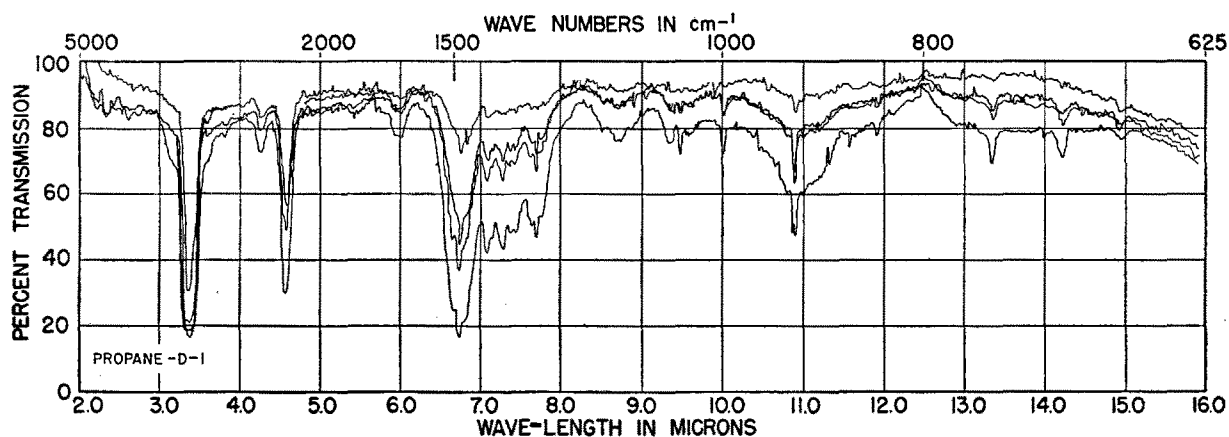


FIG. 2.

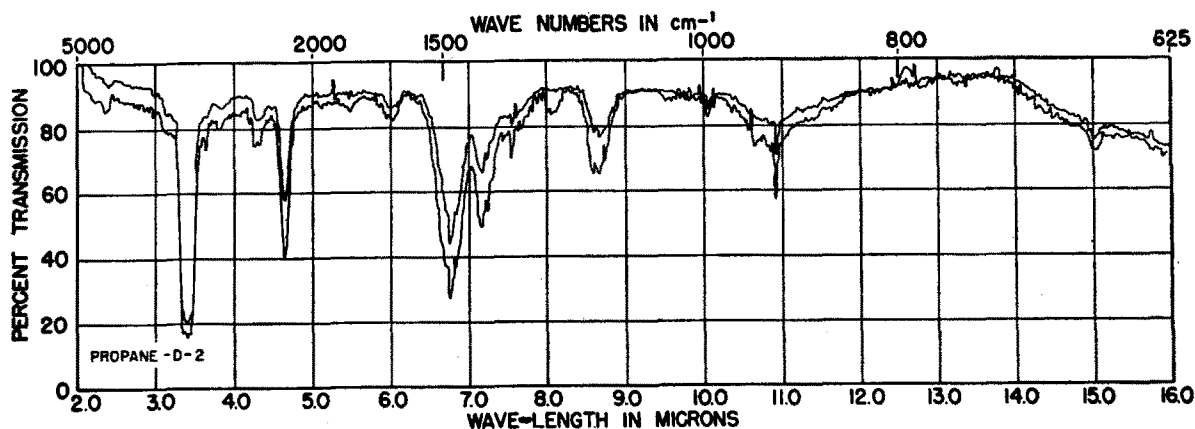


FIG. 3.

for peak of this band are 2980 cm^{-1} and 2970 cm^{-1} for propane-D-1 and propane-D-2 respectively. The difference is not significant in view of an estimated experimental error of 16 cm^{-1} in measurement of frequency in this region of the spectrum. Further discussion of the absorption in this region must await measurements under higher resolution. Fox and Martin⁷

⁷ J. J. Fox and A. E. Martin, Proc. Roy. Soc. London **175**, 208 (1940).

have examined, under high resolution, CCl_4 solutions of various hydrocarbons containing CH_3 groups without CH_2 or molecules containing CH_2 groups and no CH_3 groups. They first observed a shift from lower to higher frequency on going from CH_2 to CH_3 stretching vibrations. Two bands were observed in each case and assigned to symmetrical and unsymmetrical vibrations at 2853 cm^{-1} and 2926 cm^{-1} for CH_2 and 2885 cm^{-1} and 2960 cm^{-1} for CH_3 respectively. Thus both frequencies

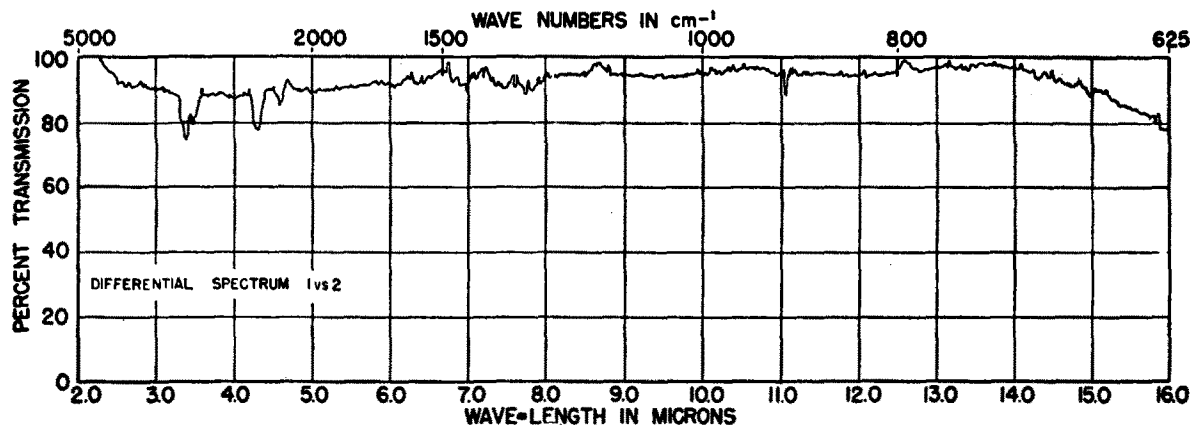


FIG. 4.

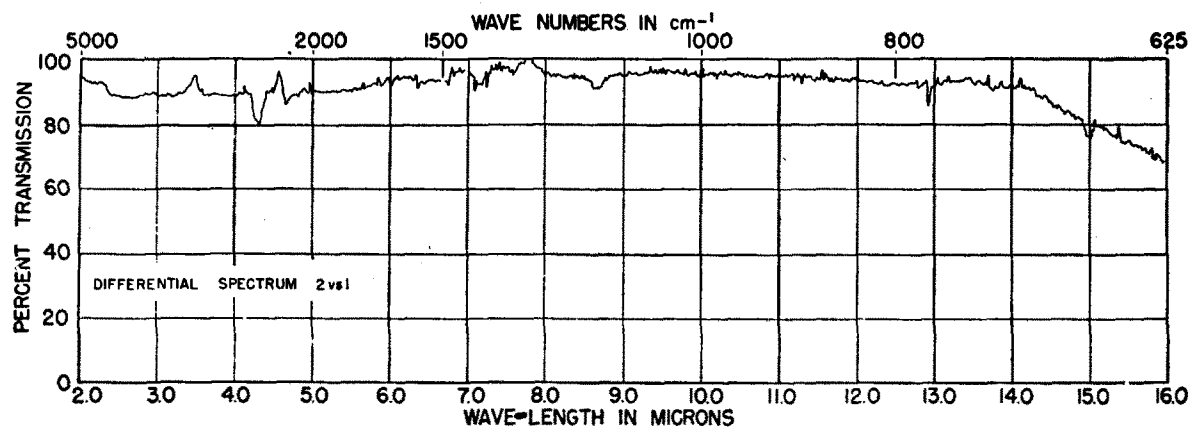


FIG. 5.

shift by approximately 30 cm^{-1} on going from CH_2 to CH_3 groups. In the case of propane which contains CH_2 and CH_3 groups in the same molecule the observed shift is only 12 cm^{-1} (Wu and Barker). The smaller difference between CH_2 and CH_3 in propane must be due to some type of coupling between the CH_2 and CH_3 oscillations. The 4.3μ band is due to absorption by atmospheric carbon dioxide present in the instrument. It is present when a spectrum is taken with no cells in the instrument and is seen in all figures presented.

The 4.6μ band corresponds to the C-D stretching vibration. In propane-D-1, the value is 2164 cm^{-1} and for propane-D-2 the value is 2125 cm^{-1} with an estimated error of 10 cm^{-1} . Since the difference between the observed positions of the C-D bands and the estimated error was rather small, an attempt was made to establish this difference of about 40 cm^{-1} by a more sensitive experimental approach. A difference spectrum was taken by placing a sample of the D-1 compound in one of the two beams of Baird spectrophotometer and the D-2 compound in the other optical path normally reserved for a compensating blank cell. The difference spectra for D-1 vs. D-2 and *vice versa* are presented in Figs. 4 and 5. These spectra were taken at $50 \pm 5\text{ mm.}$ pressure to minimize the effect of pressure broadening on the position of the band head.

The 4.6μ region of the spectra in Figs. 4 and 5 confirm a difference between the positions of the primary and secondary C-D stretching vibrations giving a separation of $45\text{ cm}^{-1} \pm 5\text{ cm}^{-1}$, with the secondary C-D vibration coming in at a lower frequency. An application of the simple isotope shift rule division of the C-D frequencies by $\sqrt{2}$ to obtain the difference in the C-H frequencies predicts a separation of the order of 60 cm^{-1} . The value is to be compared with the difference observed by Fox and Martin of about 30 cm^{-1} between the CH frequency in CH_3 and CH_2 and is in the proper direction, i.e., CH_2 having lower frequency. Our results and those of Fox and Martin are in disagreement with Wu and Barker who assign the higher frequency, 2980 cm^{-1} , to $\gamma_{22}(\text{CH})(b_2)$ an unsymmetrical CH_2 stretching vibration. Calculation of the C-H frequencies gives 3012 cm^{-1} for C-H secondary and 3075 for the C-H primary stretching vibrations. These values should be compared with the corresponding 2926 cm^{-1} and 2960 cm^{-1} obtained by Fox and Martin from their study of a series of hydrocarbons and 2968 and 2980 of Wu and Barker. Note, however, the reversal of the order reported by the latter workers. We can thus conclude that the coupling in protium propane which decreases the separation of the CH_2 and CH_3 frequencies to 12 cm^{-1} is removed when one goes to the monodeuterated

compounds. Furthermore a reassignment of the 2980 cm^{-1} and 2960 cm^{-1} and 2968 cm^{-1} bands in propane seem in order. The CH_2 stretching vibration $\gamma_{22}\text{CH}(b_2)$ cannot be assigned a higher frequency vibration than the unsymmetrical CH_3 stretching $\gamma_2\text{CH}(a_1)\gamma_{15}\text{CH}(b_1)$ and $\gamma_{23}\text{CH}(b_2)$. A better assignment is $\gamma_{22}\text{CH}(b_2)$ at 2968 cm^{-1} and $\gamma_{23}\text{CH}(b_2)$ at 2980 cm^{-1} .

At 6.8μ there are strong bands of approximately equal intensities in propane, propane-D-1 and propane-D-2. This band has been assigned to methyl and methylene deformation $\gamma_{17}\text{CH}_3(b_1)\cdot\gamma_4\text{CH}_2(a_1)$ and $\gamma_{24}\text{CH}_3(b_2)$ at 1465, 1468, and 1470 cm^{-1} (Tables 1 and 2). No conclusions can be drawn about the validity of the frequency assignment from observations on this band until further isotopic molecules are investigated.

In the $7.0\text{--}7.8\mu$ region there is a system of bands which show varying behavior as one goes from propane to the monodeuterated compounds. In propane the frequencies are 1390, 1380, and 1338 cm^{-1} ; in propane-D-1 they are 1407, 1370, 1350, 1335, and 1290 cm^{-1} ; while in propane-D-2 they are 1390, 1380, 1325 cm^{-1} . The assignments made for these bands in propane is $\gamma_{18}(\text{CH}_3)b_1$ to 1390 cm^{-1} and $\gamma_6(\text{CH}_3)a_1$ to 1380 cm^{-1} combination band $\gamma_{20}+\gamma_{14}$ to 1338 cm^{-1} . Since the bands at 1338, 1335, and 1325 cm^{-1} are probably this combination, they will not be discussed. The absence of a change in the band structure as one goes from propane to propane-D-2 gives credence to the assignment of the $7.0\text{--}7.8\mu$ band system to methyl deformation frequencies. Furthermore the fact that the 1390–1380 cm^{-1} band in propane and propane-D-2 are replaced by 1407 and 1370 cm^{-1} indicates that these vibrations not only involve the vibrations in methyl groups but also involve some interaction between the methyl groups in the first two compounds which is changed by the introduction of one deuterium into one of the methyl groups.

At 7.6μ there is a band which is present in propane-D-1 (1290 cm^{-1}) and is absent in the other two compounds.

At 8.4μ there are absorption bands in all three compounds at approximately the same frequency 1150 cm^{-1} . This absorption is ascribed to methyl and methylene rocking frequencies.

At approximately 9.5μ there are absorption bands in propane (1053 cm^{-1} and in propane-D-1 at (1050 cm^{-1}) and no band in propane-D-2. The assignment given to this system by Herzberg is $\gamma_{20}(b_1)$ which is methyl rocking. If it is a pure CH_3 rocking frequency it is surprising that it is missing in the propane-D-2 compound where the methyl groups are intact. On the other hand if it is a C–C stretching vibration (Rasmussen,⁸ Pitzer,⁵ Kohlraush,⁹ Kellner,¹⁰ Wu and Barker³) its absence in

propane-D-2 is even more surprising since these vibrations should be least affected by a particular deuterium substitution.

At 10μ (922 cm^{-1}) there is a weak band in both deuteropropanes which is absent in propane. This is roughly where one might expect an isotope shift on a C–H vibration in the 1400 cm^{-1} region of the spectrum would appear. On the other hand it fits the frequency calculated for C–Cb₁ stretching vibration by Rasmussen (998 cm^{-1}).

At 10.9μ (912 cm^{-1}) there is a strong band in both deuteropropanes which is present as a much weaker band in propane. This band has been assigned by Herzberg as $\gamma_{21}\text{CC}(b_1)$ a carbon-carbon stretching variation. However, Rasmussen and Wu and Barker have assigned this as a methyl rocking frequency. The fact that this band persists in all three molecules is strong evidence for the Herzberg assignment.

At 11.5μ (870 cm^{-1}) there is a band with a missing *Q* branch in propane which is apparently missing in both deuterocompounds. There is a possibility that this band was not detected in the latter compounds because of the increased intensity of the broad band at 10.9μ obscuring it. This band has been assigned as the $\gamma_8(\text{C–C})a_1$ stretching frequency on the basis of Raman data. However, it is possible that this particular carbon-carbon vibration may be coupled with a methyl rocking frequency (see Herzberg,³ p. 362).

At 13.4μ (748 cm^{-1}) there is a strong band in propane with a sharp central *Q* band. This band disappears completely in propane-D-2. This has been noted previously in a footnote by Rasmussen. In propane-D-1 there are weak bands at 744 and 702 cm^{-1} . The assignment given by previous workers for this vibration at 748 cm^{-1} is $\gamma_{26}(b_2)$ a methyl rocking. However, Rasmussen prefers to call it a CH_2 rocking frequency. Neither of these assignments explain the spectra and emphasize the fact that the vibrations of the component parts of this molecule are not independent but may be strongly coupled.

In conclusion it should be pointed out that neither a complete assignment of the 22 infra-red-permitted fundamentals of propane nor an unambiguous assignment of all of the 12 or 13 bands observed from $2\text{--}15\mu$ can be made from the data available. The two monodeuteropropanes may be readily distinguished from themselves and protium propane. Furthermore by shifting a particular C–H band or set of bands from 3.4μ to the 4.6μ region of the spectrum a means of observing relatively unperturbed carbon-hydrogen vibrations is obtained. The measurements presented indicate a difference of the order of 60 cm^{-1} between primary and secondary C–H frequencies isolated in such a manner. This corresponds to a 4 percent difference in the force constants, in agreement with the results of Fox and Martin.

⁸ R. S. Rasmussen, J. Chem. Phys. 16, 712 (1948).

⁹ K. W. F. Kohlraush and F. Koppl, Zeits. f. physik Chemie B26, 209 (1934).

¹⁰ L. Kellner, Trans. Faraday Soc. 41, 217 (1945).