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The Infra-Red Absorption Spectrum of Propane

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Of the twenty-seven internal degrees of freedom of propane, all nondegenerate, twenty-two may appear as fundamental absorption bands. These bands fall into three symmetry classes, designated A_1, B_1 and B_2, and distinguishable by their characteristic contours. Because of overlapping, however, it is impossible in many cases to determine their positions precisely. This is especially true in the regions of the C−H valence and deformation frequencies. Some ten or twelve fundamental bands may be identified with confidence as well as a number of combinations. An A_1 band at 870 cm^{-1} and a B_2 band at 748 cm^{-1} have been partially resolved, the line spacing being about 1.47 cm^{-1} in agreement with predictions based upon electron diffraction measurements. The fine structure of the B_1 bands has not been observed (the predicted spacing is 0.5 cm^{-1}) but the interval between maxima of the P and R branches is approximately 26 cm^{-1} as expected. With 24 cm-atmospheres of gas no bands were observed between 15μ and 35μ, although the symmetrical C−C deformation might be expected to produce a band of appreciable intensity within these limits. This frequency has apparently been observed in Raman spectra at 375 cm^{-1}.

SOME years ago the infra-red absorption spectrum of propane was investigated with a prism spectrometer by Bartholomé.[1] He found eleven bands between 14μ and 3.2μ, and eleven others, generally weaker, at wave-lengths below 3.2μ. They were not resolved sufficiently, however, to determine the characters of the associated motions. Several measurements of the Raman spectrum have also been reported,[2] and the distances between carbon atoms have been determined by means of electron diffraction.[3] This molecule belongs to the symmetry group C_{2v}, with the three carbon atoms forming an isosceles triangle whose vertex angle is obtuse. Twenty-seven internal degrees of freedom are indicated, without degeneracies. All the fundamental frequencies are permitted in Raman scattering, and twenty-two of the twenty-seven should be infra-red active.

Because of the relatively large moments of inertia, complete resolution of the rotational structure of the bands cannot be expected. Certain ones may be partially resolved, however, and for the others band envelopes may yield valuable information concerning the directions of oscillation of the electric moment, as has been shown by Dennison,[4] by Nielsen,[5] and by Badger and Zumwalt.[6] The last named authors have described the three different shapes of band envelopes to be expected for oscillations in different directions within the molecule. For propane $S \cong -0.90$ and $\rho \cong 2.7$ in their notation.** When the direction of oscillation of the electric moment

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[1] E. Bartholomé, Zeits. f. physik. Chemie **B23**, 152 (1933).

[2] P. Daure, Ann. de physique **12**, 375 (1929); S. Bhagavantam, Ind. J. Phys. **6**, 595 (1932); K. W. F. Kohlrausch and F. Köppl, Zeits. f. physik. Chemie **B26**, 209 (1934).

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[4] D. M. Dennison, Rev. Mod. Phys. **3**, 280 (1931).

[5] H. H. Nielsen, Phys. Rev. **38**, 1432 (1931).

[6] R. M. Badger and L. R. Zumwalt, J. Chem. Phys. **6**, 711 (1938).

** $S=(2b-a-c)/(a-c)$ and $\rho=(a-c)/b$, where a, b, and c are reciprocals of the principal moments of inertia, with $a>b>c$.

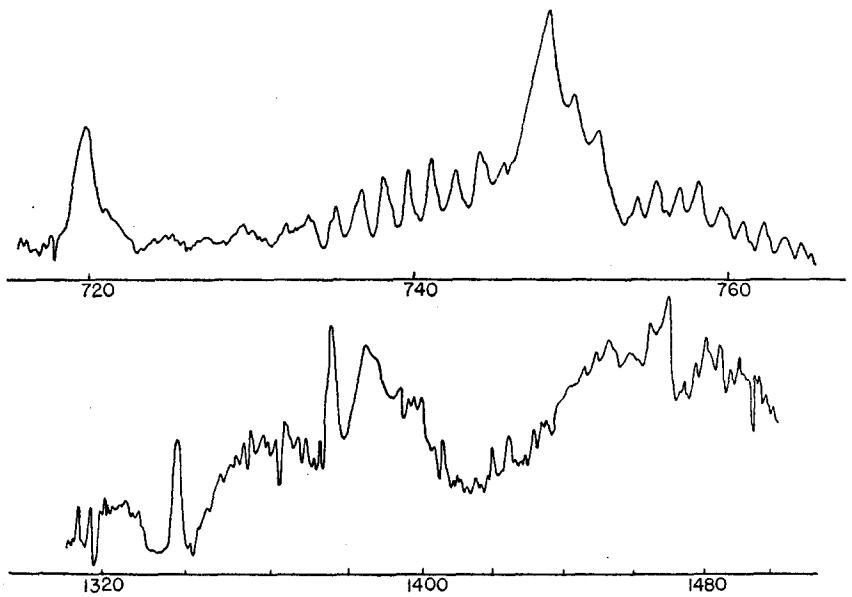

FIG. 1. The pair of B_2 bands near 13μ, and the δ_{CH} bands near 7μ.

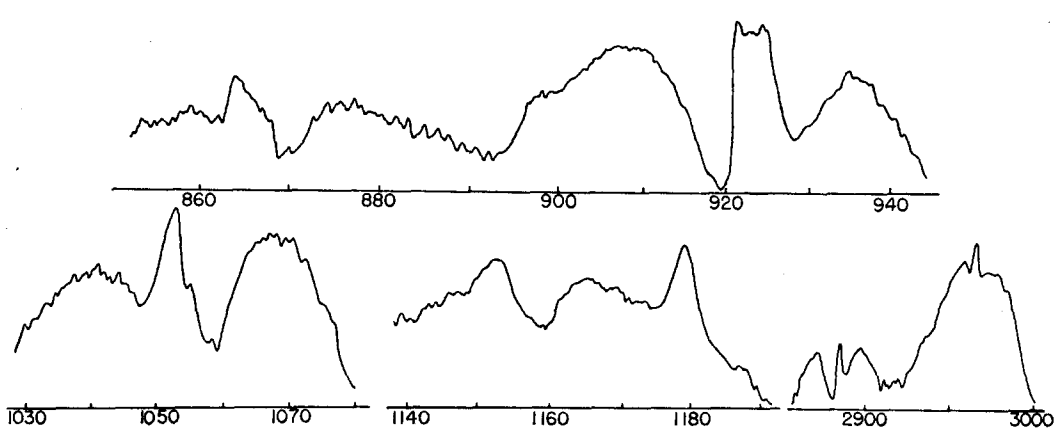

FIG. 2. Contours of several fundamental bands including the partially resolved A_1 band at 870 cm^{-1} and the B_1 combination band at 864 cm^{-1} (11.5μ).

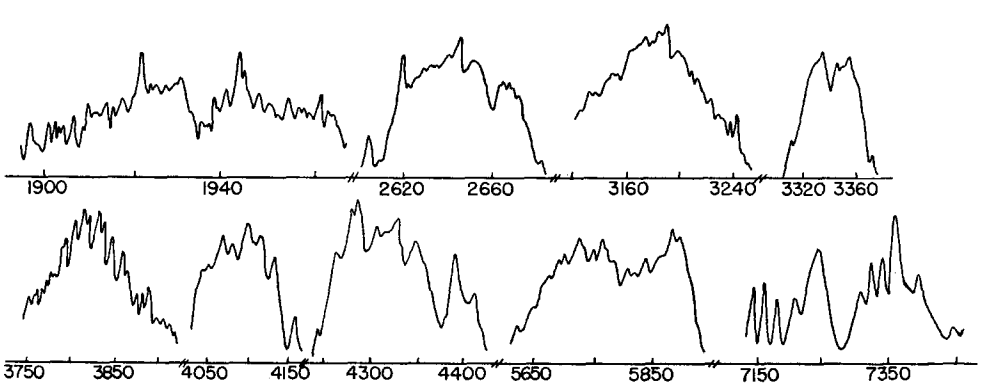

FIG. 3. Contours of harmonic and combination bands.

is along the twofold axis (the axis of the intermediate moment) the symmetrical motion falls in the class A_1, which includes nine modes of vibration. These bands are without obvious Q branches. The seven different motions in symmetry class B_1 are parallel to the plane of the carbon atoms but antisymmetric with respect to the twofold axis, hence the changes in electric moment are along the axis of minimum moment of inertia. The resulting bands have P, Q and R branches of comparable intensities, the Q branch being rather broad. The symmetry class B_2 includes six oscillations in which the changes of electric moment are along the axis of maximum moment of inertia, i.e., normal to the plane of the three carbon atoms. They give rise to bands with narrow and intense Q branches. A fourth symmetry class A_2 includes five symmetrical vibrations, none of which yield infra-red bands since they involve no change in electric moment.

Another rough but convenient classification of bands places them in three groups depending upon which particular atoms are principally involved in the motion. Only limiting cases are considered, and it must be remembered that the actual oscillations are not so simple; in general they involve linear combinations of the limiting cases. The first group includes motions primarily associated with the CH_2, the second includes the CH_3 oscillations, and the third those vibrations of the triangular structure formed by the three radicals each considered as rigid. This third group consists of nine torsional oscillations, three for each radical, and the three vibrations analogous to those of a symmetrical nonlinear triatomic molecule XY_2. The masses of the radicals being 15, 14 and 15, these last three frequencies should all lie below 1200 cm^{-1}. Dadieu and Kohlrausch[7] have predicted that the lowest one, corresponding to the symmetrical deformation, should occur at approximately 400 cm^{-1}. Subsequently Bhagavantam observed a Raman displacement at 377 cm^{-1}, and Kohlrausch and Köppl reported 373 cm^{-1}. There is in the Raman spectrum one sum band (1278 cm^{-1}) which seems to involve this frequency, but the corresponding difference has not been observed. Bartholomé failed to find any infra-red band near 375 cm^{-1}, and our own results are equally negative. It is interesting to note that the δ_{CC} vibration in propane appears to be so nearly inactive, since the corresponding infra-red band is very strong in nonlinear triatomic molecules.

[7] A. Dadieu and K. W. F. Kohlrausch, Akad. Wiss. Wien. **139**, 165 (1930).

Experimental

We have examined the spectrum of propane between 1.35μ and 35μ with a prism grating spectrometer, using an absorption cell 25 cm in length. The windows were either of NaCl or of KBr. Since the instrument is not completely enclosed, atmospheric water and carbon dioxide interfere appreciably with the measurements in some regions. Three bands have been partially resolved, the contours for several others have been determined, and a number of new bands have been located. No absorption of measurable intensity was found between 13μ and 35μ. Figures 1 to 3 present the observed results. The effective slit widths and the amount of gas used in each case are indicated in Table I, while Table II lists the positions of the various bands, their apparent symmetry characters, and possible assignments. It must be emphasized that a completely unique scheme of assignments would require more information than is as yet available. Moreover, in regions where several bands overlap it is not always possible to identify the components without ambiguity; hence the precise positions must be uncertain in some cases. This is particularly true around 1400 cm^{-1} and 3000 cm^{-1} where the C−H vibrations occur. Some assistance in the interpretation of various bands is provided by data already available upon

Table I.

Spectral Region λ in Microns	Gas Pressure in cm 25-cm Cell	Effective Slit Widths in cm^{-1}
35–15	72	0.60
13.0	25	0.43
11.5	72	0.50
10.8	72	0.84
9.5–8.5	65	0.84
7.0	5	0.50
5.1	72	0.70
3.8	65	1.85
3.4	0.5	1.28
3.0	65	1.65
2.6	72	2.0
2.4–2.3	65	3.0
1.7–1.3	65	4.5

TABLE II. *Classification of the propane bands.*

	Symmetry Classes				Analogs		
	A_1	A_2	B_1	B_2	Ethane	Ethylene	Cyclopropane
CH_2							
ν_σ				2980		3107, *3069*	3090
ν_π	2960					*3020*, 2988	
δ_π	*1450*					*1343*, 1444	*1453*, 1430
τ_σ			1152	1179		948, *943*	1020
						1015, *1035*	
τ_π		——				815	
CH_3							
ν_σ	*2966*	——	2968	2968	2980, *2965*		
ν_π	*2914*		*2942*		*2900*, 2955		
$2\delta_\sigma$	*2872*		2885	2885			
$2\delta_\pi$	*2722*						
δ_σ	1468	——	1465	1470	1461, *1463*		
δ_π	1370		1375		1375,* 1380		
τ_σ	*1149*	——	922	748	1170,* 831		
τ_π		——		——	275*		
C−C−C							
ν_σ			*1053*				
			1053				
ν_π	*867*				*993*	*1626*	*1184*, 865
	870						
δ_π	*375*						

* Not observed directly. Italics indicate Raman measurements. Subscripts π and σ indicate oscillations parallel to or perpendicular to the geometric axis of the group involved.

the analogous motions in ethane, ethylene and cyclopropane. These are also included in Table II.

Most of the A_1 frequencies are determined by Raman observations only, and for the liquid state. Two of the B_1 class also appear in Raman scattering as rather broad lines. The A_1 infra-red bands, lacking Q branches, are difficult to locate precisely unless isolated, as at 870 cm^{-1}. The methyl C−H valence vibrations apparently are complicated by resonance interaction, so that in class A_1 there are four Raman lines near 3000 cm^{-1}, and in each of the classes B_1 and B_2 at least two infra-red bands. These, of course, cannot be assigned individually to specific motions.

It is suggested that the B_2 band at 748 cm^{-1} arises from a rocking motion of the methyl radicals in a direction normal to the C_3 plane. For the corresponding motion parallel to the plane, the B_1 band at 922 cm^{-1} is proposed. Such specific assignments are perhaps hardly justified since both motions involve oscillations of the methylene also: in fact the pair of B_1 bands at 1152 and 922 cm^{-1}, and the pair of A_1 bands at 1179 and 748 cm^{-1}, are each combinations of the two limiting cases to which they have been assigned. The two normal frequencies in either case may have been quite close together, with the observed separation due to interaction.

The torsional motions τ_π of the methyl radicals around their own symmetry axes (in and out of phase) are of particular interest, but have not been identified. Their frequencies are probably low, and in consequence the excited states should be well populated. The transitions corresponding to any of the τ_σ oscillations may have somewhat different frequencies when the initial state is one of the τ_π excited levels. This would explain the broadening of the observed Q branches, particularly that of the 922 cm^{-1} band, which exhibits a second intense maximum at 925 cm^{-1}. Another possible interpretation, which, however, seems less probable, is to assign the frequencies 922 and 925 to the two infra-red τ_σ bands, and the frequency 748 to the τ_π band of type B_2.

The doublet type band at 870 cm^{-1} may be assigned with confidence to the symmetrical

TABLE III. *Observed values of $\Delta\nu_m$ for B_1 bands.*

ν	$\Delta\nu_m$	ν	$\Delta\nu_m$
923	27	1375	26
1053	26	1470	28
1152	26	2885	25

valence vibration of the C_3 framework. Apparently a second band, either of class B_1 or B_2, is superposed upon it, the Q branch appearing at 864 cm^{-1}. In the neighborhood of 1936 cm^{-1} a band is observed which, though only partially resolved, appears to be of the doublet (A_1) type, with a very irregular contour. This is probably a combination of the two B_1 bands at 922 and 1053 cm^{-1}. One other combination, observed as a Raman line, has already been mentioned; it is $1278=922(B_1)+375(A_1)$. Two moderately intense bands remain to be considered. They both have prominent Q branches, one at 1338 cm^{-1} and the other at 720 cm^{-1}; and they appear to belong to type B_2. No positive assertion regarding their origin can be made. Even the lower frequency seems much too high for the fundamental τ_π. It also seems too intense to represent the difference transition 1468–748. A possible explanation is that these two bands are sum and difference combinations of a low frequency A_2 band (τ_π) with the B_1 band at 1053. This would indicate a frequency of 333 cm^{-1} for one of the τ_π levels.

A number of other infra-red absorption regions have been observed, mostly at higher frequencies, representing multiple and combination bands. These are displayed in Fig. 3. Although some resolution is indicated, it seems hardly feasible at present to assign band centers, or to make definite assertions regarding their interpretation.

The B_2 band at 748.0 cm^{-1}, shown in Fig. 1, has been resolved into a fairly regular set of some twenty lines, almost equally spaced, as would be expected for a molecule having two nearly equal moments of inertia. By isolating the normal state a value of 1.475 cm^{-1} has been obtained for $h(a-d)/4\pi^2$, where a is the reciprocal of the smallest moment of inertia, and d is the mean of the reciprocals of the other two. The A_1 band at 870 cm^{-1} has also been partially resolved, with an average line interval in the R branch of 1.40 cm^{-1}. These frequency differences compare favorably with the value 1.47 computed for A_1 and B_2 bands using the C–C distances obtained by electron diffraction, and the C–H distance from methane. The corresponding line interval in the B_1 bands should be about 0.5 cm^{-1}, which could be observed only under very advantageous circumstances. The interval $\Delta\nu_m$ between maxima of the P and R branches in B_1 bands may be computed approximately, following Gerhard and Dennison,[8] its value being 26 cm^{-1}. Table III lists the values of $\Delta\nu_m$ observed for various B_1 bands. In Table IV the positions are given for the observed fine structure lines in the bands at 748 cm^{-1} and 870 cm^{-1}, and also for a number of the maxima appearing in the complex band near 1936 cm^{-1}.

TABLE IV. *Positions of observed lines in partially resolved bands.*

Band at 748 cm^{-1}		Band at 870 cm^{-1}		Band at 1936 cm^{-1}	
P	*R*	*P*	*R*	*P*	*R*
733.1	749.6	862.4	872.0	1914.9	1937.6
734.7	751.0	864.0	874.2	1916.8	1940.5
736.4	753.5	867.0	875.6	1918.7	1943.5
737.8	754.7		877.1	1922.3	1945.0
739.2	756.3		878.7	1924.5	1949.0
740.9	757.7		880.2	1926.0	1951.9
742.2	759.1		881.6	1927.7	1954.0
743.5	760.3		883.0	1930.6	1956.0
745.1	761.8		884.5	1934.0	
	763.4				

[8] S. L. Gerhard and D. M. Dennison, Phys. Rev. **43**, 197 (1933).