

Raman Effect in Liquid Ethane

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Raman Effect in Liquid Ethane

Further study of the Raman spectrum of ethane was considered advisable because of current controversy over the question of internal rotation in this molecule and because of variances noted in the reports of previous Raman investigations. We have measured nine Raman shifts in liquid ethane at -120°C . In Table I our values are shown in comparison with those existing in the literature.

Lines 994 , 2884 , and 2941 cm^{-1} are strong. The latter pair arise from resonance splitting¹ due to the proximity of a fundamental with the first overtone of another. The mean of the observed pair is 2913 . This corresponds to the higher fundamental. A pair of weaker diffuse lines are observed by us at 2922 cm^{-1} and 2963 cm^{-1} . These may likewise be attributed to resonance splitting. The mean value here is 2943 . Doubly degenerate frequencies² 1463 cm^{-1} (Raman active) and 1480 cm^{-1} (infra-red active) respectively could be responsible. It will be noted that the pairs overlap. Now the 2922 cm^{-1} line probably corresponds to that observed by Lewis and Houston³ at 2940 cm^{-1} . They do not record the presence of a single line corresponding to our 2963 cm^{-1} frequency, but this might well be one of the weak "Stokes lines" which they found in this region.

The diffuse line of medium strength 1463 cm^{-1} is present here; this was not found by Lewis and Houston; it was observed by Bhagavantam⁴ but was attributed by him to some impurity. Lewis and Houston's weak shift of 1344 cm^{-1} did not appear. Bartholme and Karweil⁵ list 743 cm^{-1} and 1375 cm^{-1} among the Raman active fundamentals of ethane; evidently these were deduced from specific heat data. We did not find experimental evidence for them.

Probably of isotopic origin is the weak line at 979 cm^{-1} which has been attributed to the $\text{C}^{12}-\text{C}^{13}$ molecule. This separation of 15 cm^{-1} from the corresponding frequency (994 cm^{-1}) of the normal molecule is slightly less than that reported by Bhagavantam.⁴ In measurements on four plates [8 pairs of lines] we found no separations differing more than one wave number from our value.

It is of interest to note that our values for the 994 cm^{-1} and 1463 cm^{-1} vibrations are slightly higher in frequency than are the corresponding values in the gaseous state. This reverses the shift normally observed in going from liquid to gas. However, calculations by Glockler and Wall⁶ have

shown that the force constant for the C-C bond is higher for liquids than for gases.

Raman tubes of 30 cc capacity were employed. The three prism Steinheil spectrograph gives dispersion of 8A/mm at 4358A . Eight concentric mercury-neon lamps furnished radiation. No filters were used. All Raman lines were excited by 4047 and 4358 , except for the shift 2768 cm^{-1} in which case near coincidence of lines prevents 4047 from being effective. 4078 excited only the strongest frequencies. There was little background; however, on longest exposures (16-20 hours) several unreported faint lines appeared which we have not been able to explain.

In commercial ethane the strongest lines of ethylene and propane appeared; these were not found in that prepared from EtMgBr and purified.

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Minneapolis, Minnesota,
April 6, 1938.

- ¹ E. Fermi, *Zeits. f. Physik* **71**, 250 (1931); A. Adel and E. F. Barker, *J. Chem. Phys.* **2**, 627 (1934).
² E. Bartholme and J. Karweil, *Naturwiss.* **25**, 476 (1937).
³ C. M. Lewis and W. V. Houston, *Phys. Rev.* **44**, 903 (1933).
⁴ S. Bhagavantam, *Ind. J. Phys.* **6**, 596 (1931).
⁵ G. Glockler and F. T. Wall, *J. Chem. Phys.* **5**, 813 (1937).
⁶ P. Daure, *Ann. de physique* **12**, 375 (1929).
⁷ M. M. Renfrew, *duPont Fellow* (1937-38).

The Oxygen Exchange Reaction of Glycine Hydrochloride and Water*

The oxygen exchange reaction of acetic acid and some of its derivatives with H_2O^{18} has been studied by Cohn and Urey¹ who observed complete oxygen exchange only in the case of trichloroacetic acid in slightly acidic solution. Recently we have been enabled by a grant from the Rockefeller Foundation to carry on an investigation of the oxygen exchange reaction of H_2O^{18} with various amino acids, their derivatives and with proteins.

We have observed that glycine hydrochloride exchanges its oxygen atoms 100 percent calculated on the basis of two available oxygens per molecule. This exchange took place at 100°C within 24 hr. at a pH of 1.9 or slightly less in a solution containing approximately 2 molecules of the hydrochloride to 3 molecules of water. Under the same conditions of time, temperature and molecular ratio no exchange was observable with glycine itself. Analysis of the water samples was carried out by the mass-spectrograph method of Cohn and Urey.¹ These observations are in complete agreement with the results of Dr. I. Roberts, department of chemistry, Columbia University, who has obtained complete exchange of 2 oxygen atoms at room temperature between acetic acid and H_2O^{18} in $N/10$ solution of hydrochloric acid within 30 days.

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¹ *J. Am. Chem. Soc.* **60**, 679 (1938).

TABLE I.

LIQUID ETHANE		GASEOUS ETHANE	
GLOCKLER RENFREW ⁷ (1938)	DAURE ⁶ (1929)	LEWIS HOUSTON ³ (1933)	BHAGAVANTAM ⁴ (1929)
979			975
994	990	993	993
		1344	.
1463	1460		1460
2733		2744	
2768		2778	
2884	2890	2899	2900
2922		2940	
2941	2950	2955	2955
2963		(Stokes lines)	