

LETTERS TO THE EDITOR

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The Raman Spectra of Deutero-acetones and Methyl Alcohol-*d*

Raman spectra have been photographed for a series of equilibrium solutions of the several deutero-acetones produced by means of the exchange reaction of acetone with deuterium oxide¹ and containing progressively higher deuterium fractions up to 91 percent. The results are summarized in Table I, from which the changes of frequency may be seen as a function of the isotopic composition.

Acetones (percent D)	0	4	24	51	70	91
Raman Frequencies (cm^{-1})	396		402	396	393	
	531	533	532	502	484	488
	796	790	760	714	702	706
	1068	1067	794	750	744	
	1706	1707	1047	1036	1030	1031
			1703	1703	1700	1704
		2175	2163	2126	2060	2049
			2182	2157	2104	2072
			2218	2222	2151	2113
	2918	2930		2256	2248	2219
	2970	2963	2934	2942	2948	2251
	3000	3001	2997	2992	3000	2937

As the deuterium fraction increases, the higher frequency of acetone at 2918 cm^{-1} and possibly the frequencies 2970 and 3000 cm^{-1} , increase slightly and then fade out, only the high probability parallel frequency at 2937 cm^{-1} appearing faintly in the most concentrated *d*-acetone. Simultaneously, at deuterium fraction = 4 percent, a line appears at 2175 cm^{-1} and three are found in this region when D = 24 percent. The strong lines at about 2115 , 2160 , 2219 and 2250 cm^{-1} appear at higher deuterium concentrations, with 2113 cm^{-1} becoming the strongest line at the greatest deuterium concentration; weak lines at 2049 and 2072 cm^{-1} also appear in the D = 91 percent acetone. The 1706 cm^{-1} line, ascribed to C=O, appears quite unchanged in all the acetones. The 795 cm^{-1} line splits in the intermediate acetones to give a second line at 760 cm^{-1} . This second line becomes strong, splits to give a third at about 700 cm^{-1} with the original line at 795 cm^{-1} disappearing. Finally, the 750 cm^{-1} line fades, leaving in the most concentrated *d*-acetone the 700 cm^{-1} as the strongest line. Lines at 531 cm^{-1} and 1069 cm^{-1} are gradually displaced toward the exciting line as the concentration of deuterium is increased.

We are attempting to interpret these results by the use of the equations of Rosenthal,² comparing the data with frequencies calculated for the four possible isotopic methyl groups.

The line observed at 2970 cm^{-1} with ordinary acetone is at present unexplained, CH_3 having theoretically only two frequencies near 3000 cm^{-1} .³ The usual explanation of resonance degeneracy apparently is not tenable in this case. The presence of the four strong and two weak lines at 2000 – 2250 cm^{-1} in the acetones having the greatest deuterium fraction is also of interest, since never more than the 3 hydrogen lines from 2900 – 3050 cm^{-1} appear in the acetones containing little deuterium.

Strong Raman lines appeared in acetone at 1157 , 1224 , 1340 and 1428 cm^{-1} . Lines at about these frequencies occur in the intermediate deutero-acetones and practically disappear in the 91 percent deutero-acetone. We have not tabulated these lines, however, because they may be due to excitation by the 4047 and 4078A lines of the mercury source. This point is being studied further.

The Raman spectra of methyl alcohol and methyl alcohol-*d* have been determined, using the mercury lines at 4358 and 2536A as exciting sources. Table II presents

TABLE II.

$\text{CH}_3\text{OH} (\text{cm}^{-1})$		$\text{CH}_3\text{OD} (\text{cm}^{-1})$	
From 2536	4358	2536	4358
1033	1031	1031	1034
	1056		1071
1109	1119	1153	1154
1153	1171		1179
1464	1451	1382	1370
2835	2839	2494 (Band)	2494 (Band)
2913	2914	2836	2839
2954	2948	2915	2918
2992	2982	2946	2947
3388 (Band)	3415 (Band)	2989	2986

the lines found. The OD band occurs at $2500 \text{ cm}^{-1} \pm 10$ and the OH band at $3400 \text{ cm}^{-1} \pm 20$.⁴ A line at about 1375 cm^{-1} in the CH_3OD spectra and one at 115 cm^{-1} in the CH_3OH were other differences noted. The four lines between frequencies 2840 and 3000 cm^{-1} are very strong.

J. R. BATES
LEIGH C. ANDERSON
J. O. HALFORD

University of Michigan,
Ann Arbor, Michigan,
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¹ Halford, Anderson and Bates, *J. Am. Chem. Soc.* **56**, 491 (1934); Halford, Anderson, Bates and Swisher, *ibid.*, **57**, 1663 (1935).

² Rosenthal, *Phys. Rev.* **47**, 235 (1935).

³ Adel and Barker, *J. Chem. Phys.* **2**, 627 (1934).

⁴ Redlich and Pordes, *Naturwiss.* **22**, 808 (1934).