

Infrared Spectra of Methanol and Deuterated Methanols in Gas, Liquid, and Solid Phases*

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The infrared spectra of CH_3OH , CH_3OD , CD_3OH , and CD_3OD in the five phases gas, liquid, vitreous solid, α -crystal, and (except perhaps for CD_3OH and CD_3OD for which the solid-solid transitions have not been studied) β -crystal have been recorded in the range 4000 to 300 cm^{-1} . The Raman spectrum of liquid CD_3OH has been recorded. A complete assignment of the internal modes is given, which differs somewhat from previous assignments for the CH_3 bending and rocking vibrations. No significant difference in spectrum occurred between the α -crystal and β -crystal phases. Under the full symmetry of the β -phase determined by x-ray diffraction only one OH out-of-plane bending band should occur.

1. INTRODUCTION

IN connection with a study of the intermolecular forces in CH_3OH and CH_3OD , a vibrational assignment was needed for the vapors and crystals at 0°K. The following previous investigations of the vibrational spectra of methanol and the deuterated methanols have been reported: CH_3OH : vapor infrared,¹⁻⁷ liquid infrared,⁸⁻¹² liquid Raman,¹³⁻²⁶ vapor Raman²¹; CH_3OD : vapor

Two bands are observed, and it is concluded that the carbon and oxygen atoms in one chain are not coplanar, as is required by the symmetry determined by x-ray diffraction [K. J. Tauer and W. N. Lipscomb, *Acta Cryst.* **5**, 606 (1952)], but that the chains are puckered and the x-ray symmetry arises because the puckered chains are irregularly distributed, a structure that had been previously suggested by Tauer and Lipscomb tentatively on the basis of high apparent thermal amplitudes. Bands occur in the crystal spectra near 500 cm^{-1} and 340 cm^{-1} at -180°C . These are interpreted as lattice modes, probably the two infrared-active modes that involve translations of the molecules.

infrared,^{3,4,7,8,27} liquid infrared,⁷ liquid Raman;^{15,17,19} CD_3OH and CD_3OD : vapor infrared^{3,4}; CD_3OD : liquid Raman.^{3,22} No work on the solids has been reported, except for a very brief statement about the 3- μ region of solid CH_3OH .^{28,29} There were a number of uncertainties in the assignment of the vapor frequencies. We have, therefore, recorded the infrared spectra of the four methanols CH_3OH , CH_3OD , CD_3OH , and CD_3OD , in five phases, viz., gas, liquid, vitreous solid, α -crystal, and, except perhaps for CD_3OH and CD_3OD for which solid-solid transitions have not been studied, β -crystal.

2. EXPERIMENTAL

2.1 Materials

Reagent-grade methanol was dehydrated twice by treatment with magnesium turnings and distilled through a 19-in. Vigreux fractionating column, the middle third of the constant-boiling fraction being collected. The spectrum after purification differed in no way from that of the original alcohol, and vapor chromatographic analysis showed no impurities greater than 0.1%.

The deuterated methanols were purchased from the Merck Chemical Company, Montreal. Vapor-chromatographic analysis showed them to be free from impurities within 0.1% except for a trace of xylene, which was easily removed by a simple vacuum distillation. All four alcohols were anhydrous, as indicated by the absence in the vapor and solid spectra of the strong H_2O absorption band at 1640 cm^{-1} or the corresponding D_2O absorption band at 1220 cm^{-1} . However, a trace of atmospheric moisture was often introduced into the liquid samples, which were handled with a pipette. The CD_3 groups in CD_3OH and CD_3OD were over 99% deu-

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¹ E. L. Kinsey and J. W. Ellis, *J. Chem. Phys.* **5**, 399 (1937).

² A. Borden and E. F. Barker, *J. Chem. Phys.* **6**, 553 (1938).

³ H. D. Noether, *J. Chem. Phys.* **10**, 693 (1942).

⁴ B. I. Stepanov, *J. Phys. Chem. (U.S.S.R.)* **19**, 497 (1945).

⁵ E. K. Plyler, *J. Research Natl. Bur. Standards* **48**, 281 (1952).

⁶ A. V. Stuart and G. B. B. M. Sutherland, *J. Chem. Phys.* **24**, 559 (1956).

⁷ P. Tarte and R. Deponthière, *Bull. soc. chim. Belges* **66**, 525 (1957).

⁸ J. R. Quinan and S. E. Wiberley, *J. Chem. Phys.* **21**, 1896 (1953); *Anal. Chem.* **26**, 1762 (1954).

⁹ A. M. Buswell, V. Deitz, and W. H. Rodebush, *J. Chem. Phys.* **5**, 501 (1937).

¹⁰ D. R. McMillan, Jr., *Phys. Rev.* **57**, 941 (1940).

¹¹ M. Davies, *J. Chem. Phys.* **16**, 267 (1948).

¹² F. A. Smith and E. C. Creitz, *J. Research Natl. Bur. Standards* **46**, 145 (1951).

¹³ S. Venkateswaran, *Phil. Mag.* **15**, 263 (1933).

¹⁴ B. Trumpy, *Kgl. Norske Videnskab. Selskabs Skrifter* **1**, (1934).

¹⁵ E. Bartholomé and H. Sachsse, *Z. physik. Chem.* **B30**, 40 (1935).

¹⁶ R. G. Loyarte and J. S. Fernández, *Contrib. estud. cienc. fis. y mat. (La Plata)* **1**, 3 (1935).

¹⁷ S. Mizushima, Y. Morino, and G. Okamoto, *Bull. Chem. Soc. Japan* **11**, 698 (1936).

¹⁸ J. R. Bates, L. C. Anderson, and J. O. Halford, *J. Chem. Phys.* **4**, 535 (1936).

¹⁹ J. O. Halford, L. C. Anderson, and G. H. Kissin, *J. Chem. Phys.* **5**, 927 (1937).

²⁰ J. Wagner, *Z. physik. Chem.* **B40**, 36 (1938).

²¹ J. R. Nielsen and N. E. Ward, *J. Chem. Phys.* **10**, 81 (1942).

²² M. de Hemptinne and T. Doehaerd, *Bull. Acad. roy. Belg. Ser. 5*, **30**, 189 (1944).

²³ A. L. S. Rao, *J. Indian Chem. Soc.* **22**, 260 (1945).

²⁴ P. K. Narayanaswamy, *Proc. Indian Acad. Sci.* **A26**, 121 (1947).

²⁵ W. G. Braun, D. F. Spooner, and M. R. Fenske, *Anal. Chem.* **22**, 1074 (1950).

²⁶ H. Nakamura and I. Obata, *Busseiron Kenkyu* **85**, 36 (1955); *Chem. Abstr.* **50**, 5406 (1956).

²⁷ E. F. Barker and G. Bosschieter, *J. Chem. Phys.* **6**, 563 (1938).

²⁸ M. van Thiel, E. D. Becker, and G. C. Pimentel, *J. Chem. Phys.* **27**, 95 (1957).

²⁹ G. C. Pimentel, in *Hydrogen Bonding* (Ljubljana Symposium, 1957, edited by D. Hadži, Pergamon Press, New York 1959), p. 107.

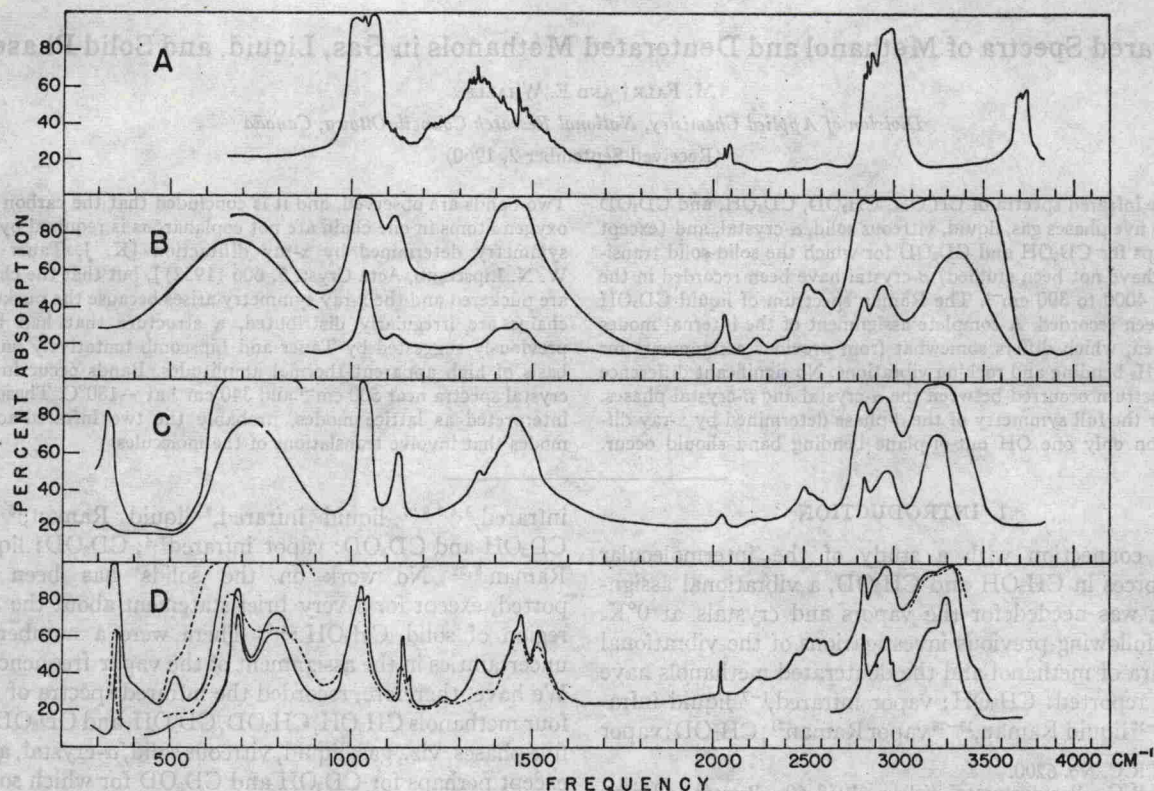


Fig. 1. Infrared absorption spectrum of CH_3OH . A—Vapor, 10-cm path-length, 80 mm Hg pressure, room temperature. B—Liquid, room temperature. Two sample thicknesses are shown, approximately 5 and 50 μ . C—Vitreous solid, -180°C . D—Crystalline solid, -180°C (full line) and -108°C (broken line, shown only where the spectrum differs appreciably from that at -180°C). Several film thicknesses are shown.

terated, as shown by an almost complete lack of absorption in the CH stretching region. The OD groups in CH_3OD were about 95% deuterated.

2.2 Spectra

The vapor spectra were recorded using a standard 10-cm gas cell filled to about 80 mm Hg methanol pressure at room temperature. The liquid films were formed by squeezing a small drop between two flat silver-chloride or cesium-bromide disks. The solid samples were prepared by condensing small amounts of vapor onto a cesium-bromide disk mounted in a silver holder in a conventional low-temperature infrared cell. The disk was pressed tightly against the holder by a spring to ensure good thermal contact. The temperature was measured to about 2°C by a copper-constantan thermocouple embedded in the cesium-bromide disk; about -180°C was normally registered with liquid nitrogen in the coolant reservoir, and the temperature registered when films of CH_3OH melted was $-97 \pm 5^\circ\text{C}$, compared with the true melting point of -98°C .

The infrared spectra were recorded on a Perkin-Elmer model-21 double-beam spectrophotometer equipped with sodium-chloride and calcium-fluoride prisms, and on a Beckman IR-4 double-beam spectrophotometer equipped with cesium-bromide and, for some spectra, lithium-

fluoride prisms. The instruments were regularly calibrated using the spectrum of water vapor and of thin polyethylene films. The Raman spectrum of liquid CD_3OH was recorded on a Cary model-81 Raman Spectrophotometer and the polarization of the bands was determined by the Edsal and Wilson technique.

3. RESULTS

Composite tracings of the infrared spectra of all four methanols in the gas and liquid phases at room temperature, the vitreous solid (see below) at -180°C , and the crystalline phases at -180°C and -108°C , are shown in Figs. 1-4. They were obtained by dividing the transmission of the cell containing the methanol sample by the transmission of the empty cell, except where the background was low and flat, when this procedure was not needed. The background noise was serious only below 350 cm^{-1} ; it was smoothed out in replotting the spectra.

The observed frequencies and rough relative intensities are listed in Tables I-IV. They are usually the means of several measurements. The accuracy of the frequencies of sharp bands above 2000 cm^{-1} is at least $\pm 4\text{ cm}^{-1}$, below 2000 cm^{-1} at least $\pm 2\text{ cm}^{-1}$, and below 500 cm^{-1} at least $\pm 1\text{ cm}^{-1}$. The centers of broad bands are measured much less accurately. The intensities of the bands below 650