

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231185958>

Deuterated methanol (99.8%) nuclear magnetic resonance thermometer

ARTICLE in ANALYTICAL CHEMISTRY · DECEMBER 1985

Impact Factor: 5.64 · DOI: 10.1021/ac00291a054

CITATIONS

16

READS

33

1 AUTHOR:



[Eddy Walther. Hansen](#)

University of Oslo

112 PUBLICATIONS 1,475 CITATIONS

SEE PROFILE

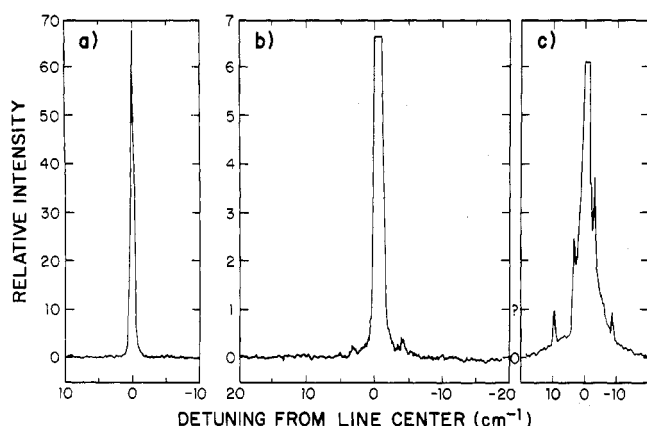


Figure 2. Spectral analyses of the dye laser output at various gains in the detection system: (a) gain $\times 1$, (b) scale expansion of Figure 2a, (c) photomultiplier tube highly saturated and gain unknown at line center.

3-mm-thick windows; there is no window in the output beam; the Brewster window sealing the grating chamber is 1.2 mm thick; and the wedged feedback spoilers are 0.7 mm thick.

Intense structure was also observed in optogalvanic spectra of the same Lu transition taken in a hollow cathode discharge when dye laser intensities were above the saturation level.

Structure in laser-generated optical spectra involving resonant intermediate states can result from laser sidebands with an intensity difficult to observe by routine optical diagnostics. Although it is difficult, without an extensive survey of available

laser systems, to estimate how general this phenomenon is, sideband generation via mode beating has been reported in other work (6-8). We suspect that the occurrence of weak sidebands on the laser output at some level is a relatively common phenomenon, but only observed under special circumstances. These sidebands may result in a significant loss in analytical selectivity when a matrix atom has a transition close to the analytical transition used. This is a very important consideration in isotope analysis.

ACKNOWLEDGMENT

Jeffrey Paisner, Lawrence Livermore Laboratory, suggested the origin of our complex spectrum. He has observed similar effects in the photoionization of uranium. We appreciate useful discussions with Dinh Nguyen and Rolf Engleman, Jr., Los Alamos National Laboratory.

Registry No. Lu, 7439-94-3.

LITERATURE CITED

- (1) Miller, C. M.; Nogar, N. S. *Anal. Chem.* **1983**, *55*, 481-488.
- (2) Downey, S. W.; Nogar, N. S.; Miller, C. M. *Int. J. Mass Spectrum Ion Processes* **1984**, *61*, 337-345.
- (3) Miller, C. M.; Nogar, N. S. *Anal. Chem.* **1983**, *55*, 1806-1808.
- (4) Miller, C. M.; Engleman, Rolf, Jr.; Keller, R. A. *J. Opt. Soc. Am. B* **1985**, *2*, 1503-1509.
- (5) Demtröder "Laser Spectroscopy"; Springer-Verlag: New York, 1981.
- (6) Paisner, J., Lawrence Livermore Laboratory, Livermore, CA, unpublished results.
- (7) Littman, M. G. *Opt. Lett.* **1978**, *3*, 138-140.
- (8) King, D. S.; Cavanagh, R. R. *Opt. Lett.* **1983**, *8*, 18-20.

RECEIVED for review May 13, 1985. Accepted August 1, 1985.

Deuterated Methanol (99.8%) Nuclear Magnetic Resonance Thermometer

Eddy Walther Hansen

Department of Chemistry, University of Oslo, P.O. Box 1033, Blindern, N-0315 Oslo 3, Norway

Different techniques have been designed in order to determine the true sample temperature in NMR experiments (1-6). Using the direct method of placing a thermocouple in the probe or in the temperature-regulating gas flow necessitates a frequent recalibration when probe geometry or gas flow rates are changed. The most general indirect method has been to make use of a "NMR thermometer", a sample such as methanol or ethylene having a strongly temperature-dependent chemical shift.

During a NMR study on the liquid phase in doped ice at sub-zero temperature (7) we found it convenient to use a "99.8% deuterated methanol thermometer" placed in a capillary inside the ice sample in order to record a temperature spectrum and a sample spectrum simultaneously. A deuterated methanol sample was chosen in order to lock the spectrometer system and to minimize the ratio of the signal from the "NMR thermometer" and the small liquid signal from the doped ice sample. Using too much nondeuterated methanol would make this ratio too big and cause dynamic range problems (8) with a consequent decrease in the reliability of quantitative measurements. On the other hand, using too little deuterated methanol would reduce the lock stability.

EXPERIMENTAL SECTION

The proton spectra were obtained on a pulse FT NMR spectrometer, Bruker CXP-200. Sixteen scans for each record were accumulated by using a bandwidth of 1.5 kHz with 16K data points giving a digital resolution of 0.188 Hz. In order to minimize

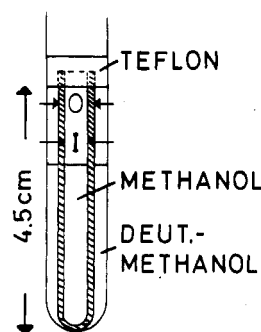


Figure 1. The lower part of the NMR tube (inner diameter 4.20 mm) showing the "methanol thermometer" placed in the capillary (i.d., $I = 0.50$ mm and o.d., $O = 2.20$ mm) and the deuterated solution kept in the annulus. The liquid height was approximately 3 cm measured from the bottom of the NMR tube.

the uncertainty in chemical shift, all the NMR spectra have been analyzed by a Lorentzian curve-fitting procedure (9). An air-saturated solution of methanol (Fluka, purum quality) containing 0.03% by volume of concentrated aqueous hydrochloric acid (in order to sharpen the NMR lines) was used as a reference thermometer (5). The temperature was calculated from the observed chemical shift separation (Δ) of the OH protons and the CH_3 protons by the generally accepted formula given by Van Geet (5) scaled to 200 MHz

$$T = 403.0 - 0.1473\Delta - (5.958 \times 10^4)\Delta^2 \quad (\Delta \text{ in Hz}) \quad (1)$$

The air-saturated 99.8% deuterated methanol solution with 0.03% by volume concentrated hydrochloric acid also contained 6% by volume of TMS.

Measurements on four identically prepared deuterated methanol samples were performed. Before any experiment was carried out the system was allowed to equilibrate for 15 min after a temperature change. Part of the experimental setup is shown schematically in Figure 1.

RESULTS AND DISCUSSION

A preliminary study in which two identical methanol samples were placed in the capillary and in the annulus gave the following results. (A) If the temperature in the sample was changed by 1 °C, the chemical shift of the residual OH proton in the deuterated methanol sample was altered by at least 1.3 Hz. Any temperature gradient across the sample would therefore give rise to a broadening of this peak. Throughout the experimental temperature region the observed line width was found to be less than 1.1 Hz (at 185 K) showing that any vertical or horizontal temperature gradient across the sample volume must be less than 0.82 °C. However, there was no observable difference between this line width and the corresponding line width of the Me₄Si peak, which indicates that field inhomogeneity was probably the main reason for the observed line broadening and that the *vertical* and/or horizontal temperature gradient was likely to be much less than 0.82 °C. (B) The probe temperature was stable to within 1.0 K over a period of 1 h at the lowest temperature setting of 185 K. (C) A horizontal temperature gradient of about 1 °C at the lowest temperature could be detected when no spinning was applied. However, after an additional 10 min of temperature stabilization the gradient was reduced to zero. (D) The spectra of the two methanol samples from the annulus and the capillary were identical, but showed a minor significant displacement relative to each other. This phenomenon is due to susceptibility effects caused by the capillary glass wall and is discussed in detail elsewhere (10). This observation is not of any importance to this work.

By substitution of the reference solution in the annulus with 99.8% deuterated methanol, the chemical-shift difference of the residual OH proton and CD₂H proton against temperature could be determined (Figure 2). No significant difference could be observed between the four different runs (Figure 2). The position of the CD₂H proton (quintet) is shifted toward higher field relative to the CH₃ protons (singlet), which is solely explained by an isotope effect (11)

$$\delta_{\text{CD}_2\text{H}} (\text{Hz}) = 653.8 + (2.03 \times 10^{-3})T + (7.285 \times 10^{-5})T^2 \quad (2)$$

relative to Me₄Si with an error (root mean square) of 0.16 Hz. A corresponding shift toward higher field is also observed for the residual OH proton in the deuterated methanol solution relative to the nondeuterated solution, which is attributed to an isotope effect similar to that discussed previously for the CD₂H proton

$$\delta_{\text{OH}} (\text{Hz}) = 1295.3 - (0.336)T - (2.511 \times 10^{-3})T^2 \quad (3)$$

relative to Me₄Si with an error (root mean square) of 1.21 Hz.

The chemical shift (Δ) in Hz between the residual protons of the CD₂H and OH group in the 99.8% deuterated methanol

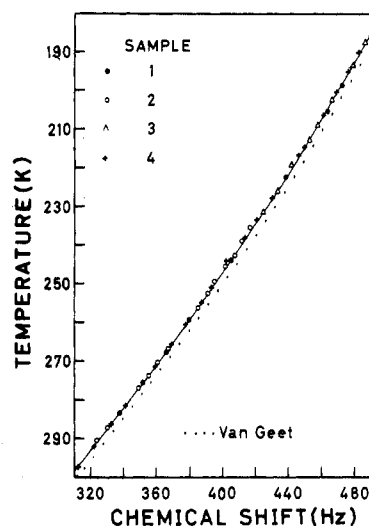


Figure 2. Temperature dependence of the chemical shift separation of CD₂H and OH proton lines of a 99.8% deuterated methanol sample measured at 200 MHz. The solid line is calculated from eq 4 and represents the best fit to the observed data while the dotted line is calculated from Van Geet's expression, scaled to 200 MHz, eq 1.

sample was correlated with temperature to give a quadratic equation, analogous to the Van Geet expression (5), with an error (root mean square) of 0.69 K.

$$T = 398.7 - 0.1347\Delta - (6.109 \times 10^{-4})\Delta^2 \quad (4)$$

The observed chemical shift difference (Δ) in deuterated methanol is systematically smaller than the corresponding value in nondeuterated methanol (Figure 2) and must be caused by an isotope effect that influences the residual CD₂H and OH proton somewhat differently.

Within experimental error the measured difference is found to be constant and therefore independent of temperature. The observed value, 4.3 Hz, is equivalent to 1.7 K and leads to the important conclusion that Van Geet's equation (eq 1) can be applied to a "deuterated methanol thermometer" by subtracting a constant equal to 1.7 K.

Registry No. Deuterated methanol, 811-98-3.

LITERATURE CITED

- (1) Slonin, I. Y.; Arshava, B. M.; Klyuchikov, V. N. *J. Phys. Chem.* **1976**, *50*, 165-166.
- (2) Kaplan, M. L.; Bovey, F. A.; Cheng, H. N. *Anal. Chem.* **1975**, *47*, 1703-1705.
- (3) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227-2229.
- (4) Raiford, D. S.; Fisk, C. L.; Becker, E. D. *Anal. Chem.* **1979**, *51*, 2050-2051.
- (5) Van Geet, A. L. *Anal. Chem.* **1980**, *42*, 679-680.
- (6) Ammann, C.; Meler, P.; Merbach, A. E. *J. Magn. Reson.* **1982**, *46*, 319-321.
- (7) Gran, H. C.; Pedersen, B.; Hansen, E. W.; Ellingsen, D. S., unpublished work, University of Oslo, 1983.
- (8) Abraham, R. J.; Lofthus, P. "Proton and Carbon-13 NMR Spectroscopy. An Integrated Approach"; Heyden: London, 1978.
- (9) Weiss, G. H.; Ferretti, J. A.; Klefer, J. E. *J. Magn. Reson.* **1982**, *46*, 69-83.
- (10) Zimmermann, J. R.; Foster, M. R. *J. Phys. Chem.* **1957**, *61*, 282-289.
- (11) Batiz-Hernandez, H.; Bernheim, R. A. *Prog. Nucl. Magn. Reson. Spectrosc.* **1967**, *3*, 63-85.

RECEIVED for review April 22, 1985. Accepted August 6, 1985.