



**HAL**  
open science

# THERMAL EXPANSION OF THE CLATHRATE HYDRATES OF ETHYLENE OXIDE AND TETRAHYDROFURAN

J. Tse

► **To cite this version:**

J. Tse. THERMAL EXPANSION OF THE CLATHRATE HYDRATES OF ETHYLENE OXIDE AND TETRAHYDROFURAN. Journal de Physique Colloques, 1987, 48 (C1), pp.C1-543-C1-549. 10.1051/jphyscol:1987174 . jpa-00226320

**HAL Id: jpa-00226320**

**<https://hal.science/jpa-00226320>**

Submitted on 4 Feb 2008

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

**THERMAL EXPANSION OF THE CLATHRATE HYDRATES OF ETHYLENE OXIDE  
AND TETRAHYDROFURAN**

J.S. TSE

*National Research Council of Canada<sup>(1)</sup>, Division of Chemistry,  
Ottawa, Ontario, K1A 0R9, Canada*

**Résumé**

Les paramètres de la cellule élémentaire des clathrates hydrates d'oxyde d'éthylène et de tétrahydrofurane ont été mesurés de 20 à 250 K par diffraction des rayons X (méthode des poudres). Les coefficients de dilatation linéaire pour les 2 clathrates hydrates sont de grandeur comparable, cependant ils sont beaucoup plus grands que pour la glace hexagonale. La plus grande dilatation thermique des hydrates indique une plus grande anharmonicité du potentiel cristallin. Un écart positif du paramètre de Grüneisen à basse température a été observé. La température de Debye caractéristique et les densités d'états vibrationnels de réseau de l'hydrate ont été à partir de la théorie quasi-harmonique.

**Abstract**

The unit cell parameters of clathrate hydrates of ethylene oxide and tetrahydrofuran have been measured from 20 to 250 K by X-ray powder diffraction. The coefficients of linear expansion for the two clathrate hydrates are of comparable magnitude and larger than that for hexagonal ice. The larger thermal expansivity in the hydrates indicates a greater anharmonicity in the crystal potential. A positive deviation of the Grüneisen parameter at low temperature was observed. The characteristic Debye temperature and the moments of the lattice vibrational density of states of the hydrate have been evaluated from quasi-harmonic theory.

**Introduction**

Clathrate hydrates are non-stoichiometric inclusion compounds with water molecules forming a three dimensional network where small atoms or molecules can be engaged in the empty voids [1]. In view of the gross similarity of the local coordination around the water molecules in the hydrates to that in hexagonal ice, it is not surprising that most of their vibrational features are very similar. However, there are growing evidences showing *anomalous* behaviour in several properties of the hydrates. The most unusual observation is that the thermal conductivity of the clathrate hydrates, depending on the temperature, is about five to twenty times lower than that of ice [2 - 7]. Since thermal resistivity is a consequence of the scattering of phonons by the anharmonic part of the crystal potential, the lower thermal conductivity suggests that the anharmonic interactions in the hydrate crystal will be quite different from that in ice. Therefore, it is very useful to measure the thermal expansivity of

<sup>(1)</sup> Issued as NRCC 26145

the clathrate hydrates. The magnitude of the thermal expansion provides direct information on the extent of anharmonicity in a crystal.

### Experimental

Structure I [8,9] ethylene oxide hydrate was prepared by slow cooling in an ice bath a saturated solution of ethylene oxide. The crystal was finely ground and loaded at liquid nitrogen temperature into a vacuum-sealed aluminium sample holder equipped with a beryllium window. Structure II hydrate [10] of tetrahydrofuran was prepared by rapidly cooling directly in the aluminium sample holder a solution of tetrahydrofuran in distilled water mixed in the ideal stoichiometric ratio (1 : 17) [11]. The samples were conditioned at  $-30^\circ$  for several days. The sample holder was then mounted on the cool tip of a closed-loop liquid helium cryostat (*Displex* model CS-202). The temperatures were measured with a gold-iron thermometer inserted into the back of the holder. A vacuum-tight seal was found to be very important as the volatile organics started to vapourize at 200 K in an unsealed sample. The powder patterns were measured with a *STOE* powder diffractometer using  $CuK_\alpha$  (1.542 Å) radiation. The variation in the unit cell parameters as a function of temperature was measured by monitoring the diffraction angles of the [222]/[321], [530] and [531] Bragg reflections in ethylene oxide hydrate, and the [115], [135], [066] and [555] reflections in tetrahydrofuran hydrate. The reproducibility of the data was ensured by cycling the temperature of the measurements. Since both hydrates have a cubic unit cell, the lattice parameter  $a$  is the only dependent variable. Because the sample position shifts with temperature, both the cell parameter  $a$  and the off-axis parameter were calculated from a least-squares fit to the positions of the Bragg peaks [12]. The average off-axis displacement of the sample was about 0.3 mm for ethylene oxide hydrate and 0.6 mm for tetrahydrofuran hydrate. We checked this procedure for Si using 8 Bragg peaks and found results within 0.001 Å or 0.02 % of published values. For the clathrate hydrates measurements, the accuracy in the derived lattice parameters is about 0.05 %.

### Results and Discussion

The variation of the unit cell parameter as a function of temperature for ethylene oxide hydrate and tetrahydrofuran hydrate is depicted in Figure 1. The data for ethylene oxide hydrate in the range 20 to 260 K can be represented by,

$$a(T)(\text{Å}) = 11.835 + 2.2173 \times 10^{-5}T(/K) + 2.2415 \times 10^{-6}T^2 (/K^2) \quad (1)$$

and for tetrahydrofuran hydrate by,

$$a(T)(\text{Å}) = 17.130 + 2.429 \times 10^{-4}T(/K) + 2.013 \times 10^{-6}T^2(/K^2) - 1.009 \times 10^{-9}T^3(/K^3) \quad (2)$$

The present results can be compared with several previous measurements at selected temperatures. The unit cell parameter of ethylene oxide hydrate was found to be 12.03(1) Å at  $-25^\circ\text{C}$  from single crystal X-ray diffraction [13], 11.89(2) Å at  $110 \pm 10$  K from X-ray powder diffraction [14] and 11.87(1) Å from single crystal neutron diffraction on a deuteriated

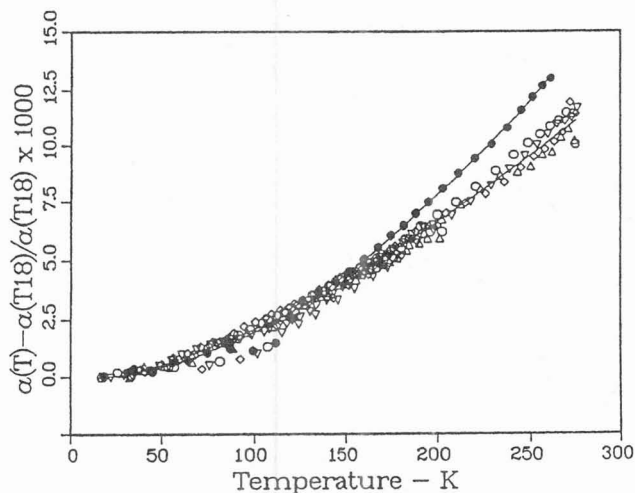


Figure 1. Thermal expansion of the lattice parameters for ethylene oxide hydrate ( $\bullet$ ) and tetrahydrofuran hydrate ( $\circ$ [115],  $\nabla$ [555],  $\triangle$ [135] and  $\diamond$ [066]).

sample [15]. Our results at the corresponding temperatures were 11.992(5), 11.865(5) and 11.850(5) Å respectively. Even though our results appear to be consistently lower, the agreements are satisfactory considering the uncertainty in the temperature measurements in the previous studies and notwithstanding the possibility that non-uniformity in the stoichiometry of ethylene oxide in hydrates may lead to small differences in the cell parameters [16]. For tetrahydrofuran hydrate, there are two independent measurements performed at  $110 \pm 20$  K using X-ray powder diffraction. The derived lattice parameters of 17.15(2) [17] and 17.13(3) Å [18] are very closed to the 11.179(9) Å determined in this work. Another measurement at 135 K gives  $a = 17.170(4)$  Å and can be compared with 17.197(6) Å obtained here. The thermal expansion of a tetrahydrofuran hydrate have been measured from 80 to 260 K using a dilatometer [19]. The coefficients of linear expansion at 100, 150, 200 and 250 K are 28, 42, 52 and 62 ( $\times 10^{-6}/\text{K}$ ) are in excellent agreement with our values of 36, 45, 54 and 61 ( $\times 10^{-6}/\text{K}$ ) evaluated at the same temperatures.

The coefficients of thermal expansion are obtained by differentiating eqn 1 and 2 and are considered accurate to about  $\pm 10\%$ . The magnitudes of the expansivities of ethylene oxide and tetrahydrofuran hydrate are found to be comparable to each other but significantly larger than ice [20]. At low temperatures, the thermal expansion of the hydrate is almost three times that of ice but the difference becomes smaller at higher temperatures. The large thermal expansivity of the hydrates is a strong indication of greater anharmonicity in the crystal potential. There are two possible factors contributing to the increase of anharmonicity in the hydrates. First, there are subtle structural differences between ice and hydrates. The distortion of the short range water molecules arrangement from ideal tetrahedral is much larger in the hydrates [11, 13, 15]. The other contributing factor arises from the intermolecular interactions between the guest molecules and the water lattice. We have investigated these possibilities by performing theoretical constant pressure molecular dynamics calculations on

the hydrates with and without the presence of guest molecules. The results show that the structural differences only plays a minor role in the expansion of the lattice. The large anharmonic potential experienced by the host lattice is mainly due to the interactions with the guest molecules.

The constant pressure heat capacity ( $C_p$ ) of tetrahydrofuran hydrate from 20 to 250 K have been measured by White [22]. Using the bulk modulus of the hydrate reported by Kieft [23] and the thermal expansivity results obtained in this work, we have converted the isobaric heat capacity ( $C_p$ ) into isochoric heat capacity ( $C_v$ ). Using these results, we deduced a Debye characteristic temperature of 198 K for the tetrahydrofuran hydrate. This value is lower than the Debye temperature of 226 K obtained for ice. We also applied the quasi-harmonic model [24] to analyse the high temperature isochoric heat capacity results. The apparent Debye temperatures  $\theta_c(T)$  were derived assuming  $3N$  degrees of freedom for the water molecules and  $8N$  degrees of freedom (3 translations, 3 rotations and 2 for the internal ring puckering motions) for the encaged tetrahydrofuran molecules and neglecting the small correction due to anharmonic contributions. The mean of the moments,  $\bar{\nu}^2$ ,  $\bar{\nu}^4$  and  $\bar{\nu}^6$ , are 168, 198 and 215  $\text{cm}^{-1}$  respectively. These results are to be compared with the corresponding values 190, 212 and 225  $\text{cm}^{-1}$  for ice. The shift to lower frequencies in tetrahydrofuran hydrate is due to the presence of low frequency rattling motions and librations from the encaged guest molecules.

We have also calculated the Grüneisen parameter for the tetrahydrofuran hydrate. The results are compared with that for ice in Fig. 2. The Grüneisen parameters for the hydrate are fairly constant from 90 to 260 K. However, instead of steady decreasing, as in the case of ice, it starts to *increase* at about 50 K. The increase of Grüneisen parameter of the hydrate is primarily due to its relatively large thermal expansivity at low temperature. This unusual behaviour in the Grüneisen parameter has been observed in disordered materials and crystals doped with impurities [25].

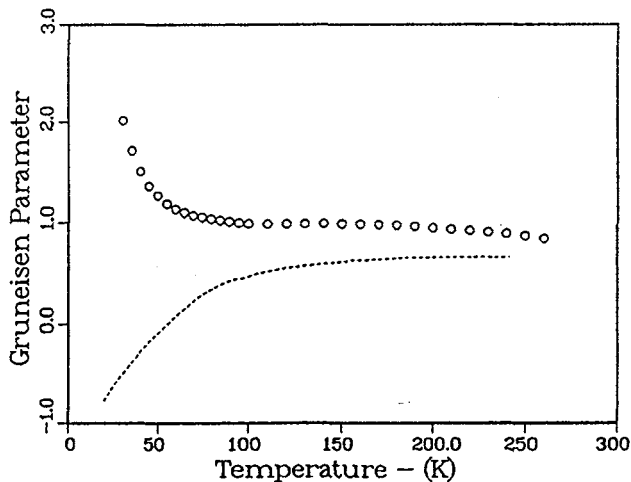


Figure 2. Grüneisen parameters for tetrahydrofuran hydrate (full circle) and ice (dash line).

## Concluding Remarks

We found that the thermal expansivity of the hydrates are significantly larger than that of ice. The increase in the expansivity is attributed to greater anharmonicity in the crystal potential due to intermolecular interactions between the water and the guest molecules. We also found that there is *anomalous* temperature dependency of the Grüneisen parameter. However, more precise measurement of the thermal expansion at low temperature is needed to substantiate this observation. The accuracy of the X-ray powder diffraction method at low temperature is inferior to most conventional methods [25]. However, it offers several advantages over the other techniques. Since only a small quantity of powder sample is required, this method can be applied to many unstable hydrates that do not form large single crystal. Moreover, impurities present in the sample can be detected easily and will not affect the accuracy of the measurements.

## Acknowledgements

The author wishes to thank Drs. J. Dahn and R. McKinnon for technical assistance and M. Marchi for communicating the results on the constant pressure molecular dynamics calculations before publication.

## References

- (1) D.W. Davidson, "*Water - A Comprehensive Treatise*", vol. 3, ed., F. Franks, Plenum Press, New York (1973).
- (2) R.G. Ross, P. Andersson and G. Backström, *Nature*, **290**, (1981) 322-323.
- (3) R.G. Ross and P. Andersson, *Can. J. Chem.*, **60**, (1982) 881-892.
- (4) J.G. Cook and M.J. Laubitz, "*Proceedings of the 17th International Thermal Conductivity Conference*", Gaithersburgs, Maryland (1981).
- (5) J.G. Cook and D.G. Leaist, *Geophys. Res. Lett.*, **10**, (1983) 397-9.
- (6) P. Andersson, R.G. Ross and G. Backström, *J. Phys.*, **C16**, (1985) 1423-1427.
- (7) T. Ashworth, L.R. Johnson and L.P. Lai, *High Temp. Hig. Press.*, **7**, (1985) 413-419.
- (8) M. von Stackelberg, and H.R. Müller, *Z. Elektrochem.*, **58**, (1954) 25-39.
- (9) M. von Stackelberg, *Naturwiss.*, **36**, (1949) 327-333, 359-362.
- (10) M. von Stackelberg and H.R. Müller, *J. Chem. Phys.*, **19**, (1951) 1319-1320.
- (11) T.C.W. Mak and R.K. McMullan, *J. Chem. Phys.*, **42**, (1965) 2732-2737.
- (12) J.R. Dahn, Ph.D dissertation, Dept. of Physics, Univ. British Columbia, Vancouver, Canada (1980).
- (13) R.K. McMullan and G.A. Jeffrey, *J. Chem. Phys.*, **42** (1966) 2725-2732.
- (14) J.E. Bertie, F.E. Bates and D.K. Hendricksen, *Can. J. Chem.*, **53**, (1975) 71-75.
- (15) F. Hollander and G.A. Jeffrey, *J. Chem. Phys.*, **66**, (1977) 4699-4705.

- (16) J.A. McIntyre and D.R. Petersen, *J. Chem. Phys.*, **47**, (1967) 3850-3852.
- (17) J.E. Bertie and S.M. Jacobs, *J. Chem. Phys.*, **69** (1978) 4105-4113.
- (18) D.F. Sargent and L.D. Calvert, *J. Phys. Chem.*, **70**, (1966) 2689-2691.
- (19) R.B. Roberts, C. Andrikidis, R.J. Tarnish and G.K. White, "*Proceedings 10th Internat. Cryogenic Eng. Conference*", Helsinki, Butterworth (1984) 409-412.
- (20) Y.S. Touloukian, R.K. Kirby, R.E. Taylor and J.Y.R. Lee, "*Thermophysical Properties of Matter*", vol. 13, Plenum Press, New York (1977).
- (21) S. Nošé and M.L. Klein, *J. Chem. Phys.*, **78**, (1983) 6928-6939.
- (22) M.A. White and M.T. Maclean, *J. Phys. Chem.*, **89**, (1985) 1380-1383.
- (23) H. Kiefte, M.J. Cloutier and R.E. Gagnon, *J. Phys. Chem.*, **84**, (1985) 3103-3108.
- (24) A.J. Leadbetter, *Proc. Roy. Soc.*, **A287**, (1965) 403-425.
- (25) T.H.K. Barron, J.G. Collins and G.K. White, *Adv. Phys.*, **29**, (1980) and references therein, 609-730.

#### COMMENTS

Remarks of E. GAFFNEY :

1. Your identification of another clathrate hydrate structure strengthens the analogy between clathrate hydrates and zeolites, for which dozens of structures are known. This may be the tip of the iceberg. It could be very important for planetary applications.

2. Jonathan Lunine has predicted from theoretical considerations that H<sub>2</sub> should form a hydrate with a pair of hydrogen molecules in a large (?) cage. This occurrence, if confirmed, would have important implications for the geochemical evolution of outer solar system bodies.

---

J.P.DEVLIN

You have seemed to stress the similarities in vibrational frequencies (density of states) for the hydrate and ice. I was under the impression that the predicted (simulated) spectra of the C.H.'s is quite different from the published spectra which are quite similar to ice.

Answer :

the MD simulated density of vibrational states for the hydrates are indeed very similar to that of ice. However, the similarity of the simulated infra-red spectra are not as strong.

---

B. HALE

In your simulations, how many water molecules did you use ? Did you find that the water was solid-like or liquid-like ?

Answer :

We employed a simulation box consisting of 128 water molecules arranged in such a way that there is not net dipole moment. Over the range of temperatures studied, the water remains solid-like.

---

T. HONDOH

Do you think that the smaller guest molecule is included in the smaller cages but not in the larger ones of structure II ?

Answer :

Yes. I anticipate the small guest molecules will occupied both the small and large cages of structure II hydrate.

---

R. GAGNON

Has any consideration been given to pressurized ice system, with regard to hydrates ?

Answer : No.

---

M.A. WHITE

Can you tell us what the melting points of the new-structure clathrate hydrates are, relative to the structure I and structure II clathrate hydrates ?

Answer :

It is difficult to remove the ice contamination from the hydrate sample. Therefore, we do not know the precise melting points of the new-structure hydrates.