Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

SEARS: Clathrates of Dianin's Compound: An Inelastic Neutron Scattering Investigation

Mary Anne White [a] , Brian M. Powell [b] & Varley F. Sears [b]

[a] Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada, B3H 4J3

[b] AECL Research, Chalk River Laboratories, Chalk River, Ontario, Canada, KOJ 1J0

Version of record first published: 27 Oct 2006.

To cite this article: Mary Anne White , Brian M. Powell & Varley F. Sears (1992): SEARS: Clathrates of Dianin's Compound: An Inelastic Neutron Scattering Investigation, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 211:1, 177-182

To link to this article: http://dx.doi.org/10.1080/10587259208025817

Mol. Cryst. Liq. Cryst. 1992, Vol. 211, pp. 177–182
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

CLATHRATES OF DIANIN'S COMPOUND: AN INELASTIC NEUTRON SCATTERING INVESTIGATION

MARY ANNE WHITE
Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

BRIAN M. POWELL and VARLEY F. SEARS
AECL Research, Chalk River Laboratories, Chalk River, Ontario, Canada K0J 1J0

(*Received July 12, 1991*)

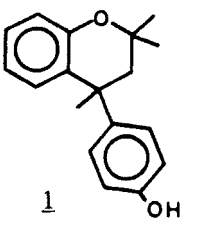
Abstract: The incoherent inelastic neutron scattering spectra of Dianin's compound and its ethanol and CCl_4 adducts have been measured, and the resulting velocity spectra are reported. The results show the insensitivity of the lattice dynamics of this host lattice to the presence of guests in its cages.

Keywords: clathrate, inelastic neutron scattering, lattice dynamics, guest-host interactions

INTRODUCTION

Clathrates offer an exceptional opportunity to examine the physical properties of isolated molecules, in the relatively isotropic environment that the host lattice provides. One unanswered question in the study of clathrates is: does the guest species influence the lattice dynamics of the host lattice? The present investigation sought to answer this question for one clathrate system.

In most clathrates, such as β-quinol[1] and the clathrate hydrates[2], the guest molecules are required to "prop open" the host lattice; without the guests, the lattice collapses to a completely different structure. However, there are a few clathrates known in which the structure appears to be much the same with or without the guest molecules. One such clathrate is the inclusion compound of 4-(*p*-hydroxyphenyl)-2,2,4-trimethylchroman (1 below), commonly known, after its discoverer[3], as Dianin's compound. The unusual stability of this structure arises from intermolecular hydrogen bonding of the phenolic groups, giving hexamers of 1, with alternate monomers pointing up and down relative to the plane of the phenolic ring. The hexamers are stacked on top of each other, giving hourglass shaped cavities



1

suitable for enclathration of small molecules. Because the structure is supported by hydrogen bonds between Dianin molecules and van der Waals interactions between hexamers, these cavities (11 Å long, 6.3 Å at the broadest) exist even in the absence of guest species[4].

The physical properties of Dianin's compound and its adducts have been the subject of several recent investigations, including the following: dynamics of the CCl_4 guest by NQR[5]; photochemistry of molecules enclathrated by Dianin's compound[6]; heat capacity of small molecules enclathrated by Dianin's compound[7]; the rôle of the guest species in thermal expansion[8,9], thermal conductivity[10] and derived thermodynamic quantities such as the Grüneisen parameter[11]; the concerted "dance" of the phenolic hydrogens[12]. Although it is known that the structure of Dianin's compound is the same both with and without guest molecules in the cages[4], from ^{13}C nmr it is known that there are some subtle differences[13]. To check the assumption of lack of influence of the guest on this host lattice on which the thermal properties analysis is predicated[7,10], we have measured the incoherent inelastic neutron scattering (IINS) spectra of Dianin's compound and two of its adducts.

EXPERIMENTAL

Unsolvated Dianin's compound and its ethanol and CCl_4 adducts were prepared in powdered form and characterized as described elsewhere[7,9,11]. From density determinations the guest occupancy was determined to be 1.94 ± 0.01 guests per hexamer of host molecules for the ethanol adduct, 1.01 ± 0.01 for the CCl_4 adduct, and fewer than 0.02 for the unsolvated host lattice.

IINS experiments were performed on the N5 spectrometer at the NRU reactor of Chalk River Laboratories. IINS spectra were measured with 2.0 Å neutrons at 300 K for all three powder samples with wavevector transfer Q = 5.0 $Å^{-1}$ and resolution (FWHM) 0.32 THz. Each spectrum was corrected for absorption.

RESULTS

Figure 1 shows the background-subtracted, transmission-corrected IINS spectrum for unsolvated Dianin's compound. The background subtraction includes an approximate

correction for multiphonon scattering. The contributions of S_0 (elastic component), S_1 (one-phonon component) and S ($=S_0+S_1$) for unsolvated Dianin's compound are shown

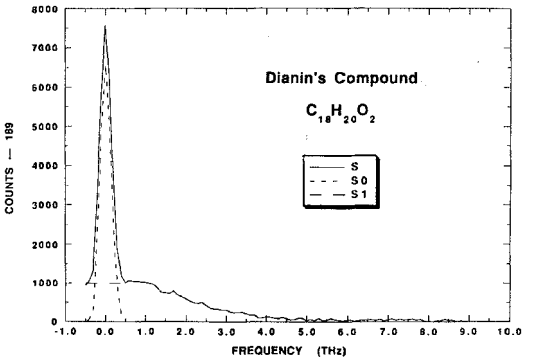


Figure 1 IINS spectrum of unsolvated Dianin's compound

in Figure 1. The one-phonon scattering is proportional to the velocity spectrum, $f(\omega)$, which is given by:

$$f(\omega) = \frac{1}{N_o\, n_H} \sum_{\nu} \sum_{\lambda} \langle |\hat{Q}\cdot\vec{e}_{\nu}(\lambda)|^2 \rangle\, \delta(\omega-\omega_{\lambda}) \qquad (1)$$

where N_0 is the number of unit cells in the sample, n_H is the number of hydrogen atoms in the unit cell (since the incoherent scattering is totally dominated by hydrogen scattering), ν labels the scattering atoms in the unit cell (1 to s), λ labels the normal modes of vibration, $\hat{Q}$ is a unit vector along the wavevector transfer, $\vec{e}_{\nu}(\lambda)$ is the Eigenvector of atom ν in mode λ (i.e. the polarization vector). Since our samples were powders, $f(\omega)$ is averaged over all directions of $\hat{Q}$ and:

$$\langle |\hat{Q}\cdot\vec{e}_{\nu}(\lambda)|^2 \rangle = \frac{1}{3} |\vec{e}_{\nu}(\lambda)|^2 \quad . \qquad (2)$$

The usual phonon density of states, $g(\omega)$, is defined as:

$$g(\omega) = \frac{1}{3\, N_0\, s} \sum_{\lambda} \delta(\omega-\omega_{\lambda}) \qquad (3)$$

and if we define an averaged polarization vector, $\vec{e}_{\nu}(\omega)$, averaged over all λ at frequency ω, such that the orthonormality relation can be written as:

$$\sum_{\nu} |\vec{e}_{\nu}(\omega)|^2 = 1 \tag{4}$$

then the powder velocity spectrum, $f(\omega)$, and the phonon density of states, $g(\omega)$, are approximately equal. (Note, however, that because the scattering is incoherent this is really the hydrogen frequency distribution, but in fact the hydrogens here should be most sensitive to the influence of the guest on the host lattice phonon density of states.) The velocity spectrum for unsolvated Dianin's compound is shown in Figure 2.

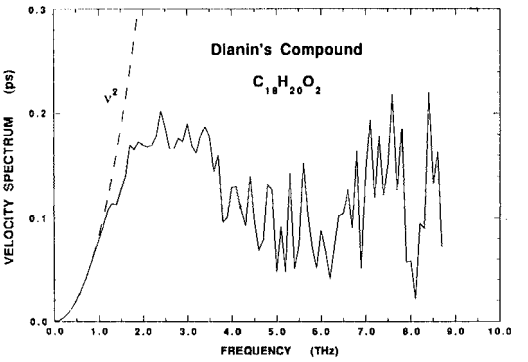


Figure 2 Final velocity spectrum for unsolvated Dianin's compound

The corresponding velocity spectra for the ethanol and CCl_4 adducts of Dianin's compound are shown in Figures 3 and 4, respectively.

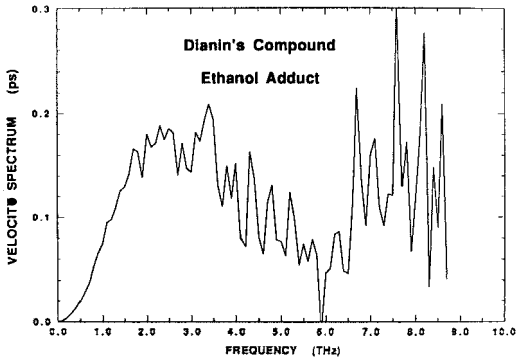


Figure 3 Final velocity spectrum for ethanol adduct of Dianin's compound

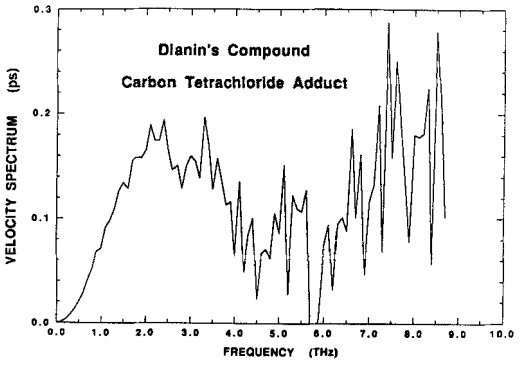


Figure 4 Final velocity spectrum for CCl_4 adduct of Dianin's compound

DISCUSSION

From Figures 2, 3 and 4, it can be seen that in the low-frequency regime the velocity spectra for all three samples are proportional to ν^2, as one would expect if the low-frequency modes are all acoustic phonons. Furthermore, the proportionality to ν^2 appears to be the same for all three compounds, which is consistent with the Debye analysis of the heat capacities which shows little influence of the guest species[11]. Although the distributions are not highly resolved, the broad peak in the velocity spectra between 1 and 4 THz appears to be real, as is the minimum at 5 to 6 THz. The fluctuations due to statistics for frequencies greater than *ca.* 7 THz preclude any definitive statements about the spectra in that region.

The most important finding from this investigation is that the velocity spectra (i.e. phonon density of states) for unsolvated Dianin's compound (Figure 2) and its ethanol adduct (Figure 3) and CCl_4 adduct (Figure 4) are essentially indistinguishable (within reasonable errors) at room temperature. This corraborates the finding that the structure is insensitive to the presence of the guest[4]. However, that result was based on the static structure; the present result takes the information a step further, as it includes dynamical information. This result is especially important in justifying our analysis of thermal properties of Dianin's clathrate: the lattice dynamical view of the host lattice is insensitive to the presence of the guest, so any observed changes in thermal properties must be attributable solely to the presence of the guest, not its influence on the host lattice *per se*.

ACKNOWLEDGEMENTS

The samples were prepared by Dr. M. Zakrzewski and we acknowledge useful discussions with him. This work was supported by the Natural Sciences and Engineering Research Council of Canada and the Canadian Institute for Neutron Scattering (through grants to MAW).

REFERENCES

1. H.M. Powell in Non-stoichiometric Compounds, edited by L. Mandelcorn (Academic Press, New York, 1964), Chapt. 7.
2. D.W. Davidson in Water - A Comprehensive Treatise, edited by F. Franks (Plenum, New York, 1973), Vol. 2, pp. 115-234.
3. A.P. Dianin, J. Russ. Phys. Chem. Soc., 46, 1310 (1914).
4. D.D. MacNicol, in Inclusion Compounds, edited by J.L. Atwood, J.E.D. Davies, D.D. MacNicol (Academic Press, London, 1984), Vol. 2, Chapt. 1.
5. L. Pang, A.C. Lucken and G. Bernardinelli, J. Am. Chem. Soc., 112, 8754 (1990).
6. P.C. Goswami, P. De Mayo, N. Ramnath, G. Bernard, N. Omkaram, J.R. Scheffer and Y.-F. Wong, Canad. J. Chem., 63, 2719 (1985).
7. M.A. White and M. Zakrzewski, J. Incl. Phenom. Molec. Recog. Chem., 8, 215 (1990).
8. M. Zakrzewski, M.A. White and W. Abriel, J. Phys. Chem., 94, 2203 (1990).
9. W. Abriel, A. du Bois, M. Zakrzewski and M.A. White, Canad. J. Chem., 68, 1352 (1990).
10. M. Zakrzewski and M.A. White, to be published.
11. M. Zakrzewski and M.A. White, J. Phys.: Cond. Matter, in press (1990).
12. T. Bernhard, H. Zimmerman and U. Haeberlen, J. Chem. Phys., 92, 2178 (1990).
13. F. Lee, E. Gabe, J.S. Tse and J.A. Ripmeester, J. Am. Chem. Soc., 110, 6014 (1988).