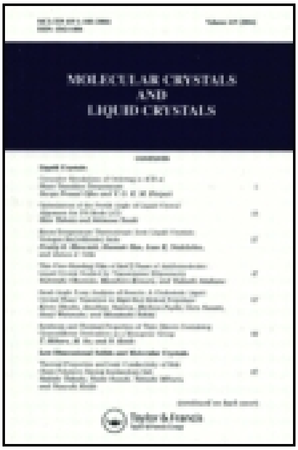

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

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

Raman and IR Studies on Proton-Related Dynamics in π -Molecular Crystals

Yutaka Moritomo [a], Yoshinori Tokura [a], Toyoshi Oohashi [b], Takashi Kojima [b] & Akira Itsubo [b]

[a] Department of Physics, University of Tokyo, Tokyo, 113, Japan

[b] Advanced Materials lab., Mitsubishi Petrochemical co., LTD, Tsukuba, 300-03, Japan

Version of record first published: 24 Sep 2006.

To cite this article: Yutaka Moritomo , Yoshinori Tokura , Toyoshi Oohashi , Takashi Kojima & Akira Itsubo (1992): Raman and IR Studies on Proton-Related Dynamics in π -Molecular Crystals, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 216:1, 223-228

To link to this article: http://dx.doi.org/10.1080/10587259208028777

Mol. Cryst. Liq. Cryst. 1992, Vol. 216, pp. 223–228
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

RAMAN AND IR STUDIES ON PROTON-RELATED DYNAMICS IN π-MOLECULAR CRYSTALS

YUTAKA MORITOMO and YOSHINORI TOKURA
Department of Physics, University of Tokyo, Tokyo 113, Japan.
TOYOSHI OOHASHI, TAKASHI KOJIMA, and AKIRA ITSUBO
Advanced Materials lab., Mitsubishi Petrochemical co., LTD, Tsukuba 300-03, Japan.

ABSTRACT Infrared absorbance (IR) spectra and Raman scattering spectra were measured as a function of pressure for molecular crystals of several 1,3-diketones, which are composed of hydrogen-bonded π-molecular chains. An unconventional proton-related band is commonly observed in the IR spectra around 1800-2000cm^{-1} in these compounds. We ascribed the observed band to proton vibration localized around **kink-** (or **antikink-**) **solitons**. The intensity of the band rapidly increases with application of hydrostatic pressure, suggesting increase in number of the solitons-like defects of the molecular chains via deformation of the double-well type proton potential.

I Introduction

Dynamics of protons and their interaction with the constituent molecular (or ionic) units governs, in general, physical properties of the hydrogen-bonded molecular (or ionic) crystals. Therefore, application of hydrostatic pressure, which deforms the double-well type proton potential, is expected to significantly affect dynamical behavior of protons and hence physical properties of the hydrogen-bonded crystals[1].

Here, we have experimentally investigated several molecular crystals composed of hydrogen-bonded π-molecular chains, which is schematically represented in Fig.1(a) and (b). In these molecular chains, the chemical bond between the molecule and hydrogen induces π-bond alternation within the molecule due to a strong proton-molecule interaction (see Fig.1). This makes a sharp contrast with ionic systems like ice, in which proton-ion interaction is considered to be sufficiently weak.

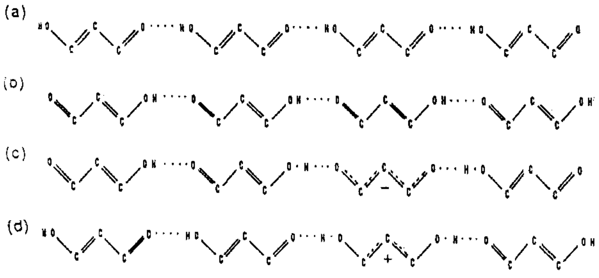

Fig.1: Schematic structure of hydrogen-bonded π-molecular chain ((a) and (b)) and kink- (or antikink-) solitons ((c) and (d)).

II Hydrogen-bonded π-molecular crystals

Crystals of several 1,3-diketones, such as 1,3-cyclopentanedione (abbreviated as CPD) and 1,3-cyclohexanedione (CHD), are known to consist of hydrogen-bonded enol-formed molecular chains, as schematically shown in Fig.2. These molecular chains are weakly connected by van der waals force to form molecular crystals; details of the crystal structures have been reported elsewhere[2-5].

In Table I, we classify these compounds by their hydrogen-bond configurations. In the table, the hydroxyl orientation is specified first and the carbonyl hydrogen-bond orientation second. In CPD, for example, the configuration is 'anti-anti' since both the hydroxyl and carbonyl orientations are 'anti'. The inter-oxygen distance, which is one of the crucial parameters to determine dynamics of protons, is also listed for each compound. The proton potential is considered to be of a double-well type in all the compounds, since the inter-oxygen distance is much longer than the empirically-derived critical value (~2.45A)[6] below which the potential is of a single-well type.

III Proton-related bands in IR spectra

Figure 2 shows IR spectra measured at 300K for the above-mentioned four compounds in the frequency region of 1700-3700cm^{-1}, where the spectral profiles are dominated by proton-related vibrational modes. Spectral profiles are similar to each others in this spectral range: The spectra consist of the broad O-H stretching mode around 2500cm^{-1} (indicated by vertical lines) and a lower-lying small band (marked with an arrow; we call the band "S band"). Intensities of the S band relative to the O-H stretching mode are listed in Table I.

Compounds		Hydrogeng-bond Conformation	O-O distance (A)	S band intensity relative to the main band
CPD	1,3-Cyclopentandione	anti-anti planar	2.542(8) at R.T.	0.26
CHD	1,3-Cyclohexanedione	anti-anti planar	2.561(4) at R.T.	0.06
PMDA	Phenylmalondialdehyde	anti-anti planar	2.575(2) at 111K	0.02
Dimedone	5,5-Dimetyl -1,3-Cyclohexanedione	sin-sin helix	2.593(2) at R.T.	0.11

Table I: Configuration of hydrogen-bonds and the inter-oxygen distance in crystals of several 1,3-diketones with hydrogen-bonded molecular chains.

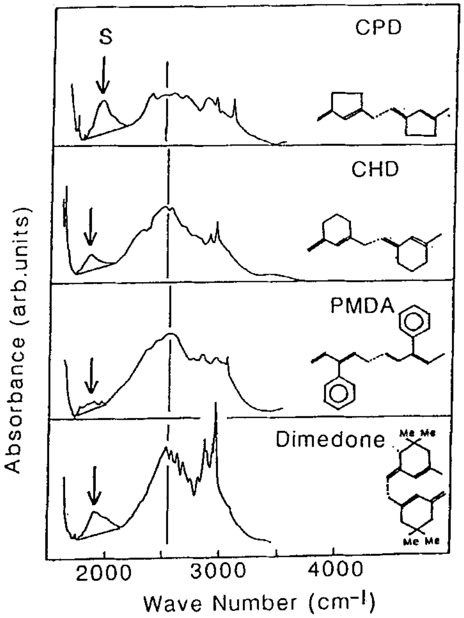

Fig.2: IR spectra for typical 1,3-diketone crystals with hydrogen-bonded molecular chains at 300K.

The S band cannot be ascribed to the ordinal intramolecular vibrations of C- or O-atom, because these modes are expected to appear below ca. 1700cm^{-1}. In fact, in case of PMDA, deuteration of the crystal seems to erase the S band as well as the ordinary O-H stretching mode (a vertical line in Fig.2). Therefore, the S band is considered to be originated in a proton vibration in somewhat different environment. Here, we propose that the S band arises from a proton vibration localized around kink-type defects of the molecular chains or the so-called solitons[7,8], which are schematically represented in Fig.1(c) and (d). Because the force constant between the proton and oxygen is considered to be reduced around these solitons due to disappearance of the π-bond alternation.

Such solitons may be generated in the hydrogen-bonded chains, since the ground state structure of the molecular chain is doubly-degenerated (see Fig.1(a) and (b)). It may be easily anticipated that the shorter the inter-oxygen distance becomes, the more easily the solitons are generated, since energy of the soliton is expected to reduce under hydrostatic pressures via reduction in the barrier height of the double-well type proton potential[7,8]. In accordance with the expectation, the S band becomes stronger with decreasing the inter-oxygen distance (d_{OO}), i.e., in going PMDA(d_{OO}=2.575A[4]) → CHD(2.561A[3]) → CPD(2.542A[2]) with the same hydrogen-bond configurations (see Fig.2 and Table I).

Let us proceed to the problem of hydrostatic pressure effects on IR spectra. Figure 3 shows pressure dependence of IR spectra at 300K for three compounds; (a)PMDA, (b)CHD, and (c)Dimedone. In all the compounds, frequency of the broad O-H stretching mode decreases with pressure (indicated by vertical lines), indicating reduction in the inter-oxygen distance under hydrostatic pressures[6]. The reduction in the inter-oxygen distance anomalously influences the S band (indicated by an arrow) in all the compounds: The intensity rapidly increases with pressure[9]. Such a behavior may be accounted for increase in number of the kink- (or antikink-) solitons in the molecular chains[7,8] via deformation of the double-well type proton potential.

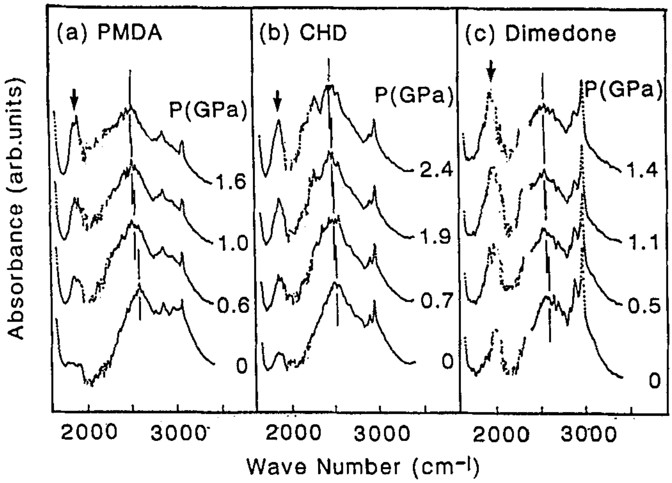

Fig.3: Pressure dependence of IR spectra at 300K: (a)PMDA, (b)CHD, and (c)Dimedone.

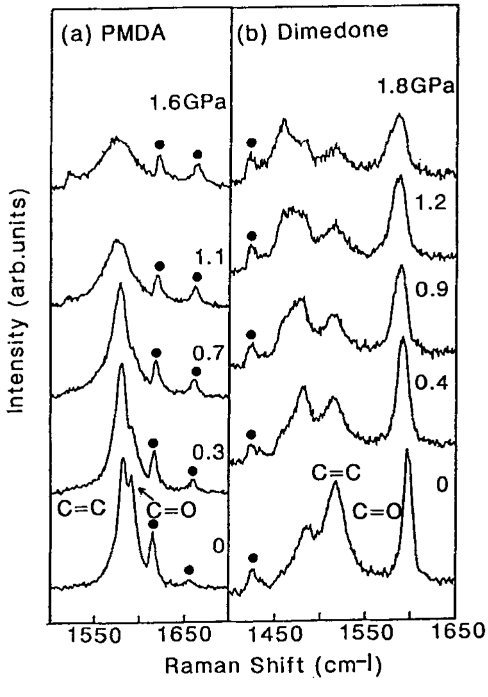

Fig.4: Pressure dependence of Raman spectra at 300K for (a)PMDA and (b)Dimedone single crystals.

IV Pressure-induced change in Raman bands

Figure 4 shows pressure dependence of Raman spectra at 300K for (a)PMDA and (b)Dimedone single crystals. The observed bands in both spectra are ascribed to the intramolecular vibrations, such as C=O and C=C stretching modes. Application of hydrostatic pressure significantly influences the spectral shape of these Raman bands in both the compounds: The C=O and C=C stretching modes show a prominent broadening accompanied by a slight red-shift (indicated by broken lines), making a sharp contrast with the other bands indicated by closed circles. These observations imply changes in the π-electron distribution in the molecules under pressures, which may be favorable for formation of the soliton-like defect.

REFERENCES

1. For example, Y.Moritomo, S.Koshihara, and Y.Tokura, J.Chem.Phys., 93, 5429 (1990): Y.Moritomo, T.Katsufuji, and Y.Tokura, J.Chem.Phys., 95, 2244 (1991).
2. A.Katrusiak, Acta.Cryst. C46, 1289 (1990).
3. M.C.Etter, Z.Urbanczyk-Lipkowska, D.A.Jahn, and J.S.Frye, J.Ame.Chem.Soc., 108, 5871 (1986).
4. D.Semmingsen, Acta.Chem.Scand. B28, 169 (1974).
5. D.Semmingsen, Acta.Chem.Scand. B31, 114 (1977).
6. C.Hamilton and J.A.Ibers, Hydrogen-Bonding in Solids, (Benjamin, New York, Amsterdam, 1968).
7. V.Ya.Antonchenko, A.S.Davydov, and A.V.Zolotariuk, Phys.Stat.Sol., B115, 631 (1983).
8. Y.Kashimori, T.Kikuchi, and K.Nishimoto, J.Chem.Phys., 77, 1904 (1982).
9. Y.Moritomo, S.Koshihara, Y.Tokura, Y.Iwasa, T.Koda, N.Iwasawa, G.Saito, T.Oohashi, T.Kojima, and A.Itsubo, Synthetic Metals 41-43, 3275 (1991).