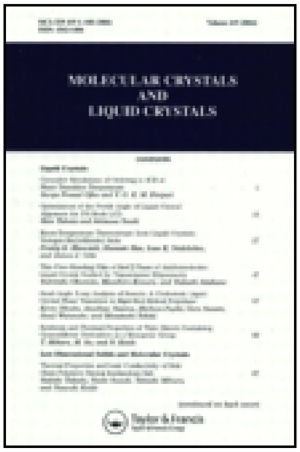

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Optical-Spectroscopy of Interacting Protons in H-Bonding System

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Version of record first published: 04 Oct 2006.

To cite this article: Tadaoki Mitani (1990): Optical-Spectroscopy of Interacting Protons in H-Bonding System, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 183:1, 139-142

To link to this article: http://dx.doi.org/10.1080/15421409008047448

Mol. Cryst. Liq. Cryst., 1990, vol. 183, pp. 139–142
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Printed in the United States of America

OPTICAL-SPECTROSCOPY OF INTERACTING PROTONS IN H-BONDING SYSTEM

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Abstract Design of a new type of 1-D charge-transfer Mott-insulator stabilized by interchain H-bonding is presented. The proton dynamics of this system are discussed on the basis of the experimental results.

INTRODUCTION

Quasi-one-dimensional (1-D) electronic states with fractional charge have structural instability due to the Peierls distortion. Control of this instability is essential for design of a novel molecular function in the 1-D system. Recently, it has been demonstrated that the Peierls instability can be suppressed by introducing strong interchain H-bonding in the mixed-valenced metal complexes, and then the system is transformed into a 1-D Mott insulator, where the electron-electron repulsive energy (U) is responsible for gap-opening.[1] This give us a unique opportunity to investigate cooperative interaction between electron and proton in H-bonded crystals, since the magnitude of U effectively depends on the charge distribution in surrounding molecules, which is sensitive to displacement of the proton in the H-bonding. Thus, the control of proton motion is expected to play a significant role in determining the physical properties of the 1-D Mott insulator.[2]

The basic idea for design of a cooperative electron-proton system using D-A pair-molecules is presented in this report, and its experimental verification by investigation of the O-H vibrational mode of quinhydrone CT complexes under hydrostatic pressures.[3] The polarized absorption spectra in the mid-gap energy region of these crystals under high pressures reflect the cooperative electron-proton interaction, suggesting the possibility of formation of "protonic" soliton-like kinks in the 1-D semiquinone-type crystals. Some improvements by chemical modification of quinhydrone(and N-salicylideneaniline) are now in progress.

DESIGN OF H-BONDED 1-D ELECTRONIC STATES

In an isolated H-bonding as shown in Figure 1 (a), the potential energy (E) for the displacement (u_l) of a proton is in general asymmetric, except in the limit of extremely strong-coupled H-bonding, so that proton tunneling between minima of a double well potential would be negligible.

Proton transfer in a carboxylic acid dimer, however, has a considerably large probability, since resonant electronic configurations exist as shown in Figure 1 (b). In this system, quantum-mechanical motion of the proton, presented by Γ_R in the figure, has been demonstrated by NMR measurements on the crystals.^{4}

Stacking donor-acceptor (D-A) molecular-pairs linked by H-bonding are shown in Figure 1 (c), and a simultaneous proton-electron transfer similar to that observed in carboxylic acid dimers is expected to take place. As the result, neutral radical pairs are formed, in which electrons and protons might be cooperative.

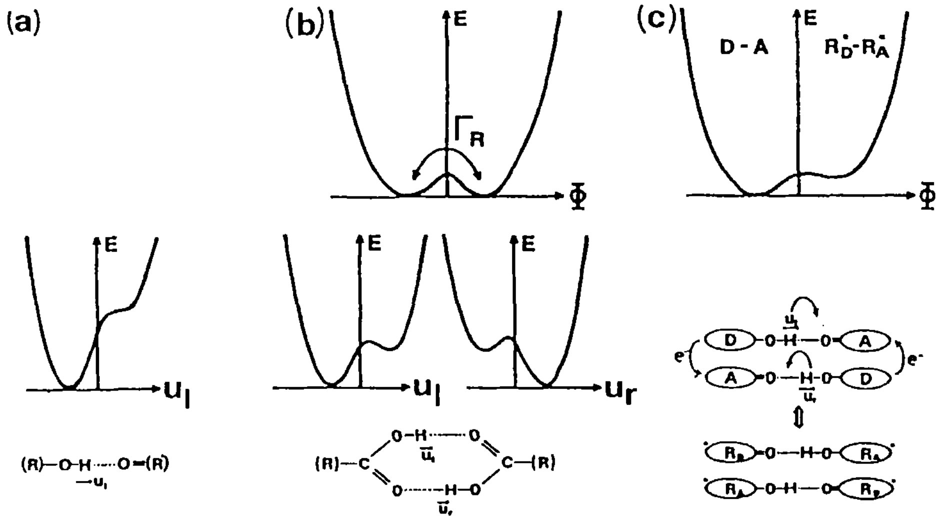

Figure 1. Potential energy for various proton-transfer system; (a) single H-bonding, (b) carboxylic dimer, and (c) D-A molecular pairs.

Quinhydrone CT complex composed of hydroquinone as a donor and benzoquinone as an acceptor has been found to exhibit a transformation from quinhydrone to semiquinone complex, i. e. from the normal CT complex to the Mott-type phase, by application of hydrostatic pressure. According to vibrational spectroscopy of the O-H stretching mode of quinhydrone crystals, two different types of O-H bands are observed, even at an ambient pressure[3]; one is the strong broad band, which is recognized as strongly damped vertical transitions in the u_1 coordinate of the quinhydrone system, and the other is the weak but sharp multistructure band, which can be assigned to the self-traped excitations[5], or the transitions to the relaxed states accompanying with the electron transfer. Coexistence of both bands possibly indicates the presence of quantum-mechanical motion (Γ_R) between the two system.

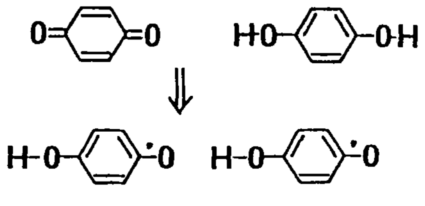

Figure 2. Molecular structures of quinhydrone and semiquinone.

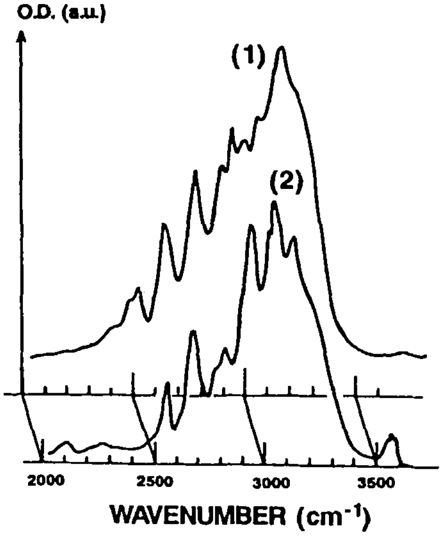

Figure 3. Comparison of the O-H vibrational spectra of (1) quinhydrone under pressure (11 kbar) and (2) CD_3COOH vapor(Ref. 6).

When pressure is applied to quinhydrone crystals, the potential energies for the quinhydrone and semiquinone phases are expected to be energetically balanced, as suggested in Figure 1 (b) and (c). For an experimental demonstration of such a balanced state, a comparison of the O-H vibrational spectra of quinhydrone at 11 kbar and CD_3COOH vapor reported by Hofacker, Marechal and Ratner[6] is presented in Figure 3. Good agreement between these two spectra supports a model of strong electron-proton cooperation in the CT lattice.

With application of increased pressure, the system will enter the semiquinone phase, where the topologically degenerated electronic states with respect to freedom of proton transfer are formed[7]. In Figure 4, pressure dependencies of the absorption edge of the CT exciton are presented. It should be noted that the absorption coefficient is suddenly enhanced only for light parallel to the CT axis, after a lower energy shift of the absorption edge of the CT exciton with increase of pressure. This could be responsible for the formation of some kind of soliton-like defects associated with the phase mismatching of the proton transfer.

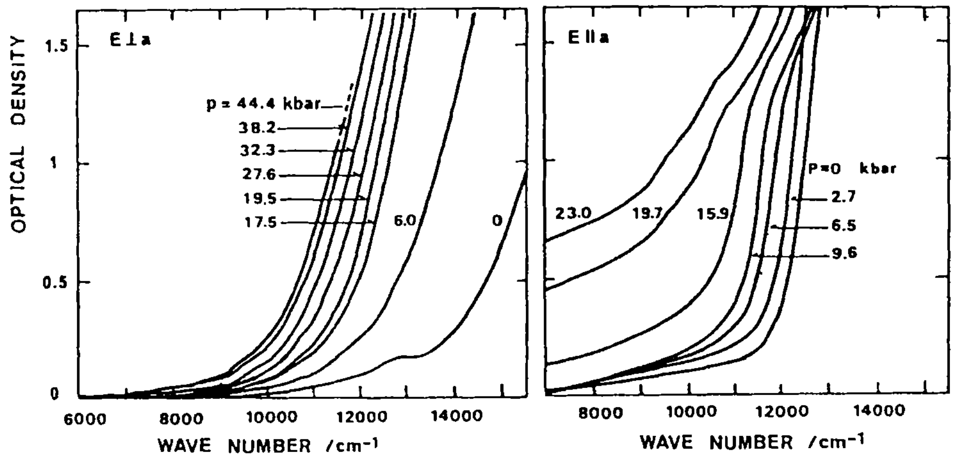

Figure 4. Pressure dependencies of the polarized absorption spectra near the CT exciton edge of quinhydrone crystals for light perpendicular (a) and parallel (b) to the CT axis.

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