Far Infrared Spectra of Tunnelling Protons in Bromo- and Iodo-hydroxyphenalenone at Low Temperature

T. Matsuo, O. Yamamuro#, A. Inaba, M. Ohama, T. Mochida* and T. Sugawara**
Department of Chemistry, Graduate School of Science, Osaka University
*Department of Chemistry, Faculty of Science, Toho University
**Department of Basic Science, Graduate School of Art and Science, The University of Tokyo
tmatsuo@bc4.so-net.ne.jp

Quantum mechanics of nuclear motion was first introduced in ferroelectricity in 1957 in an attempt to explain the strong isotope effect on the Curie temperature of some hydrogen bonded ferroelectrics, notably KH₂PO₄ (KDP) and KD₂PO₄ [1]. Tunnelling of the proton on the hydrogen bond is the key concept by which the light and heavy isotopes of hydrogen are distinguished. Tunnelling splits the two-fold degeneracy corresponding to the classical two-fold positional disorder of the hydrogen atom on a hydrogen bond into separate levels. Evidence for the tunnelling states has been sought in KDP and isomorphous crystals, without a definite result for more than four decades. A few years ago we found a strong infrared absorption in an intramolecularly hydrogen-bonded molecular crystal bromo-hydroxyphenalenone (BHP) at 83 cm⁻¹ and assigned it to the dipole-allowed transition from the ground to the excited state of the tunnel-split pair of the states [2]. The assignment is based on the observation that the absorption does not occur for bromo-deuteroxy phenalenone (BDP) and that the temperature dependence of the peak is distinctly different from that of the vibration peaks.

In the present paper we report the analysis of the tunnel spectra of BHP and iodo-hydroxyphenalenone (IHP) with respect to the frequency and line width of the peaks in their temperature dependence. Figures 1 and 2 show the far infrared spectra of BHP, IHP and their deuterated analogs BDP and IDP at 5 K [2,3]. The strong peaks at 83 cm⁻¹ for BHP and 68 cm⁻¹ for IHP are due to proton tunnelling. These are absent from the BDP and IDP spectra, while the sharp vibrational peaks at 95-100 cm⁻¹ occur for all of the four spectra.

Fig. 1. Far IR spectra of BHP and BDP at 5 K.

Fig. 2. Far IR spectra of IHP and IDP at 5 K.

The temperature dependence of the peaks was analyzed by comparison with the near-by vibrational transition. Interestingly, the tunnel peaks shifted to higher frequencies with increasing temperature, unlike the vibrational transitions. The large widths of the tunnel peaks are also notable. At 5 K they are independent of temperature and represent a residual width [4].

# Present address: Institute of Solid State Physics, The University of Tokyo.