Available online at www.sciencedirect.com

SCIENCE DIRECT

Chemical Physics 323 (2006) 479–489

Chemical Physics

www.elsevier.com/locate/chemphys

Vibronic model for H/D isotopic “self-organization” effects in hydrogen bond cyclic trimeric systems: 4-Bromopyrazole crystal IR spectra

Henryk T. Flakus *, Aleksandra Pyzik

Institute of Chemistry, University of Silesia, 9 Szkolna Street, 40-006 Katowice, Poland

Received 15 July 2005; accepted 6 October 2005
Available online 11 November 2005

Abstract

In this paper, a theoretical model has been proposed, aiming to explain a new kind of H/D isotopic effects concerning hydrogen bond systems, i.e. the H/D isotopic “self-organization” effects, recently deduced from the IR spectra of molecular crystals. The problem of existence of these kinds of co-operative effects was considered in the limits of a vibronic model in the Herzberg–Teller approximation, for cyclic trimeric systems of hydrogen bonds. It was shown that non-conventional attraction forces between three identical hydrogen isotope atoms, resulting from the vibronic mechanism, are responsible for excess stabilization energy of cyclic hydrogen bond trimers.

The H/D “self-organization” effects were deduced to be negligible in the case of non-symmetric HDD, or HHD-type trimers, containing both, hydrogen and deuterium bonds in one ring trimer. The symmetric trimers of the HHH and of the DDD-type should be more stable, when compared with the HDD, or the HHD-type trimer properties. This thermodynamic effect explains the IR spectral properties of molecular crystals containing cyclic trimers of hydrogen bonds in their lattices, accompanying to isotopic dilution. The results of the theoretical considerations were confronted with the IR spectra of 4-bromopyrazole crystals, which were measured in a wide temperature range (from 298 to 77 K), using polarized light, in the frequency ranges of the proton or deuterium stretching vibrations bands.

Keywords: Hydrogen bond cyclic trimers; H/D isotopic effects in the IR; Isotopic dilution; H/D isotopic “self-organization” effects; Herzberg–Teller vibronic coupling; Molecular crystals; Co-operative effects; “Strong-coupling” model; Band shape analysis

1. Introduction

The IR spectroscopy is still considered as a basic tool in the hydrogen bond research. During the last 50 years, the main interest of the investigators has been focused on the $\nu_{\mathrm{X-H}}$ proton stretching vibration band properties for X–H...Y bonds and on the band fine structure patterns as well (the X and Y symbols denote the heavy atoms like O, N, F, S, P participating in hydrogen bonds) [1–4].

The contemporary theoretical models, proposed for quantitative description of spectral properties of hydrogen bond systems, namely the “strong-coupling” theory [5–8], or the much novel “relaxation” theory [9–14], were generally able to satisfactorily explain some basic spectral properties of hydrogen bonds, including a quantitative reproduction of the $\nu_{\mathrm{X-H}}$ band shapes. However, there are a number of spectral effects in the vibrational spectra, which seems to be beyond the reach of a purely vibrational approach assumed by these two models. It appeared that some spectral effects were connected with vibronic coupling mechanisms, involving the proton stretching motions and the electronic movement in the hydrogen bonds of the associated complexes. This remark concerns spectral properties of even so simple hydrogen bond systems as cyclic, centrosymmetric dimers [14].

Explanation of H/D isotopic effects observed in the IR spectra is the most severe test for the modern quantitative theoretical models. When investigating the H/D isotopic effects in the spectra, the $\nu_{\mathrm{X-D}}$ bands for deuteron stretching motions in deuterium X–D...Y bonds, were traditionally the objects of routine studies. In contrast, practically

---

* Corresponding author. Fax: +48 32 2599 978.
E-mail address: flakus@ich.us.edu.pl (H.T. Flakus).

0301-0104/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.chemphys.2005.10.011

no interest was made to investigate the residual ν_{X-H} band spectral properties for partially deuterated samples. These bands are the attributes of the residual protons in these samples. However, the latest studies on the residual ν_{X-H} bands have suggested that a new kind of H/D isotopic effects for hydrogen bond systems existed, namely the so called isotopic "self-organization" effects [15–19]. For the first time these effects were revealed for cyclic, centrosymmetric dimeric systems of hydrogen bonds, for which the shapes of residual ν_{X-H} bands remained almost invariant, when the deuterium substitution rate increased; such behavior remained in contrast with predictions of the most recent advanced theoretical models [5–13,20,21].

The H/D isotopic "self-organization" effects appeared not to be restricted exclusively to the cyclic dimeric systems of hydrogen bonds. For a number of crystalline systems, characterized by infinite open chains of hydrogen bonds in their lattices, similar effects as for cyclic hydrogen bond dimers, have also been observed [22–24]. In these cases, the idea of a non-random distribution of the hydrogen isotopes in chain structures was strongly supported also by detection of linear dichroic effects for the residual ν_{X-H} bands [22–24]. The linear dichroic effects differentiated properties of the longer- and the shorter-wave branch of the residual ν_{X-H} bands [25,26]. The only explanation of this effect was that the residual protons were grouped in domains in fragments of open chains of hydrogen bonds. However, in the case of the alcohol crystal spectra, isotopic dilution was responsible for strong evolution of the residual ν_{O-H} band shape [22–24], that was directly connected with a random distribution of protons and deuterons, in open chains of alcohol crystals.

Explanation of the nature of isotopic H/D "self-organization" effects seems to be beyond the reach of the most advanced quantum chemistry methods, based on the Born–Oppenheimer approximation, as such theoretical approach does not differentiate hydrogen and deuterium atoms. Therefore, it seems that a proper theoretical model, adequate for the explanation of these new H/D isotopic effects, must incorporate dynamical couplings between the electronic and the vibrational motions in the hydrogen bond systems.

In the case of cyclic dimers, the main source of the H/D "self-organization" effects was most probably a difference in the hydrogen bond energy between dimers of the HH or the DD-type, in comparison with the energy of non-symmetrical dimers of the HD-type. It was estimated by model calculations that the latter dimer should be less stable, as the Gibbs thermodynamic potential ΔG for the hydrogen isotope exchange reaction

$$1/2\ \mathrm{HH} + 1/2\ \mathrm{DD} = \mathrm{HD},$$

between the dimers was estimated to be approximately equal to 1.5 kcal [15].

The basic principles of the H/D isotopic "self-organization" effects for cyclic dimeric hydrogen bond systems were deduced only recently [27]. These effects were ascribed to mechanisms of dynamical vibronic couplings, involving the proton stretching vibrations and the electronic motions in dimers. A similar formal treatment, with only slight necessary modifications, should also be valid in the case of other hydrogen bond systems, e.g. in the case of chain systems in crystalline lattices. This paper has been devoted to the H/D "self-organization" effects for cyclic hydrogen bond trimeric systems. Such cyclic trimers are sometimes being formed in the lattices of molecular crystals, e.g. in 4-bromopyrazole crystals [28].

Despite the fact that the cyclic trimeric hydrogen bond systems in crystal lattices were found as much more rare, when compared with the cyclic dimers as the crystal structural units, they also seem to be interesting from the theoretical point of view. This therefore brings to attention the problem of the influence of the increasing number of mutually coupled hydrogen bonds in cyclic *n*-mers, on the H/D "self-organization" mechanism. Most probably, when a cycle dimension grows, some essential restrictions in the H/D isotopic "self-organization" mechanisms should appear, as only some of the chain systems exhibited these effects in their IR spectra [22,24]. In the spectra of another group of the chain systems these effects were absent [20,21,29]. Therefore our aim was also to check experimentally, if the H/D isotopic "self-organization" effects appeared in the IR spectra of the trimer hydrogen-bonded model, in the way predicted by the proposed theoretical model.

2. A single hydrogen bond in a cyclic trimer

We propose the simplest model of a single hydrogen bond participating in a cyclic trimer, formed by identical hydrogen bonds, labeled by A, B and C. For a single hydrogen bond, let us assume that only the coupling between the proton stretching vibrational motion with the electronic movement in the hydrogen bond is responsible for the discussed properties of hydrogen bond systems. This coupling basically involves electrons on the non-bonding orbitals of the proton acceptor atom Y, as well as the electrons of atoms from the closest neighborhood of the hydrogen bond in an associated molecular complex. Other vibrational modes are not taken into account as being most probably not so strongly coupled with the electronic movement. Let us assume further that this vibronic coupling can be satisfactorily expressed in the Herzberg–Teller approximation, when assuming a linear term dependence of the electronic hamiltonian of the system upon the proton vibration normal coordinate [30]. This model is simpler when compared with the recently discussed vibronic model of a dimer, as it does not take into the account the C–H bond stretching vibrations in the formalism [30].

In this case, the vibronic hamiltonian of a single hydrogen bond takes the following form:

$$H(q,Q) = T_{\mathrm{N}}(Q) + T_{\mathrm{el}}(q) + U(q,Q_0) + \left(\frac{\partial H_{\mathrm{el}}(q,Q)}{\partial Q}\right)_0 Q, \tag{1}$$