



Effect of the resonance of the C–H and O–H bond stretching vibrations on the IR spectra of the hydrogen bond in formic and acetic acid

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ABSTRACT

It is shown that the resonance of the O–H and C–H bond stretching vibrations is responsible for a noticeable intensity redistribution effect in the IR spectra of associated formic acid molecules in the gaseous phase. This effect is manifested by a considerably high growth in intensity of the $\nu_{\text{C-H}}$ band, which overlaps the $\nu_{\text{O-H}}$ band contour in the spectra. A vibronic coupling of the Herzberg–Teller-type expressed by the second order term in the perturbation theory is the most probable source of these spectral effects. The presented mechanism explains the variation of the effect magnitude accompanying the phase transitions. The proposed model also facilitates the understanding of the H/D isotopic effects in the spectra as well as the essential difference in the corresponding spectral properties between the formic and the acetic acid.

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1. Introduction

The hydrogen bonding is responsible for the appearance of spectacular changes in IR spectra of associated molecules. This remark particularly concerns the $\nu_{\text{X-H}}$ proton stretching vibration bands, which are the attribute of the X–H atomic groups in the X–H...Y bridges. The main effects depend on a considerable low-frequency $\nu_{\text{X-H}}$ band shift, on the band integral intensity growth by even two orders of magnitude and on a noticeable increase of the band-width [1–5]. The $\nu_{\text{X-H}}$ bands often exhibit well-developed fine structure patterns. Qualitatively similar spectral effects characterize the $\nu_{\text{X-D}}$ bands attributed to deuterium-bonded species [1–5].

The contemporary quantitative theoretical models, elaborated for describing IR spectra of the hydrogen bond in diverse associated molecular systems (the “strong-coupling” theory [6–8] and the “relaxation” or the “linear response” theory [9,10]) aimed to explain the intensity distribution in the $\nu_{\text{X-H}}$ bands. They also explain the basic H/D isotopic effects in the spectra expressed by the relation between the $\nu_{\text{X-H}}$ and $\nu_{\text{X-D}}$ band contour shapes. However, on the basis of these most sophisticated theoretical models the more complicated H/D isotopic effects connected with the replacement of hydrogen atoms of C–H bonds in molecular skeletons by deuterium atoms have not been considered. Solving this problem seems to be justified since some noticeable differences between the IR crystalline spectra of the hydrogen bond of isotopomer molecular

systems (with C–H or C–D bonds) have been observed [11–16]. This suggests that undoubtedly a coupling involving the X–H and C–H bond (or the X–D and C–D bond) stretching vibration influences the spectra of the hydrogen (or deuterium) bonds formed in the molecular systems. Let us call these isotopic effects the “long-range” H/D isotopic effects.

Lack of reports on systematic studies of the “long-range” H/D isotopic effects in literature is somewhat surprising. Over the last four decades researchers have focused mainly on the influence of the Fermi resonance mechanism on the main band generation mechanism in quantitative theoretical models describing the $\nu_{\text{X-H}}$ and $\nu_{\text{X-D}}$ band shapes in the spectra of hydrogen bonded systems. The effect of other normal vibrations of associated molecules on their hydrogen bond spectra was considered in a similar way. These models assumed the Fermi resonance mechanism involving the X–H (or the X–D) bond stretching vibrations with some other vibrations of the associated molecules in their combination states. Most frequently the $\delta_{\text{X-H}}$ proton “bending-in-plane” vibrations in their first overtone state were assumed to strongly couple in an anharmonic way with the stretching protonic motion [9,10,17–19]. The possibility of the coupling involving the C–H (or C–D) bond stretching vibrations in their first excited state with the proton (or deuterium) stretching vibration fundamental has not been practically analyzed as yet.

The first attempt at tackling this problem was made ca. three decades ago. It concerned the interpretation of the IR spectra of the hydrogen bond in the gaseous formic acid HCOOH [20]. On assuming a dipole–dipole interaction model involving the C–H and O–H stretching vibration transition moments the effect of the $\nu_{\text{C-H}}$

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band intensity increase, near 3000 cm^{-1} , was explained. A similar coupling mechanism the C–D and O–D stretching vibrations was assumed for the explanation of the $\nu_{\text{C-D}}$ band intensity growth in the spectra of the gaseous formic acid isotopomer DCOOD [20]. However, the magnitude of the coupling energy of the two normal vibrations, resulting from the *dipole–dipole* interaction model seems to be strongly overestimated and therefore non-realistic.

The next attempt at solving the problem of the “*long-range*” H/D isotopic effects was made when analyzing the spectra of diverse imidazole isotopomer crystals [21]. They were ascribed to a *Herzberg–Teller*-type vibronic coupling in the second order of the perturbation theory [22]. The product of the two normal vibration coordinates of the two interacting motions expressed the coupling term.

To elucidate the mechanisms responsible for the generation of the “*long-range*” H/D isotopic effects the consequences of the hypothetical coupling between the C–H and O–H (or the C–D and O–D) bond stretching vibrations should be analyzed in the limits of an appropriate model. On the basis of the model the effect of the coupling involving the $\nu_{\text{O-H}}$ (or $\nu_{\text{O-D}}$) band contour shapes should be predicted. For this purpose a possibly simple model of molecular systems should be chosen. It seems that the simplest associated carboxylic acid molecules, *i.e.*, those of formic and acetic acid may be treated as the optimum model systems for the studies of spectral consequences of the hypothetical coupling of the two kinds of normal vibrations. There are some advantages of this choice. Both molecular systems are characterized by a relatively low number of vibrational freedom degrees. Moreover, each molecular system exists in the form of four popular isotopomers. Both substances in the gaseous phase form cyclic hydrogen-bonded dimers while in the solid state they form infinite hydrogen-bonded chains of the same space-symmetry group of the orthorhombic system [23–25]. On the other hand the corresponding spectra of the two systems substantially differ one from another. These effects yield mathematical constrains, which could potentially allow us to choose an optimum theoretical model for the description of these phenomena.

There is also another advantage of choosing these two systems, mainly they constitute the most frequently investigated model in the history of the hydrogen bond research. Since the beginning of the research on hydrogen bonds the IR spectra of the acetic and formic acid have often been used for diverse experimental methods. The subsequently introduced theoretical models [26–49] also interpreted them theoretically which included, the quantitative way as well [50,51]. Hence due to this fact we gain comprehensive knowledge about the mechanism of the spectra generation of cyclic hydrogen dimers formed by the molecules of these two carboxylic acids.

However it should be mentioned that in the case of the formic acid molecule the hypothetical coupling effects of the C–H and O–H bond stretching vibrations do not result from a particularly advantageous structure of the “*G*” matrix. “*G*” is the matrix of the kinematic coefficients in the classic *Wilson’s* theory of molecular normal vibrations [52]. In the “*G*” matrix the corresponding non-diagonal elements for the two different internal vibrational coordinates of the two motions vanish. This implies that the resonance of the two vibrations, provided it takes place, has a different source than a purely mechanical coupling.

Both the experimental and theoretical facts listed above have inspired us to re-investigate the source of the appearance of intense $\nu_{\text{C-H}}$ and $\nu_{\text{C-D}}$ bands in the spectra of the HCOOH and DCOOD formic acid isotopomers. In the spectra of the corresponding acetic acid isotopomers, CH_3COOH and CD_3COOD , these bands are of a practically negligible intensity. The undertaken studies should also explain the role of the peripheral C–H or C–D groups in the $\nu_{\text{C-H}}$

and $\nu_{\text{C-D}}$ band generation mechanism in the IR spectra of associated molecular systems.

2. Experimental

Formic acid HCOOH and its DCOOH, HCOOD and DCOOD isotopomers, acetic acid CH_3COOH and its deuterium derivatives, CD_3COOH , CH_3COOD and CD_3COOD , used in our studies were commercial substances (Sigma–Aldrich).

The spectra of gaseous samples of formic and acetic acid isotopomers (saturated vapor over a droplet of liquid sample) were measured in gas cell (glass tube with a pathlength of 10 cm) equipped with NaCl windows. The liquid phase spectra were measured for thin liquid films formed between NaCl plates tightly squeezed together.

Monocrystalline layers of the compounds were obtained by crystallization of liquid samples occurring between two closely-spaced CaF_2 windows. The IR spectra of gaseous, liquid and crystalline samples of the compounds were recorded in the frequency ranges of the $\nu_{\text{O-H}}$ and $\nu_{\text{O-D}}$ bands with a 2 cm^{-1} resolution by the transmission method, using a FT-IR Nicolet Magna 560 spectrometer.

3. The results of the spectral studies

The IR spectra of formic acid and its deuterium isotopomers in three condensation states of the matter, in the $\nu_{\text{O-H}}$ and $\nu_{\text{O-D}}$ band frequency ranges, are shown in Fig. 1.

The comparison of the spectra of acetic acid in the three different condensation states of the matter, in the $\nu_{\text{O-H}}$ and $\nu_{\text{O-D}}$ band frequency ranges is presented in Fig. 2.

The IR spectra of gaseous formic acid and d_2 -formic acid, recorded in the O–H and C–H or in the O–D and C–D stretching frequency regions, respectively, are shown in Fig. 3. In this picture the corresponding spectra of two gaseous acetic acid isotopomers, CH_3COOH and CD_3COOD are also presented.

The IR spectra of formic acid isotopomers measured for the gaseous phase samples have proved the domination of the associated cyclic, centrosymmetric dimeric form of the associates. The wide and intense $\nu_{\text{O-H}}$ bands in the spectra of HCOOH and DCOOH, found in the frequency range of 2400 cm^{-1} – 3400 cm^{-1} , and the $\nu_{\text{O-D}}$ bands of qualitatively similar properties appearing in the spectra of HCOOD and DCOOD, in the range of 1900 cm^{-1} – 2600 cm^{-1} , provide conclusive evidence of this statement (see Fig. 1).

On comparing the $\nu_{\text{O-H}}$ band contours of gaseous HCOOH and DCOOH as well as the $\nu_{\text{O-D}}$ bands of DCOOD and HCOOD some noticeable differences in the corresponding band fine structure patterns can be distinguished. The spectra of formic acid isotopomers with identical hydrogen isotope atoms in the C–X groups (where X = H or D) and in the hydroxyl groups, differ when compared with the spectra of molecules of a mixed isotope content (Fig. 1). These differences are expressed by the appearance of intense and narrow spectral lines, $\nu_{\text{C-H}}$ or $\nu_{\text{C-D}}$, which perturb the $\nu_{\text{O-H}}$ or $\nu_{\text{O-D}}$ band contours, respectively. These lines are marked at the frequencies of 2938 cm^{-1} and 2212 cm^{-1} and appear at a surprisingly high intensity (Fig. 3). Each line, $\nu_{\text{C-H}}$ or $\nu_{\text{C-D}}$, arises from the background determined by the complex fine structure pattern of the $\nu_{\text{O-H}}$ or $\nu_{\text{O-D}}$ band contour, respectively. Therefore the baselines of the $\nu_{\text{C-H}}$ and $\nu_{\text{C-D}}$ bands are uncertain as shown in Fig. 3. It is also noteworthy to mention that the compared band contours also differ slightly outside the $\nu_{\text{C-H}}$ or $\nu_{\text{C-D}}$ band line region.

There is no counterpart of this effect in the corresponding spectra of other carboxylic acids. An analogous spectral effect, depending on the $\nu_{\text{C-H}}$ and $\nu_{\text{C-D}}$ intensity growth, is also absent in the IR spectra of the hydrogen bond of the acetic acid isotopomers,

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