Title: Theoretical modeling of hydrogen bond infrared spectra in molecular crystals of 2-thiopheneacetic acid : Fermi resonance and Davydov coupling effects

Author: N. Issaoui, H. Abdelmoulahi, Henryk T. Flakus, H. Ghalla, B. Oujia

Citation style: Issaoui N., Abdelmoulahi H., Flakus Henryk T., Ghalla H., Oujia B. (2016). Theoretical modeling of hydrogen bond infrared spectra in molecular crystals of 2-thiopheneacetic acid : Fermi resonance and Davydov coupling effects. "Macedonian Journal of Chemistry and Chemical Engineering" (Vol. 35, np. 2 (2016), s. 157-168), doi: 10.20450/mjcce.2016.1081

Macedonian Journal of Chemistry and Chemical Engineering, Vol. **35**, No. 2, pp. 157–168 (2016)
MJCCA9 – 710
ISSN 1857-5552
e-ISSN 1857-5625
DOI: 10.20450/mjcce.2016.1081
Received: October 23, 2016
Accepted: November 9, 2016
Original scientific paper

THEORETICAL MODELING OF HYDROGEN BOND INFRARED SPECTRA IN MOLECULAR CRYSTALS OF 2-THIOPHENEACETIC ACID: FERMI RESONANCE AND DAVYDOV COUPLING EFFECTS

N. Issaoui[1*], H. Abdelmoulahi[2], H. T. Flakus[3], H. Ghalla[1], B. Oujia[1,4]

[1]*Quantum Physics Laboratory, Faculty of Sciences, University of Monastir, Tunisia*
[2]*Laboratory for Physical Chemistry of Materials, Faculty of Sciences, Tunisia*
[3]*Institute of Chemistry, University of Silesia, 9 Szkolna Street, 40-006 Katowice, Poland*
[4]*King Abdul-Aziz University, Faculty of Science, Saudi Arabia*
issaoui_noureddine@yahoo.fr

A quantum theoretical approach, within the adiabatic approximation and taking into account a strong non-adiabatic correction via the resonant exchange between the fast mode excited states of the two moieties of the dimer. The intrinsic anharmonicity of the low-frequency mode through a Morse potential, direct and indirect damping, and a selection rule breaking mechanism for forbidden transitions, is applied to reproduce the $\upsilon_{X\text{-}H}$ IR line shape of cyclic dimers of moderately *H*-bonded species in the crystalline phase. The results are used to gain an insight into the experimental spectral line shapes obtained by the transmission method. This approach fits satisfactorily the experimental line shape of 2-thiopheneacetic acid and predicts their evolution with isotopic substitution. Numerical calculations show that mixing of all these effects allows one to reproduce the main features of the experimental IR line shapes.

Keywords: 2-thiopheneacetic acid dimer; Davydov coupling; Fermi resonance; Morse potential; hydrogen bond; IR spectral density

ТЕОРЕТСКО МОДЕЛИРАЊЕ НА ИНФРАЦРВЕНИТЕ СПЕКТРИ НА ВОДОРОДНАТА ВРСКА ВО МОЛЕКУЛСКИТЕ КРИСТАЛИ НА 2-ТИОФЕНОЦЕТНА КИСЕЛИНА: РЕГМИЕВА РЕЗОНАНЦА И ДАВИДОВ ЕФЕКТ НА КУПЛИРАЊЕ

Разработен е квантнотеориски пристап во рамките на адијабатска апроксимација, а земајќи ја предвид силната неадијабатска корекција преку резонантна размена меѓу брзите модови на возбудени состојби на двете единки од димерот. Применета е сопствената анхармоничност на ниско-фреквенцискиот мод преку Морзеов потенцијал, директното и индиректно придушување и механизам на селекционо правило на прекршување за да се репродуцира $\upsilon_{X\text{-}H}$ IR профилот на циклични димери на умерено *H*-поврзани видови во кристална фаза. Резултатите се користат за да се добијат сознанија за експериментално добиените профили на спектралните ленти, добиени со трансмисиониот метод. Со овој пристап задоволувачки се усогласува профилот на лентите на 2-тиофеноцетна киселина и може да се предвиди нивната еволуција при изотопска супституција. Нумеричките пресметки покажуваат дека мешањето на сите овие ефекти овозможува да се репродуцираат основните карактеристики на експерименталниот профил на IR лентите.

Клучни зборови: димер на 2-тиофеноцетна киселина; куплување на Давидов; Фермиева резонанца; Морзеов потенцијал; водородна врска; спектрална густина на IR

1. INTRODUCTION

Hydrogen bonding (X-H…Y) is an interaction between a covalently bound H atom (X-H), with some tendency to be donated, and a region of high electron density on an electronegative atom or group of atoms (Y), which can accept the proton [1–3]. A hydrogen bond is said to be intermolecular or intermolecular depending on whether the atoms (or groups of atoms) X and Y belong to the same molecule or not. It is the most important interaction in chemical and biochemical systems. Hydrogen bonds are of fundamental importance in the structure of DNA [4, 5], in the secondary and tertiary structures of proteins, and in many chemical and biological processes. The nature of hydrogen bonding can be most conveniently studied in acid-base systems where the molecules are hydrogen bonded. Such systems are known as hydrogen-bonded complexes (HY complexes). The properties of hydrogen bonds have been widely investigated theoretically and experimentally, and have been the subject of several monographs [6, 7]. Many theoretical models have been proposed to describe the unusual features of hydrogen bond stretching bands in IR spectra [8–14].

The vibrational spectra of hydrogen-bonded dimers have been the subject of numerous experimental and theoretical studies [15–18]. The investigation of the vibrational spectra of hydrogen-bonded systems in crystalline phases is an important topic in physics and chemistry, as well as biology. These spectra are, as a rule, complicated as a result of significant anharmonic effects. The problem of anharmonicity in high frequency intermolecular vibrations in crystals has been studied for many years. There are two aspects that complicate this problem. The first of these is Fermi resonance (FR), which occurs between a fundamental vibration and a combination (or overtone) of the molecule. The second is splitting, which arises from intermolecular interactions and transmission of vibrational excitation from one molecule to another in a crystal. As a result, according to Davydov [19], one non-degenerate vibration of the free molecule may be split in the crystal into a multiplet of bands. The number of components is equal to the number of molecules in the crystal unit cell and the polarization of these bands can be different. Such an effect was named as Davydov splitting (DS) [20]. There have been also numerous studies of Fermi resonance in hydrogen-bonded complexes and crystals [21–23]. In this work, we present a theoretical study of polarized infrared spectra of 2-thiopheneacetic acid 2-TAA and its O-D derivative. We compare theoretical calculations to the experimental results. The theoretical model was used to simulate O–H(D) stretching bands. Recent polarized infrared spectra of hydrogen bonded 2-TAA have been studied experimentally and interpreted theoretically by Flakus *et al*. [24].

At room temperature, 2-TAA is a crystal and its melting point is at 336–337 K. The system that draws our attention in the present study is the 2-TAA dimer. 2-TAA crystals are monoclinic with space group P21/c and Z = 4. The lattice constants at 100 K are a = 27.063(9) Å, b = 4.452(4) Å, c = 10.7811(9) Å and β = 100.540(17)° [24]. In crystalline systems, associated molecules form hydrogen-bonded cyclic, centrosymmetric dimers. There are two centrosymmetric hydrogen-bonded dimers in each unit cell, linked by 2.669 Å long hydrogen bonds. The anharmonic coupling between the high frequency X–H stretching and low frequency intermolecular hydrogen bond vibrations, described by Maréchal and Witkowski [8], is an important mechanism for shaping the fine structure of ns bands in hydrogen-bonded systems. The most important mechanism influencing the fine structure of vibrational spectra of hydrogen-bonded systems is Fermi resonance. The theoretical model of Fermi resonance was used by Witkowski and Wojcik [9].

In this study, we present a quantitative description of infrared spectra in the O-H stretching region of the hydrogen-bonded 2-TAA dimer. This work is a continuation of our previous studies of hydrogen bonding [16]. We present a theoretical interpretation of the fine structure of the ν_s(OH) stretching band of 2-TAA and its deuterated derivative. For simulation of the fine structure, we used an adiabatic coupling between the high-frequency O–H(D) stretching and the low frequency intermolecular O· · ·O stretching modes, linear and quadratic distortions of the potential energies for these modes in the excited state of the O–H(D) stretching vibration, resonance interaction between the two hydrogen bonds in the dimer and the Fermi resonance between the fundamental $\nu_{O\text{-}H(D)}$ stretching and the overtone of the $\delta_{O\text{–}H(D)}$ bending vibrations. The present theoretical approach allows for the fitting of the experimental polarized $\upsilon_{X\text{–}H}$ IR line shapes of the cyclic 2-TAA dimer and its deuterated derivative using a minimum number of parameters.

2. THEORETICAL FORMULATION OF THE MODEL

2.1. *Basic parameters*

The 2-TAA dimer is formed by two hydrogen bonds that are cyclic centrosymmetric in interaction. Therefore, in cyclic symmetric dimers of hydrogen bonds, there are two degenerate high frequency modes (fast modes) and two degenerate low frequency H-bond vibrations (low modes). The two parts of the dimer are labeled as *r* = 1, 2. The computation of the spectral density requires knowledge of the following physical parameters:

$\omega°$ (Ω): vibration angular frequency of the two degenerate fast (slow) mode moieties,

$\alpha°$: dimensionless strong anharmonic coupling parameter,

β_e: dimensionless parameter characterizing the Morse potential width,

D_e: dissociation energy of the hydrogen bond bridge,

$\gamma°$ (γ): direct (indirect) damping parameter,

$V°$: Davydov coupling parameter,

γ_i^δ: damping parameter of the bending mode,

ω_δ: angular frequency of the bending mode,

f_i: Fermi coupling parameter,

Δ_i^0: angular frequency gap between the fast bending modes,

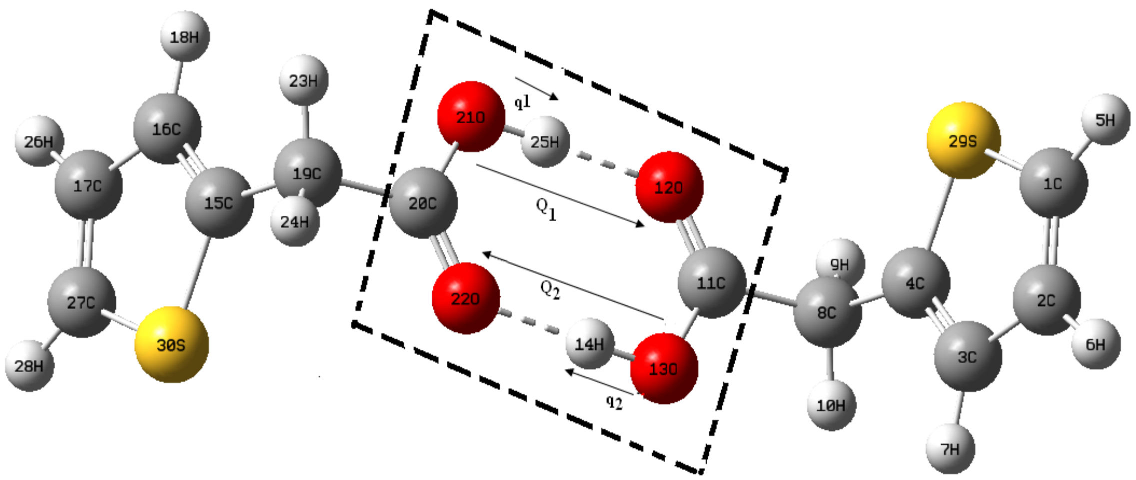
T: absolute temperature.

2.2. Computational approach

In the present approach, we treat hydrogen bonds as three atom systems composed of two heavier atoms, X and Y (these are usually oxygen, nitrogen, chloride, fluoride or sulfur), and hydrogen or deuterium atom in between these two. We assume that the basic physical mechanism responsible for the energy and intensity distributions is an anharmonic-type coupling between the high-frequency X-H(D) stretching vibration and the low frequency hydrogen bond X…Y stretching vibration in an isolated hydrogen bond.

Scheme 1 shows the geometry of the 2-TAA dimer optimized at the B3LYP/6-311G++ level. In this case, the two hydrogen bonds of the dimer are related by the symmetry operation C_2, corresponding to the two-fold symmetry axis. Because of the symmetry of the dimer, there is a symmetry C_2 parity operator that exchanges the two moieties of the system. This operator exchanges the coordinates Q_i of the two hydrogen bond bridges of the cyclic dimer according to:

$$C_2Q_1 = Q_2 \text{ and } C_2Q_2 = Q_1 \qquad (1)$$



Scheme 1: Geometry of the 2-TAA dimer optimized at the B3LYP/6-311G++ level

Within the linear response theory [25, 26], the IR spectral density I(ω) of the hydrogen bond dimer system may be related to the autocorrelation function (ACF, G(t)) of the transition dipole momentum of the fast mode X-H, through the following Fourier transform:

$$I(w) = 2\,\mathrm{Re}\int_0^{+\infty} G(t)e^{-iwt}dt \qquad (2)$$

The ACF of the dipole moment operator is written, in a general way, as:

$$G(t) = \mathrm{tr}\{\rho(0)\mu(0)\mu(t)\} \qquad (3)$$

where ρ(0) is the equilibrium Boltzmann density operator, μ(0) is the dipole moment operator at initial time and μ(t) is the same operator at time (t). Within the Heisenberg representation, this last operator is given by:

$$\mu(t) \propto \exp\left\{-i\frac{H.t}{\hbar}\right\}\mu(0)\exp\left\{i\frac{H.t}{\hbar}\right\} \quad (4)$$

where H is the full Hamiltonian of the hydrogen bonded dimer system. In the presence of direct damping, the ACF G(t) may be written as [27]:

$$G(t) = G°(t)\exp(-\gamma°t) \quad (5)$$

where $\gamma°$ is the direct damping parameter of the fast mode and G°(t) is the time dependent ACF without damping.

In order to obtain the spectral density (given in Eq. (2)), we need to construct and diagonalize the full Hamiltonian of the system.

Working within the strong anharmonic coupling theory, the high frequency mode is assumed as a harmonic potential, whereas the slow one is described by a Morse potential. The corresponding Hamiltonians of the slow and high frequency modes of the two moieties of the dimer are, respectively, given using dimensionless operators with the following expressions:

$$[H_{Slow}]_i = (1/2)P_i^2\hbar\Omega + D_e[1 - e^{(-\beta_e Q_i\sqrt{M\Omega/\hbar})}]^2; \quad i=1,2 \quad (6)$$

$$[H_{Fast}]_i = (1/2)(p_i^2 + q_i^2)\hbar\omega(Q_i); \quad i=1,2 \quad (7)$$

where P_i is the dimensionless conjugate moment of the hydrogen bond bridge dimensionless coordinates Q_i of the two moieties, whereas p_i and q_i are the dimensionless coordinates and the conjugate moment of the two degenerate high frequency modes of the two moieties. Ω and M are the angular frequency and reduced mass of the hydrogen bond bridge, respectively, whereas $\omega(Q_i)$ is that of the high frequency mode, which is supposed to depend on the coordinate of the hydrogen bond bridge. D_e is the dissociation energy of the hydrogen bond bridge.

There are two experimental correlations [28, 29] which show that the effective angular frequency of the fast mode $w(Q)$ and its equilibrium position q_e are assumed to be strongly dependent on the slow mode stretching coordinate. Based on these two correlations, a hypothesis was made in the literature that there exists within a given H-bond, a modulation of the angular frequency of the fast mode $w(Q)$ and its equilibrium position $q_e(Q)$ by the hydrogen bond distance Q, represented by two expansions to the second order:

$$\omega(Q) = \omega° + \alpha Q + \beta Q^2 \quad (8)$$

$$q_e(Q) = q_e^{\circ} + f°Q + g°Q^2 \quad (9)$$

These two hypotheses are at the origin of the strong anharmonic coupling theory, developed initially by Maréchal and Witkowski [8], and in another sense by Hofacker et al. [30]. Maréchal and his coworker Witkowski [8] have shown that consideration of the only parameter α ($\beta = f° = g° = 0$) allows us to reproduce the main characteristics of the envelope of spectra, especially their widths, asymmetry, as well as change of bands related to the deuteration. After that, the majority of consecutive works neglect the modulation of the equilibrium position of the fast mode and the quadratic dependence of its frequency. On this basis, following Maréchal and Witkowski, we consider only the expansion to the first-order of the angular frequency of the fast mode with respect to the coordinate of the hydrogen bond bridge, leading to:

$$\omega(Q_i) = \omega° + \alpha°\Omega Q_i \quad (10)$$

where ω° is the angular frequency of the two degenerate fast modes when the corresponding hydrogen bond bridge coordinates are at equilibrium, whereas α° is a dimensionless parameter that appears to be an anharmonic coupling parameter.

In the presence of damping, the thermal bath may be described by an infinite set of harmonic oscillators, and its coupling with the hydrogen bond bridge is described by terms that are linear in the position coordinates of the bridge and of the bath oscillators:

$$H_{Damp} = \sum(1/2)[\tilde{p}_r^2 + \tilde{q}_r^2]\hbar\omega_r + \sum\tilde{p}_r[Q_1 + Q_2]\hbar g_r \quad (11)$$

where q_r are the dimensionless position coordinate operators of the oscillators of the bath. p_r is the corresponding conjugate moment, obeying the usual quantum commutation rules, ω_r are the corresponding angular frequencies and g_r is the coupling between the hydrogen bond bridges and the oscillators of the bath.

For a cyclic symmetric dimer of hydrogen bonds, there are two degenerate high frequency modes and two degenerate low frequency H-bond vibrations, as shown in Scheme 1. The adiabatic approximation leads to a description of each moiety by effective Hamiltonians of the hydrogen bond bridge. For a single hydrogen bond bridge, this effective Hamiltonian is described by an harmonic oscillator if the fast mode is in its ground state, or with a driven harmonic oscillator if the fast mode is excited. When one of the two identical fast modes is excited, then, because of the symmetry of the cyclic dimer, and of te coupling V_{12} between the two degenerate fast mode excited states, an interaction occurs (Davydov coupling), leading to an exchange between the two identical excited parts of the dimer. Certainly, this interaction between degenerate excited states is of a non-adiabatic nature, although the adiabatic approximation has been performed in order to separate the high and low frequency motions. Therefore, within the adiabatic approximation, the Hamiltonian of each moiety of the dimer takes the form of the sum of effective Hamiltonians that depend on the degree of excitation of the fast mode according to:

$$[H_{Adiab}]_i = \sum [H^{\circ\{k\}}]_i \left| \{k\}_i \right\rangle \left\langle \{k\}_i \right| ;\ i=1,2;\ k=0,1 \quad (12)$$

$$[H^{\circ\{k\}}]_i = (1/2)P_i^2 \hbar\Omega + D_e[1-\exp(-\beta_e Q_i \sqrt{M\Omega/\hbar})]^2 + k\alpha^\circ Q_i \hbar\Omega + k\hbar\omega^\circ \quad (13)$$

An excitation of the fast mode of one moiety of the dimer is resonant with the excitation of the other moiety. Thus, a strong non-adiabatic correction [31], i.e., Davydov coupling occurs between the two resonant states after excitation of one of the two fast modes. The full Hamiltonian of the two moieties is given by the following equations:

$$H = [H_{Adiab}]_1 + [H_{Adiab}]_2 + V_{12} + H_{Damp} \quad (14)$$

with

$$V_{12} = \hbar V^\circ [\left| \{1\}_1 \right\rangle \left\langle \{0\}_2 \right| + \left| \{0\}_1 \right\rangle \left\langle \{1\}_2 \right|] \quad (15)$$

where V° is the Davydov coupling parameter.

Because of the symmetry of the system, it is suitable to use the following symmetrized coordinates and eigenvectors [31]:

$$Q_g = \frac{1}{\sqrt{2}}\{Q_1 + Q_2\}\ ;\ Q_u = \frac{1}{\sqrt{2}}\{Q_1 - Q_2\} \quad (16)$$

$$\left|\{k\}_g\right\rangle = \frac{1}{\sqrt{2}}\left[\left|\{k\}_1\right\rangle + \left|\{k\}_2\right\rangle\right];\ \left|\{k\}_u\right\rangle = \frac{1}{\sqrt{2}}\left[\left|\{k\}_1\right\rangle - \left|\{k\}_2\right\rangle\right] \quad (17)$$

Using the symmetry of the system (centrosymmetric cyclic dimer), the ACF may be split into symmetric parts (g) and antisymmetric parts (u). The ACF may be written using the following expression:

$$G(t) \propto [G(t)]_g [[G^+(t)]_u + [G^-(t)]_u] \quad (18)$$

In this equation, $[G(t)]_g$ is the *g* ACF of the dipole moment operator of the fast mode, which is affected by the strong anharmonic coupling and the indirect damping of the hydrogen bond bridge, i.e., the interaction of the two hydrogen bonds of the dimer with their environment.

The reduced g ACF can be written [31], after taking into account the natural line width of the excited state of the fast mode, in the following closed form:

$$[G(t)]_g \propto e^{i\omega^\circ t} e^{-i\frac{\alpha^\circ}{2}\Omega t} e^{-i\left[\frac{\beta}{\sqrt{2}}\right]^2 \Omega t} e^{-i\left[\frac{\beta}{\sqrt{2}}\right]^2 [\langle n \rangle + 1/2](2e^{-\gamma t/2}\cos\Omega t - e^{-\gamma t})} e^{i|\beta|^2 e^{(-\gamma t/2)} \sin\Omega t} \quad (19)$$

where, <n> and β are, respectively, the thermal average of the occupation number and the effective dimensionless anharmonic coupling parameter related to α°.

Alternatively, $[G^+(t)]_u$ and $[G^-(t)]_u$ are the two uACFs dealing with the corresponding (u) part, which are affected only by the Davydov coupling and the anharmonicity of the hydrogen bond bridge. They are given by [31]:

$$[G^\pm(t)]_u \propto \sum_n \sum_{n_\mu} e^{-(n\hbar\Omega/kT)} [1 \pm (-1)^{n_\mu+1} \cdot + \eta\ [1-(-1)^{n_\mu+1}]^2]^2 \times \left|C^\pm_{n_\mu,\mu}\right|^2 e^{i\omega^\pm_\mu t} e^{-in_\mu \Omega t} \quad (20)$$

where η is a dimensionless parameter reflecting the fact that in the real cyclic dimers, it is not possible to rigorously split the equations of the system into g and u parts. This parameter is similar to the breaking of the IR selection rule forbidding the Ag transition in cyclic dimers of carboxylic acids [32]. $C^\pm_{n_\mu,\mu}$ are the expansion coefficients of the eigenvectors on the basis of the eigenstates |n> of the Hamiltonian of the quantum harmonic oscillator.

The spectral densities are computed by Eq. (2) after constructing and diagonalizing the full Hamiltonian involving Davydov coupling and damping mechanisms in a truncated basis.

The previous treatment was developed with neglect of the Fermi resonances. Now, we suppose a situation where this effect is taken into account. It results from the interactions occurring between the first excited state of the high frequency mode and the first harmonic of some bending modes. As stated by Maréchal and Witkowski [8], if Fermi resonances are taken into account, one has to consider one fast mode, one slow mode and one bending mode for each hydrogen bond of the cyclic dimer. If we take into account Fermi resonances [33], they affect only the g state of the system. As a consequence, the $[G^{-}(t)]_u$ ACFs are not modified. In the presence of Davydov coupling and Fermi resonances, the ACF can be written as [33]:

$$[G(t)]_g \propto \sum_n \sum_\mu e^{-\lambda m} \left| a_{\{\mu,0,m\}_g} \right|^2 \left[e^{i\{\omega_\mu\}_g t/\hbar} \right] e^{-im\Omega t} \quad (21)$$

where $\{\omega_\mu\}_g$ are the eigenvalues appearing in Eq. (22) and $a_{\{\mu,0,m\}g}$ are the expansion coefficients defined by Eq. (18).

$$\left[H_D^F\right]_g \left|\phi_\mu\right\rangle_g = \hbar \left|\phi_\mu\right\rangle_g \{\omega_\mu\}_g \quad (22)$$

with

$$\left|\phi_\mu\right\rangle_g = \sum_m \sum_g \{a_{\mu,l,m}\} \left|\Psi_{l,m}\right\rangle_g \quad (23)$$

The g states involved in the above expansions are defined by:

$$|\{\Psi_{0,m}\}_g\rangle = |\{1\}_g\rangle|\{0_1\}_g\rangle|[0_2]_g\rangle|(m)_g\rangle, \quad (24)$$

$$|\{\Psi_{1,m}\}_g\rangle = |\{0\}_g\rangle|\{2_1\}_g\rangle|[0_2]_g\rangle|(m)_g\rangle, \quad (25)$$

$$|\{\Psi_{2,m}\}_g\rangle = |\{0\}_g\rangle|\{0_1\}_g\rangle|[2_2]_g\rangle|(m)_g\rangle. \quad (26)$$

where the kets $|\{k\}_g\rangle$, $|(m)_g\rangle$ and $|[l]_g\rangle$ are the *g* eigenstates of, respectively, the symmetrized high frequency quantum harmonic oscillator, the slow frequency quantum harmonic oscillator and the bending frequency quantum harmonic oscillator. The Fermi resonance mechanism, characterized by the coupling parameter f_i, is described by the following coupling operators $\hbar f$, which express the non-resonant exchanges between the state $|\{1\}_j\rangle$ of the *jth* fast mode and second damped excited state $|[2]_j\rangle$ of the *jth* bending mode. The introduction of the Fermi resonance coupling effects in the line shape is presented by the complex angular frequency gap Δ_i:

$$\Delta_i = \Delta_i^\circ - i\gamma_i^\delta \quad (27)$$

with

$$\Delta_i^\circ = -\omega^\circ - 2\omega_i^\delta \quad (28)$$

where ω_i^δ is the frequency of the bending modes (i=1,2,...n_F). The imaginary part in this gap is related to the lifetime of the corresponding excited states. Recall that the Hamiltonian of the dimer involving Davydov coupling and Fermi resonances between the g excited state of the fast mode and the g first harmonics of the bending mode, together with the damping of these excited states is:

$$[H_{Fermi+Dav}]_g = \begin{pmatrix} [H^{\{1\}}] & \hbar f_1 & \hbar f_2 & \hbar f_3 & \cdots & \hbar f_{nF} \\ \hbar f_1 & H^{\{0\}} + \hbar\Delta_1 & & & & \\ \hbar f_2 & & H^{\{0\}} + \hbar\Delta_2 & & & \\ \hbar f_3 & & & H^{\{0\}} + \hbar\Delta_3 & & \\ \cdots & & & & \cdots & \\ \hbar f_{nF} & & & & & H^{\{0\}} + \hbar\Delta_{nF} \end{pmatrix} \quad (29)$$

with

$$H^{\{0\}} = \left[a^+ a + \frac{1}{2}\right]\hbar\Omega \quad (30)$$

and

$$\left[H^{\{1\}}\right]_g = \left[\left(a^+ a + \frac{1}{2}\right) + \alpha\left(a^+ + a\right)\right]\hbar\left(\Omega - i\frac{\gamma}{2}\right) + \hbar\omega^\circ - \frac{\alpha}{2}\hbar\Omega \quad (31)$$

In these two last equations, a^+ and a are the boson operators obeying $[a^+, a] = 1$ and $i^2 = -1$.

3. LINE SHAPE OF CRYSTALLINE 2-THIOPHENEACETIC ACID

We propose here to apply the present model to the $\upsilon_{O\text{-}H}$ IR line shapes of polarized 2-TAA crystal and its deuterated form in the crystalline phase. In this study, we have supposed that the 2-TAA forms a centrosymmetric cyclic dimer in the crystalline phase. In addition, due to the complex generation mechanism of the $\upsilon_{X\text{-}H}$ bands in IR spectra of centrosymmetric H-bond dimers formed in associated carboxyl groups, any structural changes in the molecular associated should influence the band spectral properties, intensity distribution in the band included. For the cyclic, centrosymmetric dimeric structure, the forbidden transition sub-band in the proton stretching band is located in the lower frequency part of the band. In this study, according to which this model may apply to crystalline 2-TAA dimers, is based on the quantum mechanisms we have chosen to take into account the influence of the medium on the irreversible behavior of the 2-TAA of the dipole moment operator of the fast mode: the quantum direct damping is caused by the dipole-dipole interaction of one hydrogen bonded species with the other ones, whereas the indirect damping is related to the damping of one H-bond bridge because of collisions. The experimental polarized spectra of 2-TAA and its deuterated form are obtained by Flakus [24], where it was measured for two orientations of the electric field vector $\vec{E}$, with respect to this axis, the first one parallel (Pol=0°) and the last one perpendicular to the axis (Pol=90°). The spectral densities are computed by Eq. (2) after constructing and diagonalizing the total Hamiltonian H_{Tot} involving Davydov coupling and damping mechanisms in a truncated basis. Before starting the reproduction of IR spectra of 2-TAA, it is of interest to comment on the importance of the parameters used to fit the experimental line shapes. We have selected for the dissociation energy of the H-bond bridge, values D_e=2100 cm^{-1} and β_e = 0.189 [33]. These parameters are used to describe the Morse potential. The $\upsilon_{X\text{-}H}$ of the fast mode of the 2-TAA used in the calculation is around 3000 cm^{-1}. Note that, according to the Maréchal and Witkowski theory [8], the angular frequency ω° of the high frequency mode must decrease on *D* isotopic substitution of the proton involved in the H-bonds.

In the object of the study of the combined effect of Fermi resonances and Davydov coupling in the reproduction of the IR spectra of 2-TAA and its deuterated derivatives dimers, we show firstly the effect of the Davydov coupling parameter and then the effect of multiple Fermi resonances in the reproduction of the IR spectra. Among the myriad of results that we found, we identify the most acceptable physically case, which led to the reproduction of the experimental spectra of the concerned compounds. The theoretical spectra found are compared with those measured by Flakus *et al.* [24]. Note that the experimental spectra have a complex structures and shift towards lower frequencies in the case of the deuterated species. To reproduce the experimental spectra, we proceeded to vary the physical parameters, which will be discussed in the following, to reach an agreement between the theoretical and experimental spectra. The sets of parameters used to fit the experimental line shapes are reported in Tables 1 and 2.

Table 1

Parameters used for fitting experimental H(D)-2-TAA spectra

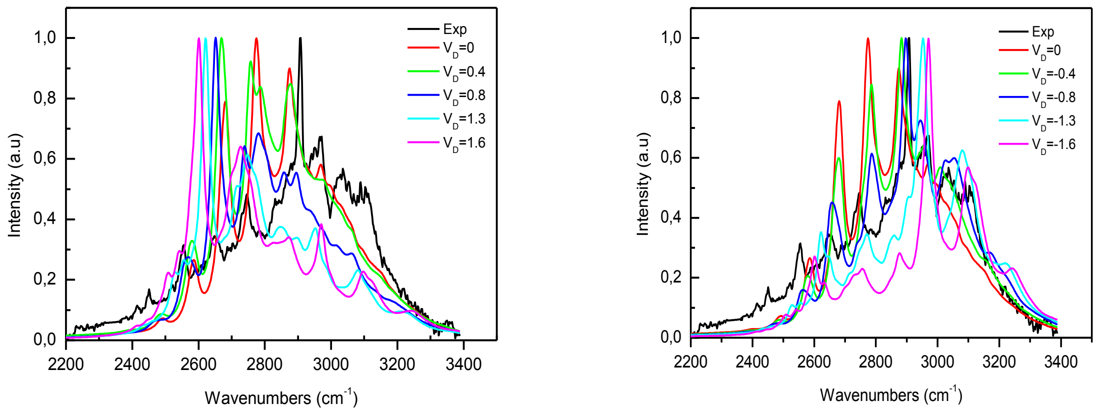
	T(K)	Pol(°)	ω° (cm^{-1})	Ω(cm^{-1})	α°	γ° (Ω)	γ (Ω)	V°	η
2-TA(H)	77	0	2995	80	1.25	0.35	0.12	–1.6	0.4
		90	3150	95	1.45	0.22	0.15	–0.8	0.25
	293	0	3140	95	1.45	0.19	0.015	–0.8	0.2
		90	3050	88	1.31	0.16	0.19	–1.3	0.30
2-TA(D)	77	0	2207	72	0.351	0.17	0.14	–0.78	0.72
		90	2206	71	0.346	0.16	0.16	–0.78	0.75
	293	0	2204	69	0.328	0.13	0.17	–0.95	0.50
		90	2204	70	0.328	0.16	0.18	–0.95	0.50

Table 2

Fermi parameters (in cm^{-1}) used to reproduce the theoretical H(D)-2-TAA line shapes

	T	Pol°	Δ_1	Δ_2	Δ_3	Δ_4	f_1	f_2	f_3	f_4	γ_1^δ	γ_1^δ	γ_3^δ	γ_4^δ
2-TA(H)	77	0°	100	70	30	70	25	25	25	10	0.2	0.18	0.15	0.01
		90°	65	-110	-200	55	20	5	10	20	0.02	0.01	0.01	0.01
	293	0°	75	-100	-200	75	20	10	20	10	0.02	0.01	0.01	0.01
		90°	110	45	30	60	10	12	25	05	0.2	0.4	0.35	0.01
2-TA(D)	77	0°	67	50	30	90	32	6	9	05	0.05	0.05	0.06	0.1
		90°	66	50	30	90	30	9	10	05	0.09	0.05	0.06	0.1
	293	0°	65	40	25	90	24	20	12	10	0.2	0.09	0.08	0.1
		90°	65	40	20	90	24	20	9	10	0.02	0.09	0.05	0.1

Before going very far in the reproduction of the experimental spectra, it is more appropriate to have an idea about the effect of the Davydov coupling parameter. In Figure 1, we present the evolution of spectral density function of Davydov coupling parameter V_D. In this figure, we show the effect of the increase of this parameter (from 0 to ±1.6). One may see that when this parameter becomes stronger, the intensity of the theoretical line shape changed and became more and more intense in the tails of the spectra. The intensity became more intense in the tail of haut frequencies when these parameters take a negatives values and inversely when this values became positive. The analyses of these spectra show that there is good agreement between the whole features of the theoretical and experimental line shapes when this parameter is close to the unity with a negative value. Such findings for the important effect of the Davydov coupling parameter in reproducing the fine structure of the IR spectra have been recently showed by Rekik et al. [34].



V_D>0 **V_D<0**

Figure 1: Davydov coupling effects on the IR SD of perpendicular polarized 2-TAA (Pol=90°) at 77 K when the slow modes were described by a Morse potential and Multiple Fermi resonances were taken account. The experimental (black line) and theoretical (colored lines) spectra. The corresponding parameters are given in Tables 1 and 2.

To precisely study the effect of Fermi resonances on the theoretical line shapes of crystalline 2-TAA, we performed numerical experimentation by increasing progressively the number of Fermi resonances n_F. The number of Fermi resonances n_F increases from zero (without Fermi resonances) to 4 (n_F = 0, 1, 2, 3 and 4). Figure 2 shows that when the number of Fermi resonances increases, the effect of Fermi resonance coupling becomes minimal. This may be explained by the fact that the Fermi resonance mechanism may involve the O-H bond in-plane bending vibrations in their first overtone states. Thus, the coupling between the electronic systems with the electrons of the associated carboxyl groups implies a stabilization of the dimers. Alternatively, each deformation of the dimers provides a destruction of this stabilization mechanism. This is the most probable source of the anharmonic coupling involving the proton stretching and proton bending-in-plane vibrations in the dimers of carboxylic acids.

In order to obtain good agreement with the experimental line shapes, we have taken into account some breaking of the IR selection rule for the centrosymmetric cyclic dimer, via a large amount (η=0.65…0.95) of forbidden A_g transition. Recall that in a general way, the quality of the fitting is weakly improved by taking small values for η which lying between 0 and 1. This assumption was initially introduced by Flakus [35]. This is a general trend which has been observed recently in the cases of the centrosymmetric cyclic dimers of gaseous acetic acid [12]. Note that according to the Flakus hypothesis, the lack of a "forbidden" transition ought to be stronger in the solid state than in the gaseous one, and we must keep in mind that the Flakus assumption has been seen by this author to be unavoidable in diverse crystalline H-bonded carboxylic acids, such as for cinnamic acid [35], and particularly in centrosymmetric H-bonded dimers, such as 2-hydroxybenzothiazole [36]. The problem of the "selection rule breaking" in the spectra is, in our opinion, a real problem. Flakus [37] found a predictable correlation in the spectra of diverse carboxylic acid crystals, between the forbidden transition probability and the electronic structure of carboxylic acid molecules. If carboxyl groups are linked directly with aromatic rings, or with other large pi-electronic systems, the forbidden transition is three times higher intensity than in the case when the same pi-electronic systems are separated from carboxyl groups by methylene groups.

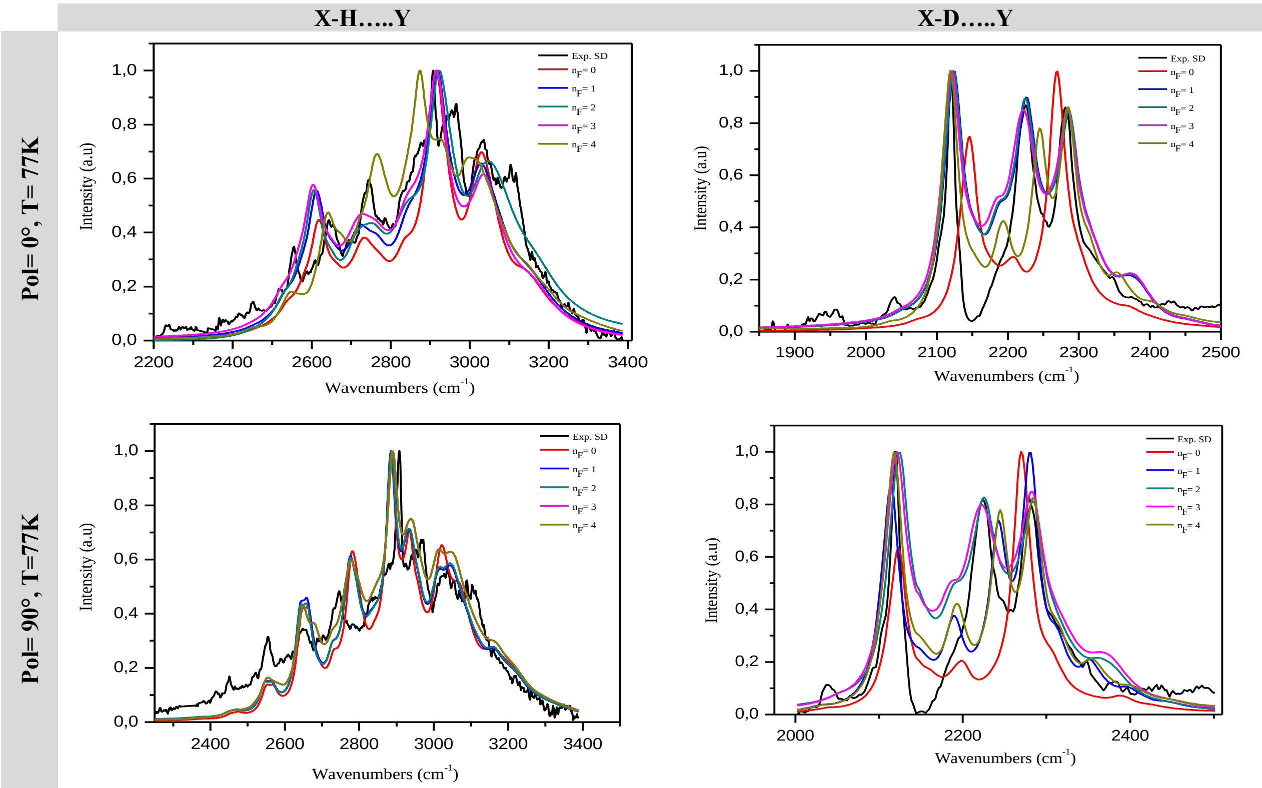


Figure 2: Multiple Fermi resonance effects on the IR SD of polarized 2-TAAwhen the slow modes were described by a Morse potential. The number of Fermi resonances n_F increases from zero (without Fermi resonances) to four. Comparison between the experimental (black line) and theoretical (colored lines) spectra. The corresponding parameters are given in Tables 1 and 2.

The effect of the symmetry breaking parameter η is illustrated in Figure 3. In this figure, we present the evolution of the spectral densities of 2-TAA with the symmetry-breaking parameter η. The lower spectral density represents the situation where η is zero, and then the parameter increases going upwards. The examination of Figure 3 shows the important role played by the parameter η in the reproduction of the polarized IR spectra. Finally, we can say that to obtain a good agreement with the experimental line shapes, we must take into account some breaking of the IR selection rule for the centrosymmetric cyclic dimer, via a large or a small amount (η=0.2…0.75) of forbidden Ag transition.

Consider now the general physical situation in which Davydov coupling and Fermi resonances occur and for which the spectral density is given by Eqs. (2, 18 and 20). The procedure we have used is the fitting of the experimental line shapes by optimizing the values of the basic parameters. We have performed numerical experimentation by increasing progressively the number of Fermi resonances.

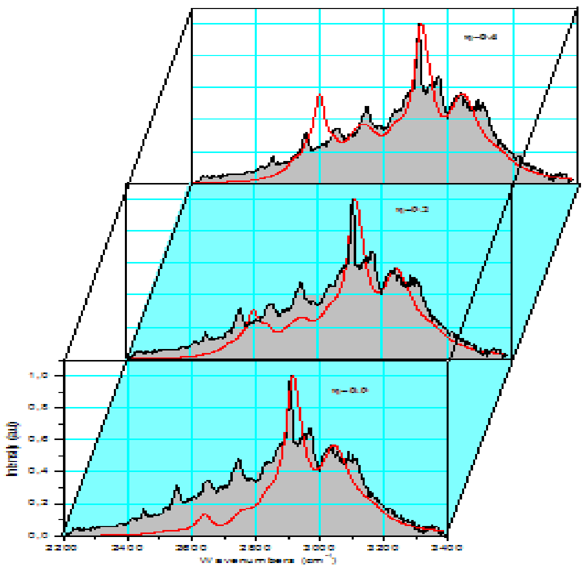
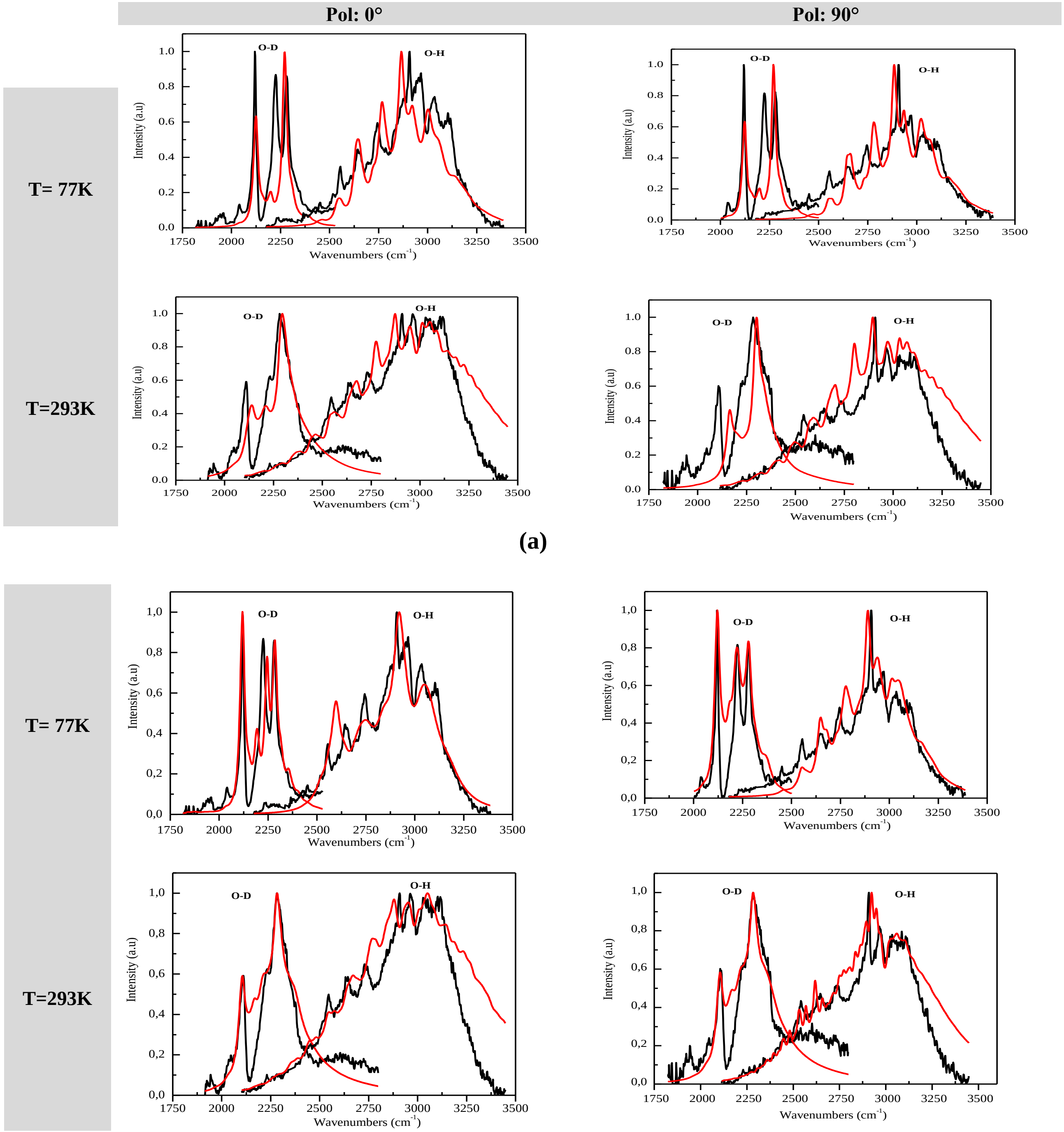


Figure 3: Effect of the forbidden transition parameter η on the SD of perpendicular polarized 2-TAA(Pol=90°) at 77 K. Theoretical SDs: red line shapes. Experimental SDs: black line. The corresponding parameters are given in Table 1.

We have observed that the quality of the fitting increases progressively with this number. We have observed that a good compromise between this number and the accuracy of the fitting may be the use of three Fermi resonances.

The numerical simulation shows that this model reproduces satisfactorily the main features of the experimental IR line shapes the of crystalline of 2H(D)-TAA dimers for two different temperatures of 77 and 293 K. Figure 4 deals with the comparison of theoretical and experimental line shapes for hydrogenated $\upsilon_{O\text{-}H}$ and deuterated $\upsilon_{D\text{-}H}$ crystalline 2-TAA at 0° and 90° polarizations and 77 and 293 K, when it is assumed that Fermi resonances are missing and when they are taken into account.



(b)

Figure 4: Effects of temperature and isotopic substitution on the spectral densities of 2-TAA at different polarizations without (a) and with four Fermi resonances (b). Experiment: black line spectra. Theoretical: red line spectra. The corresponding parameters are given in Tables 1 and 2

The comparison in Figure 4 shows good agreement between theory and experiment when Fermi resonances are taken into account. It shows that the introduction of multiple Fermi resonances improves the resolution of the fine structure of the spectra of 2-TAA dimer, in particularly in the high-frequency bands. In addition, Fermi resonances and Davydov coupling appear to play an important role in reproducing the theoretical infrared spectra of 2-TAA dimer and its deuterated derivative, especially when the slow modes are described by anharmonic potentials (Morse potential).

4. CONCLUSIONS

In the present work, we have reproduced the IR spectrum absorption of the O-H(D) stretching vibration of the 2-TAA dimer, involving two hydrogen bonds in interaction, with a quantum theoretical approach. This approach was developed within the strong anharmonic coupling theory between the high frequency modes and the slow frequency modes taking into account multiple Fermi resonances, Davydov coupling and the direct and indirect damping. It appears that this quantum approach satisfactorily reproduces the main features of the experimental IR line shapes of crystalline hydrogenated and deuterated 2-TAA. The inability to reproduce some more details of the fine structure has yet to be dealt with for precedent approaches using similar models and dealing with other more complex molecules. This may be explained by the fact that the model used ignored the quadratic dependence of the angular frequency of the fast mode and its equilibrium position on the H-bond bridge elongation and some of another important approximations, especially the electrical anharmonicity.

REFERENCES

[1] D. Hadzi, H. W. Thompson, Eds. *Hydrogen Bonding*, Pergamon: London, 1959.

[2] W. C. Hamilton, J. A. Ibers, *Hydrogen Bonding in Solids, W.* A. Benjamin: New York, 1968.

[3] P. Schuster, G. Zundel, C. Sandorfy, Eds. *The Hydrogen Bond. Recent Developments in Theory and Experiments;* Vol. 1–3, North-Holland: Amsterdam, 1976.

[4] D. Zanuy, C. Aleman, *J. Phys. Chem. B* **112** (2008) 3222. DNA-conducting polymer complexes: a computational study of the hydrogen bond between building blocks. DOI: 10.1021/jp711010t

[5] V. V. Prabhu, L. Young, K. W. Awati, W. Zhuang, E. W. Prohofsky," Defect-mediated hydrogen-bond melting in B-DNA polymers", *Phys. Rev. B* **41** (1990). DOI: 10.1103/PhysRevB.41.7839

[6] D. Hadzi (Ed.), *Theoretical Treatments of Hydrogen Bonding, J. Wiley, Chichester,* 1997.

[7] P. Gilli, G. Gilli, *The Nature of the Hydrogen Bond, Oxford University Press, Oxford*, 2009.

[8] Y. Maréchal, A. Witkowski, Infrared Spectra of H-Bonded Systems, *J. Chem. Phys.* **48** (1968) 3697. DOI:10.1063/1.1669673

[9] A. Witkowski, M. Wójcik, Infrared spectra of hydrogen bond a general theoretical model, *Chem. Phys.* **1** (1973) 9. DOI:10.1016/0301-0104(73)87017-X

[10] N. Issaoui, N. Rekik, B. Oujia, M. J. Wójcik, Theoretical infrared line shapes of H-bonds within the strong anharmonic coupling theory and Fermi resonances effects, *Int. J. Quant. Chem,* **110** (2010) 2583. DOI: 10.1002/qua.22395.

[11] N. Issaoui, N. Rekik, B. Oujia, M. J. Wójcik, Anharmonic effects on theoretical IR line shapes of medium strong H(D) bonds, *Int. J. Quant. Chem,* **109** (2009) 483. DOI: 10.1002/qua.21839

[12] P. Blaise, M. J. Wójcik, O. Henri-Rousseau, Theoretical Interpretation of the Line Shape of the Gaseous Acetic Acid Dimer, *J. Chem. Phys.* **122** (2005) 064306. DOI:10.1063/1.1847491

[13] M. Z. Brela, J. Stare, G. Pirc, M. Sollner Dolenc, M. Boczar, M.J. Wójcik and J. Mavri, Car-Parrinello Simulation of the Vibrational Spectrum of a Medium Strong Hydrogen Bond by Two-Dimensional Quantization of the Nuclear Motion: Application to 2-Hydroxy-5-Nitrobenzamide, *J. Phys. Chem. B* **116** (2012) 4510. DOI: 10.1021/jp2094559

[14] N. Issaoui, H. Ghalla, B. Oujia, A Theoretical model for polarized infrared spectra of crystals of 2-naphthyl acetic acid in the OH-stretching region *J. Appl. Spectro.*. **80** (2013) 15. doi:10.1007/s10812-013-9714-7

[15] S. Detoni, D. Hadzi, Hydroxyl bands in the infra-red spectra of organophosphoric and phosphinic acids, *Spectrochim. Acta* **20** (1964) 949. DOI:10.1016/0371-1951(64)80095-3

[16] N. Issaoui, H. Ghalla, B. Oujia, Theoretical study of hydrogen and deuterium bond in glutaric acid crystal dimer, *Int. J. Quant. Chem.* **112** (2012) 1006. DOI: 10.1002/qua.23085

[17] H. Ghalla, N. Issaoui, B. Oujia, Theoretical study of the polarized infrared spectra of the hydrogen bond in 2-furoic acid crystal dimer, *Int. J. Quant. Chem,* **112** (2012) 1373. DOI: 10.1002/qua.23117

[18] L. González, O. Mó, M. Yáñez, J. Elguero, Very strong hydrogen bonds in neutral molecules: the phosphinic acid dimers, *J. Chem. Phys.* **109** (1998) 2685. DOI: 10.1063/1.476868

[19] A. S. Davydov, *Theory of Molecular Excitons,* McGraw Hill, New York, 1962.

[20] H. Winston, The Electronic Energy Levels of Molecular Crystals, *J. Chem. Phys.* **19** (1951) 156. DOI:10.1063/1.1748150

[21] S. Bratoz, D. Hadzi, Infrared Spectra of Molecules with Hydrogen Bonds, *J. Chem. Phys.* **27** (1957) 991. DOI:10.1063/1.1743982

[22] D. Chamma, O. Henry-Rousseau, IR spectral density of weak H-bonded complexes involving damped Fermi

resonances. II. Numerical experiments and physical discussion, *Chem. Phys.* **229** (1998) 51. DOI:10.1016/S0301-0104(97)00361-3

[23] M. P. Lisitsa, N. E. Ralko, A. M. Yaremko, Exciton splitting and Fermi resonance in solid solutions, *Phys. Lett., A* **48** (1974) 241. DOI:10.1016/0375-9601(74)90486-1

[24] H. T. Flakus, N. Rekik, A. Jarczyk, Polarized IR Spectra of the Hydrogen Bond in 2-Thiopheneacetic Acid and 2-Thiopheneacrylic Acid Crystals: H/D Isotopic and Temperature Effects, *J. Phys. Chem. A*, **116** (2012) 2117. DOI: 10.1021/jp210950n

[25] R. Kubo, Statistical-Mechanical Theory of Irreversible Processes. I. General Theory and Simple Applications to Magnetic and Conduction Problems, J. Phys. Soc. Japan. **12**, (1957) 570. DOI:10.1143/JPSJ.12.570

[26] R. Kubo, in: *Lectures in theoretical physics* I, W. E. Brittin and L. G. Dunham (Eds.), Interscience, Boulder 1958.

[27] N. Rosch, M. Ratner, Model for the Effects of a Condensed Phase on the Infrared Spectra of Hydrogen Bonded Systems, *J. Chem. Phys.* **61**, (1974) 3344. DOI:10.1063/1.1682497

[28] A. Novak, Hydrogen Bonding in Solids Correlation of Spectroscopic and Crystallographic Data *Structure and Bonding* **18** (1974) 177.

[29] I. Olovsson, P.-G. Jonsson, in: *The hydrogen bond*, P. Scheuster, G. Zundel, C. Sandorfy (Eds.), Amsterdam 1976.

[30] G. Hofacker, Y. Marechal, M. Ratner, in: P. Schuster, G. Zundel, C. Sandorfy (Eds.), *The Hydrogen Bond*, North-Holland Publ. Co, Amsterdam, 1976

[31] M. El-A. Benmalti, D. Chamma, P. Blaise, O. H. Rousseau, Theoretical Interpretation of the Infrared Lineshape of Gaseous Propynoic and Acrylic Acid Dimers, *J. Mol. Struct,* **785** (2006) 27. doi:10.1016/j.molstruc.2005.09.036

[32] H. T. Flakus, On the Vibrational Transition Selection Rules for the Centrosymmetric Hydrogen-Bonded Dimeric Systems, *J. Mol. Struct. (Theochem),* **187** (1989) 35. DOI:10.1016/0166-1280(89)85148-6

[33] K. Belhayara, D. Chamma, O Henri-Rousseau. Infrared spectra of weak H-bonds: Fermi resonances and intrinsic anharmonicity of the H-bond bridge, *J. Mol. Struct.* **648** (2003) 93. DOI:10.1016/S0022-2860(02)00618-X

[34] N. Rekik, F. A. Al-Agel, H. T. Flakus, Davydov coupling as a factor influencing the H-bond IR signature: Computational study of the IR spectra of 3-thiopheneacrylic acid crystal, *Chem. Phys. Lett.* **647** (2016) 107. DOI:10.1016/j.cplett.2016.01.042

[35] H. T. Flakus, A. Miros, "Infrared Spectra of the Hydrogen Bonded Glutaric Acid Crystals: Polarization and Temperature Effects" *J. Mol. Struct*. **484** (1999) 103. doi.org/10.1016/S0022-2860(98)00907-7

[36] H. T. Flakus, M. Jabłonska, Study of Hydrogen Bond Polarized IR Spectra of Cinnamic Acid Crystals, *J. Mol. Struct.* **707** (2004) 97. DOI:10.1016/j.molstruc.2004.06.032

[37] H. T. Flakus, A. Miros, P.G. Jones, Influence of molecular electronic properties on the IR spectra of dimeric hydrogen bond systems: polarized spectra of 2-hydroxybenzothiazole and 2-mercaptobenzothiazole crystals, *J. Mol. Struct.* **604** (2002) 29. DOI:10.1016/S0022-2860(01)00620-2