

Theoretical model of infrared spectra of hydrogen bonds in molecular crystals of 2-thiopheneacetic acid: Fermi resonance and Davdov coupling effects.

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Abstract

A general quantum theoretical approach of the ν X-H IR lineshape of cyclic dimers of moderately H-bonded species in the crystalline phase is proposed. In this model, the adiabatic approximation is performed for each separate H-bond bridge species of the dimer, a strong non-adiabatic correction is introduced into the model via the resonant exchange between the fast mode excited states of the two moieties, 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 in IR. The present model reduces satisfactorily to many models in the literature dealing with more special situation. It has been applied to the cyclic dimers of 2-thiopheneacetic acid (2-TAA) and his deuterated derivative in the crystalline phase. It correctly fit the experimental line shape of the hydrogenated compound and predicts satisfactorily the evolution in the line shapes with isotopic substitution. Numerical calculations show that mixing of all these effects allows one to reproduce satisfactorily the main features of the experimental IR line shapes of hydrogenated and deuterated 2-TAA crystals and is expected to confirm the importance of the Fermi resonances and Davydov coupling in reproducing the experimental spectra.

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1. Introduction

Hydrogen bonding ($X-H\cdots Y$) 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]. The hydrogen bond is said to be intramolecular or intermolecular; that is whether the atoms (or groups of atoms) X and Y belong to the same molecule or not. It is the most important interactions in chemical and biochemical systems. Hydrogen bonds are of fundamental importance in the structure of DNA [4,5], in secondary and tertiary structures of proteins, and in many chemical and biological processes. Hydrogen-bond nature 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 subject of several monographs [6,7]. Many theoretical models have been proposed to describe unusual features of hydrogen bond stretching bands in the IR spectra [8–13]. Vibrational spectra of hydrogen bonded dimers have been a subject of numerous experimental and theoretical studies [14–17]. The investigation of the vibrational spectra of hydrogen bonded systems in crystalline phases is an important topic in physics and chemistry, and also for biology. These spectra are as a rule complicated as a result of significant anharmonic effects. The problem of anharmonicity in the high frequency intermolecular vibrations in crystals has been studied over 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 interaction and transmission of vibrational excitation from one molecule to another in a crystal. As a result, according to Davydov [18], 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 [19] as Davydov splitting (DS). There have been also numerous studies of Fermi resonance in hydrogen bonded complexes and crystals [20–22]. In this paper, we present a theoretical study of polarized infrared spectra of 2-TAA and its O-D derivative. We compare our 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. [23]. At room temperature 2-TAA is a crystal, its melting points is at 336–337 K. System which draws our attention in the present paper is 2-TAA dimer. 2-TAA crystals are monoclinic, space group is $P2_1/c$ 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 $\beta = 100.540(17)^\circ$ [23]. In crystalline systems, associated molecules form hydrogen-bonded cyclic, centrosymmetric dimers. There are two centrosymmetric hydrogen bonded dimers in each unit cell, linked 2.669 Å ° long hydrogen bonds. An 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 shaping fine structure of ns bands in hydrogen-bonded systems. The most important mechanism influencing the fine structure of vibrational spectra of hydrogen bonded system is Fermi resonance. Theoretical model of Fermi resonance was used by Witkowski and Wojcik [9]. In this paper, we present quantitative description of infrared spectra in the O–H stretching region of hydrogen bonded 2-TAA dimer. This paper is a continuation of our previous studies of hydrogen-bond [15]. We present a theoretical interpretation of the fine structure of the $\nu_s(OH)$ 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 $O\cdots O$ 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 Fermi resonance between the fundamental $\nu_{O-H(D)}$ stretching and the overtone of the $\delta_{O-H(D)}$ bending vibrations. The present theoretical approach allows fitting the

experimental polarized $\nu_{\text{X-H}}$ IR line shapes of cyclic 2-TAA dimer and its deuterium derivative by 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 in 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 $r = 1, 2$. The computation of the spectral density requires the knowledge of the following physical parameters, namely:

- $\omega^\circ (\Omega)$: the vibration angular frequency of the two degenerates fast (slow) modes moieties,
- α° : the dimensionless strong anharmonic coupling parameter,
- β_e : the dimensionless parameter characterizing the Morse potential width,
- D_e : the dissociation energy of the hydrogen bond bridge,
- $\gamma^\circ (\gamma)$: the direct (indirect) damping parameter,
- V° : the Davydov coupling parameter,
- γ_i^δ : the damping parameter of the bending mode,
- ω_δ : the angular frequency of the bending mode,
- f_i : Fermi coupling parameter,
- Δ_i^0 : the angular frequency gap between the fast the bending modes,
- T : absolute temperature.

2.2. The computational approach

In our theoretical approach we treat hydrogen bond as a three atom systems composed of two heavy atoms X and Y (these are usually oxygen, nitrogen, chloride, fluoride or sulphur atoms) 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 isolated hydrogen bond. Scheme 1. present geometry of the 2-TAA dimer optimized at the B3LYP/6-311G++ level. In this case the two hydrogen bonds of this 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 which 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:

$$C_2 Q_1 = Q_2 \text{ and } C_2 Q_2 = Q_1 \quad (1)$$

Within the linear response theory [24,25], the IR spectral density $I(\omega)$ of the hydrogen bond dimer system may be related to the autocorrelation function $G(t)$ of the transition dipole momentum of the fast mode X-H, through the following Fourier transform:

$$I(\omega) = 2 \operatorname{Re} \int_0^{+\infty} G(t) e^{-i\omega t} dt \quad (2)$$

The autocorrelation function (ACF) of the dipole moment operator is written, in a general way:

$$G(t) = \operatorname{tr} \{ \rho(0) \mu(0) \mu(t) \} \quad (3)$$

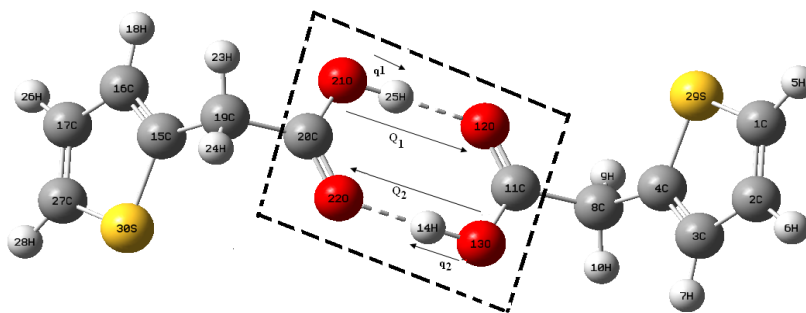
where $\rho(0)$ is the equilibrium Boltzmann density operator and $\mu(0)$ the dipole moment operator at initial time, $\mu(t)$ being the same operator at time (t) . Within the Heisenberg representation this last operator is given by:

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

In the last equation H is the full Hamiltonian of the hydrogen bonded dimer system. In the presence of direct damping, the ACF $G(t)$ may be written [26]:

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

where γ° is the direct damping parameter of the fast mode. $G^\circ(t)$ is the time dependent autocorrelation function without damping. In order to obtain the spectral density (given in eq.2), we need to construct and diagonalize the full Hamiltonian H of the system.



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

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, by the following expressions:

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

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

In these equations, P_i are the dimensionless conjugate moment of the hydrogen bond bridges 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 the reduced mass of the hydrogen bond bridge, 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 [27,28] shows that the effective angular frequency of the fast mode $\omega(Q)$ and its equilibrium position q_e is assumed to be strongly dependent on the slow mode stretching coordinate. Based on these two correlations, hypothesis was made in the literature that there exists within a given H-bond, a modulation of the angular frequency of the fast mode $\omega(Q)$ and its equilibrium position $q_e(Q)$ by the hydrogen bond distance Q , represented by two expansions to the second order:

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

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

These two hypotheses are at the origin of the strong anharmonic coupling theory, developed initially by Maréchal and Witkowski [8] and, in another spirit by Hofacker et al.[29]. Maréchal and his coworker Witkowski [8] have shown that the consideration of the only parameter α ($\beta=f^\circ=g^\circ=0$) allows to reproduce main characteristics of the envelope of spectra, especially their widths, asymmetry, as well as change of bands related to the deteuration. 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. That is way in this Work, following Maréchal and Witkowski, we consider only the expansion to first-order of the angular frequency of the fast mode with respect to the coordinate of the hydrogen bond bridge leads to write:

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

Here, 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 which will appear to be an anharmonic coupling parameter. In presence of damping, the thermal bath may be described by an infinite set of harmonic oscillators and its coupling with the hydrogen bond bridge are described by terms which are linear in the position coordinates of the bridge and of the bath oscillators:

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

where q_r are the dimensionless position coordinate operators of the oscillators of the bath. p_r are the corresponding conjugate moment, obeying the usual quantum commutation rules, ω_r are the corresponding angular frequencies and g_r are the coupling between the hydrogen bond bridges and the oscillators of the bath. For 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 description of each moiety by effective Hamiltonians of the H-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 that of a driven harmonic oscillator if the fast mode is excited. While one of the two identical fast modes is excited, then, because of the symmetry of the cyclic dimer, and of 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 nonadiabatic nature although the adiabatic approximation has been performed in order to separate the high and low frequency motions. There for, within the adiabatic approximation, the Hamiltonian of each moiety of the dimer takes the form of sum of effective Hamiltonians which are depending on the degree of excitation of the fast mode according to:

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

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

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 [30] i.e. a 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 equations:

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

with

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

Here, V° is the Davydov coupling parameter. Because of the symmetry of the system, it is suitable to use the following symmetrized coordinates and eigenvectors [30]:

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

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

Using the symmetry of the system (the centrosymmetric of the cyclic dimer), the ACF may be split into symmetric parts (g) and antisymmetric parts (u). The ACF may be written in 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, the indirect damping of the hydrogen bond bridge i.e, the interaction of the two hydrogen bond of the dimer with its environment. The reduced g ACF can be written [30], after taking into account the natural line width of the excited state of the fast mode, in the following closed form:

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

Here, $\langle n \rangle$ and β are respectively the thermal average of the occupation number and the effective dimensionless anharmonic coupling parameter related to α° . On the other hand, $[G^+(t)]_u$ and $[G^-(t)]_u$ are the two uACFs dealing with the corresponding (u) part, which are affected only by the Davydov coupling and by the anharmonicity of the hydrogen bond bridge. They are given by [30]:

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

In last equation (20), η is a dimensionless parameter reflecting the fact that in the real cyclic dimers, it is not possible

to split rigorously the equations of the system into g and u parts. This parameter looks like some breaking of the IR selection rule forbidding the Ag transition in cyclic dimers of carboxylic acids [31], $C_{n_\mu, \mu}^\pm$ are the expansion coefficients

of the eigenvectors on the basis of the eigenstates $|n\rangle$ of the Hamiltonian of the quantum harmonic oscillator.

The spectral densities are computed by eq.(2) after construct and diagonalizable the full Hamiltonian H involving Davydov coupling, damping mechanisms in a truncated basis. The previous treatment was developed with the neglect of Fermi resonances. Now suppose the situation where this later effect is taken into account. It is resulting from the interactions occurring between the first excited state of the high frequency mode and the first harmonic of some bending modes. As it was 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 [32], they affect only the g state of the system. As a consequence, the $[G^-(t)]_u$ autocorrelation functions are not modified. In the presence of Davydov coupling and Fermi resonances, the ACF can be written following [32]:

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

Here, $\{\omega_\mu\}_g$ are the eigenvalues appearing in equation (22) whereas, $a_{\{\mu, 0, m\}_g}$ are the expansion coefficients defined by equation (18).

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

$$\text{with} \\ |\phi_\mu\rangle_g = \sum_m \sum_g \{a_{\mu, 1, m}\} |\psi_{1, m}\rangle_g \quad (23)$$

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

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

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

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

Here, 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 j th fast mode and

second damped excited state $|[2]_j\rangle$ of the j th bending mode. The introduction of the Fermi resonance coupling effects in the line shape is presented by the complexes 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 ($i=1,2,\dots,n_F$).. 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, 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:

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

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

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

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

3. The lineshape of crystalline 2-thiopheneacetic acid

We propose here to apply the present model to the $\nu_{\text{O-H}}$ IR lineshapes of polarized 2-TAA crystal and its deuterated in crystalline phase. Our assumption is that the 2-TAA forms a centrosymmetric cyclic dimer in the crystalline phase. Besides, due to the complex generation mechanism of the $\nu_{\text{X-H}}$ 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 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 paper, according to which our 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 behaviour 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 are obtained by Flakus [23] were 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 equation (2) after construct and diagonalize the total Hamiltonian H_{Tot} involving Davydov coupling, damping mechanisms in a truncated basis. Before starting the reproduction of IR spectra of 2-TAA, it is of interest to comment the importance of the parameters used to fit the experimental lineshapes. We have selected for the dissociation energy of the H-bond bridge, the value $D_e=2100 \text{ cm}^{-1}$, then $\beta_e = 0.189$ [32]. These parameters are used to describe the Morse potential. The $\nu_{\text{X-H}}$ of the fast mode of the 2-TAA used in the calculation is around 3000 cm^{-1} . Note that, according to Maréchal and

Witkowski theory [8], the angular frequency ω° of the high frequency mode must be decreased 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 infrared spectra of 2-TAA and its deuterated derivatives dimers, we shows firstly the effect of Davydov coupling parameter and then the effect of multiple Fermi resonances in the reproduction of the infrared spectra. Among the myriad results 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 [23]. Note that the experimental spectra have a complex structures and shift towards the lower frequencies in the case of the deuterated species. To reproduce the experimental spectra we proceed 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 lineshapes 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

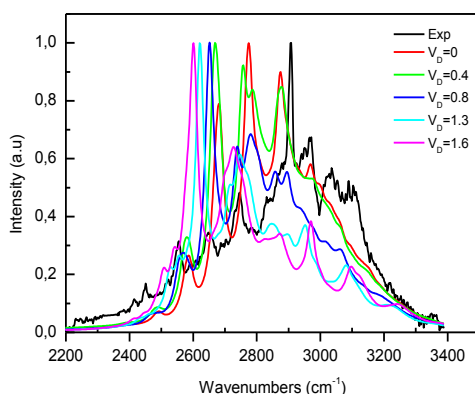
Table 2 : Fermi parameters (in cm⁻¹) used to reproduce the theoretical H(D)-2-TAA lineshapes.

	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 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 more and more strong 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 positively. The analyses of these spectra, shows that there is a 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, of the

important effect of the Davydov coupling parameter to reproduce the fine structure of the IR spectra, has been recently showed by Rekik et al.[33].

$V_D > 0$



$V_D < 0$

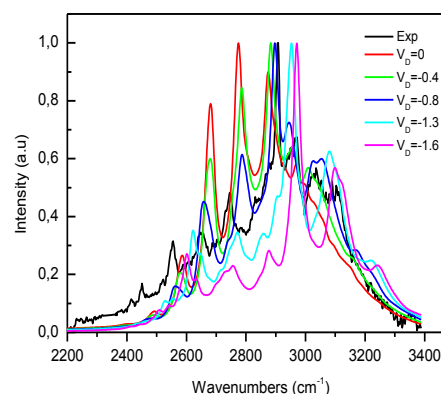


Figure 1: Davydov coupling effects on the IR SD of perpendicular polarized 2-TAA ($\text{Pol}=90^\circ$) at 77 K when the slow modes were described by a Morse potential and when Multiple Fermi resonances were taken account. The experimental (black line) and theoretical (colours lines) spectra. The corresponding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

To study precisely 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 is increasing 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. It may be explain by that Fermi resonances mechanism may involve the O-H bond in-plane bending vibrations in their first overtone states. So the coupling between the electronic systems with the electrons of the associated carboxyl groups implies a stabilization of the dimers. On the other hand, 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 the proton bending-in-plane vibrations in the dimer of carboxylic acids. In order to obtain a good agreement with the experimental lineshapes, we have take into account some breaking of the IR selection rule for the centrosymmetric cyclic dimer, via a large amount ($\eta=0.65\ldots 0.95$) of forbidden A_g transition. Recall that in 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 [34]. 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 Flakus hypothesis, the lack of "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 instance 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 of ca. three times higher intensity than in the case when the same pi-electronic systems are separated from carboxyl groups by methylene groups [38]. 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 5 shows the important role played by the parameter η in the reproduction of the polarized IR spectra. Finally we can said 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 ($\eta=0.2...0.75$) of forbidden Ag transition.

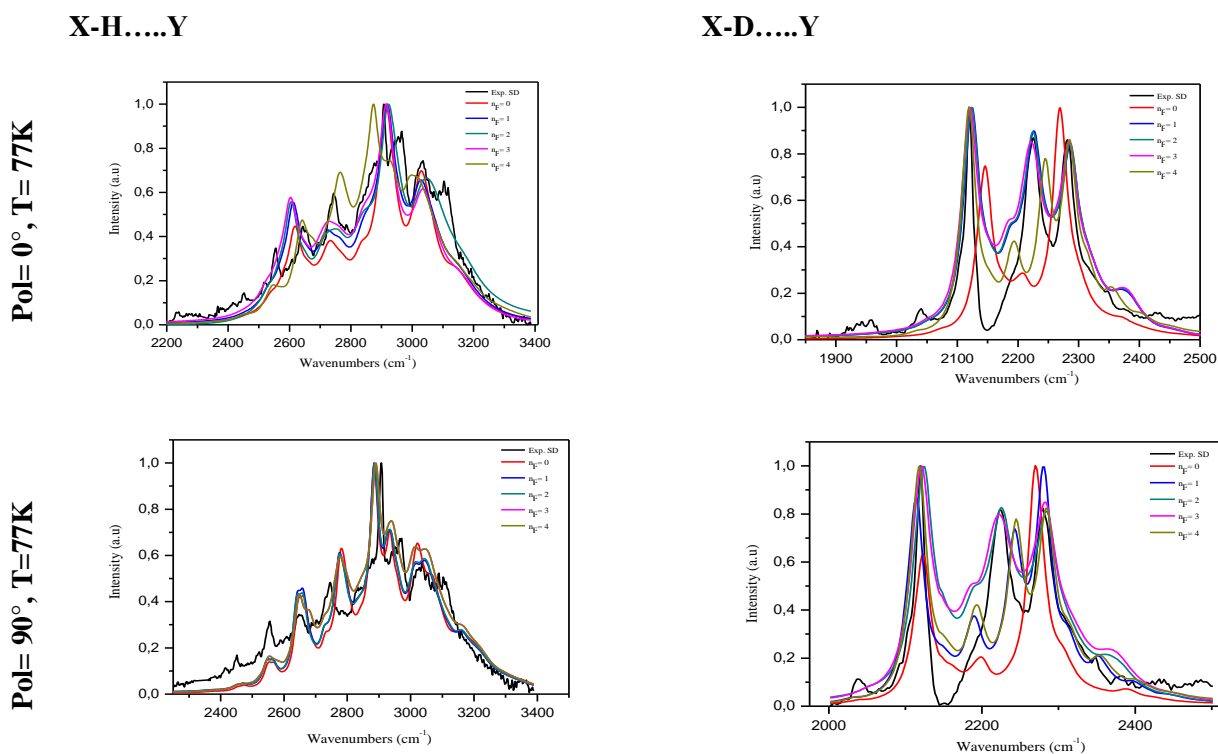


Figure 2: Multiple Fermi resonance effects on the IR SD of polarized 2-TAA when the slow modes were described by a Morse potential. The number of Fermi resonances n_F is increasing from zero (without Fermi resonances) to four. Comparison between the experimental (black line) and theoretical (colour lines)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

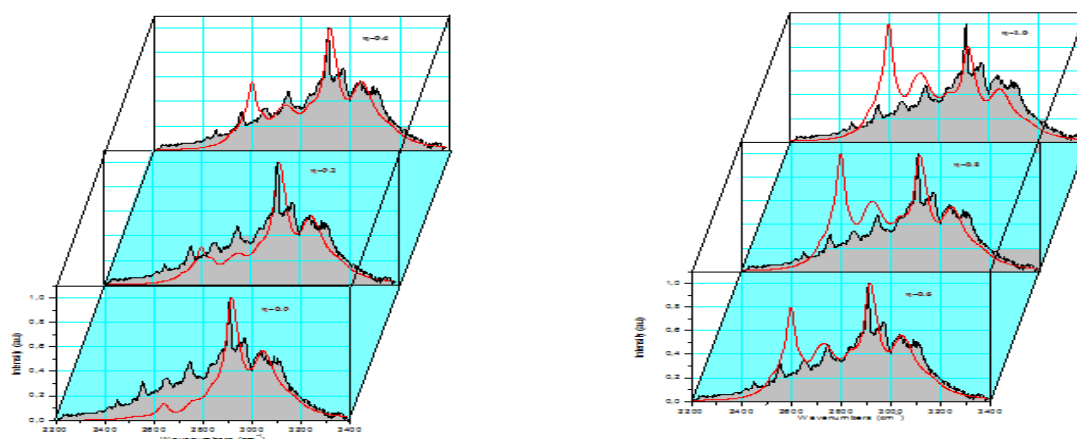


Figure 3: Effect of the forbidden transition parameter η on the SD of perpendicular polarized 2-TAA (Pol=90°) at 77 K. Theoretical SDs: red line shapes. Experimental SDs: black line. The corresponding parameters are given in Table 1

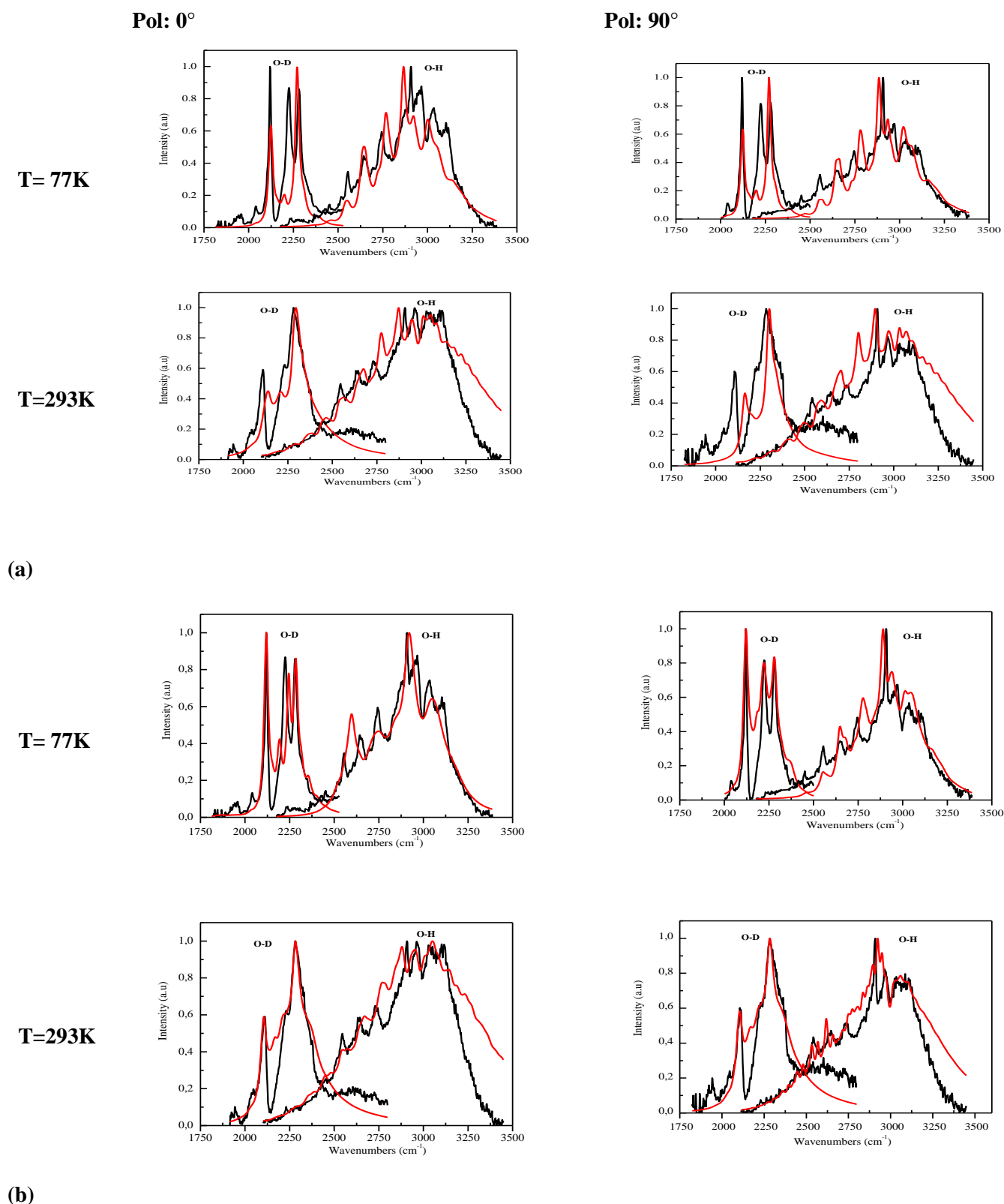


Figure 4: Effects of temperature and isotopic substitution on the spectral densities of 2-TAA at different polarizations without (a) and with four Fermi resonances (b). Experiment: black line spectra. Theoretical: red line spectra. The corresponding parameters are given in Tables 1-2

The numerical simulation shows that, this model reproduces satisfactorily the main features of the experimental IR lineshapes of crystalline 2H(D)-TAA dimers for two different temperatures 77 and 293 K. **Figure 4** is dealing with the comparison of theoretical and experimental lineshapes, for hydrogenated $\nu_{\text{O-H}}$ and deuterated $\nu_{\text{D-H}}$ crystalline

2-TAA, for 0° and 90° polarizations, at 77 and 293K, when it is assumed that Fermi resonances are missing and when it is taken account. Comparison between **Figure 4** shows a 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. Besides, Fermi resonances and Davydov coupling appear to play an important role to reproduce 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. Conclusion

In the present work, we have reproduced the IR spectrum absorption of O-H(D) stretching vibration of 2-TAA dimer, involving tow 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 resonance, Davydov coupling and the direct and indirect damping. It appears that this quantum approach reproduce satisfactorily the main features of the experimental IR line shapes of crystalline hydrogenated and deuterated 2-TAA. This inability to reproduce some more details of the fine structure was yet met for precedent approaches using similar models and dealing with other more complex molecules. It 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.

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