

See discussions, stats, and author profiles for this publication at:  
<https://www.researchgate.net/publication/229309659>

# Spectral density of H-bonds. II. Intrinsic anharmonicity of the fast mode within the strong anharmonic coupling theory

ARTICLE *in* CHEMICAL PHYSICS · NOVEMBER 2001

Impact Factor: 1.65 · DOI: 10.1016/S0301-0104(01)00470-0

---

CITATIONS

22

---

READS

17

4 AUTHORS, INCLUDING:



**Najeh Rekik**

University of Alberta

25 PUBLICATIONS 185 CITATIONS

SEE PROFILE



**A. Ceausu-Velcescu**

Université de Perpignan

27 PUBLICATIONS 103 CITATIONS

SEE PROFILE



**Paul Blaise**

Université de Perpignan

98 PUBLICATIONS 560 CITATIONS

SEE PROFILE

# Spectral density of H-bonds. II. Intrinsic anharmonicity of the fast mode within the strong anharmonic coupling theory

Najeh Rekik <sup>b</sup>, Adina Velcescu <sup>a</sup>, Paul Blaise <sup>a,\*</sup>, Olivier Henri-Rousseau <sup>a</sup>

<sup>a</sup> Centre d'Etudes Fondamentales, Université de Perpignan, 52 avenue de Villeneuve, 66860 Perpignan Cedex, France

<sup>b</sup> Laboratoire de Physique Quantique, Faculté des Sciences de Monastir, Route de Kairouan, 5000 Monastir, Tunisia

Received 15 May 2001; in final form 2 August 2001

## Abstract

A quantum theoretical 2-D approach of the IR  $\nu_{X-H}$  spectral density (SD) for symmetric or asymmetric intermediate or strong H-bonds is proposed. The presented model is based on the linear response theory; the strong anharmonic coupling theory (SACT) beyond the adiabatic approximation is used. The fast mode potential is described by an asymmetric double-well potential, whereas the slow mode is assumed to be harmonic. The slow and fast modes are assumed to be anharmonically coupled as in the SACT. The intrinsic anharmonicity of the fast mode and the anharmonicity related to the coupling between the slow and the fast modes are taken in an equal foot within quantum mechanics, without any semiclassical assumption. The relaxation is supposed given by a direct damping mechanism. When the barrier of the double-well asymmetric fast mode potential is very high, i.e. when the H-bond becomes weak, the computed theoretical SD reduces, as required, to that obtained in one of our precedent more simple approaches, dealing with weak H-bonds and working beyond the adiabatic approximation [Chem. Phys. 243 (1999) 229]. It reduces, within the adiabatic approximation, to the Franck–Condon progression of Röscher–Ratner (RR) [J. Chem. Phys. 61 (1974) 3444], and, in turn, to that of Maréchal–Witkowski (MW) [J. Chem. Phys. 48 (1968) 2697] when in this adiabatic approximation the damping is missing. When the anharmonic coupling between the slow and fast mode is missing, the behavior of the SDs is in good agreement with that which may be waited for a situation involving a 1-D asymmetric double well and thus the possibility of tunnelling. When the barrier is low, and the asymmetry is missing or weak, the changes induced by the asymmetric potential in the features of the Franck–Condon progression of the RR and MW model are more important than those in which the Fermi resonances or the Davydov coupling are acting. The model reproduces satisfactorily the increase in low frequency shift when passing from weak to strong H-bonds. The isotope effect due to the D-substitution of the H-bond bridge leads, in agreement with experiment, to a low frequency shift and a narrowing of the line shapes and simultaneously to deep changes in the features. © 2001 Elsevier Science B.V. All rights reserved.

## 1. Introduction

The most evident effect of hydrogen bonding (H-bond) are the red shift of the high frequency  $X-H \cdots Y$  stretching mode, its intensity increase and band broadening; the latter is often accompanied by the development of peculiar band-shapes.

\* Corresponding author. Tel.: +33-4-68-662108; fax: +33-4-68-662234.

E-mail address: blaise@univ-perp.fr (P. Blaise).

The number of vibrational degrees of freedom is dramatically increasing. The red shifts of the band centers may be as large as  $3000\text{ cm}^{-1}$  and the intensity increases up to 1000-fold. At last, the bandwidth increases from around  $15\text{ cm}^{-1}$  to several thousands wave numbers. The large increase of the bandwidth, the band asymmetry, the appearance of subsidiary absorption maxima and minima such as Evans windows, peculiar isotope and temperature effects are a challenge for the theories of H-bonds. For about thirty years, it has been assumed that anharmonicity plays a fundamental role in the spectral features of the  $\nu_{\text{X-H}}$  line shapes. That has been confirmed by quantum chemical calculations. This anharmonicity may manifest in different ways. There is the possibility of an anharmonic coupling between the low and high frequency modes. There are also anharmonic couplings between the first excited state of the fast mode and some harmonics or combinations of some low frequency bending modes, which are susceptible to lead to Fermi resonances. Such anharmonic couplings are in agreement with quantum studies of multidimensional potential energy surfaces involving H-bonded complexes for which it appears that there are several small amplitude vibrations strongly coupled with proton displacements. Besides, the anharmonicity of the H-bond is obvious for the slow and fast modes, since the slow mode potential is characterized by a Morse curve whereas the fast mode potential must be of double-well nature (symmetric or not).

The basic description common to all quantum theories dealing with the infrared (IR) line shapes of simple H-bonded species [1] is a 2-D quantum representation in which there is a strong anharmonic coupling between the fast X–H and the slow X–H $\cdots$ Y modes. In pure quantum theories, the slow and fast modes are both considered quantum mechanically, at the opposite of semiclassical theories in which only the fast mode is viewed obeying the quantum commutation rules. The strong anharmonic coupling theory (SACT) has been introduced by Hofacker et al. [2], Maréchal and Witkowski (MW) [3] and some other authors thirty years ago. The basic idea is the assumption of a dependence of the high frequency stretching mode on the coordinate of the H-bond bridge,

which leads to an anharmonic coupling between the two modes. The first full quantum mechanical treatment of weak H-bonds is that of MW [3]. It takes into account explicitly the anharmonic coupling between the slow and fast modes but ignores the influence of the surrounding. It leads, within the adiabatic approximation, for the special situations of single dimers, to spectral densities (SDs), involving Franck–Condon progression of Dirac delta peaks. Furthermore, Rösch and Ratner (RR) [4] have considered within the adiabatic approximation of MW, the influence of the direct relaxation of the fast mode towards the medium. They supposed that the relaxation is due to the coupling between the fluctuating local electric field and the dipole moment of the complex. The SD they obtained within the linear response theory (LRT) reduces to the Franck–Condon progression when the damping is missing. It has also been shown that the RR SD remains the same for weak H-bonds when the adiabatic approximation is removed [5]. Later, Boulil et al. [6] have studied in a full quantum mechanical way the influence of the fast mode damping. The physical idea was that, within the MW model, the slow mode becomes a coherent state just after excitation of the fast mode, so that, in the presence of indirect relaxation, the coherent state becomes damped. The SD they obtained reduces, when the damping is missing, to the MW Franck–Condon progression. More later, Boulil et al. [7,8] have improved their model. Recently [9], it has been shown that, if the quantum direct damping resulting from the RR model [4] induces a broadening of the line shapes, at the opposite, the pure indirect damping resulting from the Boulil et al. model [6] induces a narrowing of the SD, contrarily to the conclusion of the semiclassical models of indirect relaxation.

Let us return to the more fundamental theories quoted above which consider quantum mechanically both the slow and fast modes. In the pioneering work of MW [3], the SACT was introduced in order to take into account, beyond the adiabatic approximation, the main idea of Davydov couplings (4-D representation) between the excited states of symmetric double H-bond systems, such as the carboxylic acids dimers, but the relaxation was ignored. Later, Witkowski and

Wojczyk [10] have introduced 3-D representation within the SACT of MW [3], by considering the possibility of Fermi resonance in the special situations of no damping and pure resonance. In a next step, Wojczyk has considered situations where both pure Fermi resonances and Davydov coupling may occur in the absence of damping. All these approaches ignored the influence of the surrounding. More recently, in the spirit of the Witkowski and Wojczyk work, Chamma et al. [11–14] have studied, within the adiabatic approximation, multiple Fermi resonances involving descriptions lying from 3-D to 7-D, by considering the anharmonic coupling between one or several torsion or bending low frequency modes and the high frequency stretching mode, taking into account the influence of the direct dampings of both the fast and bending modes and also the possibility of non-resonant situations between the first harmonic energy levels or the combined excited states of the low frequency modes and the first excited states of the high frequency mode. These authors have also extended their study of Fermi resonances beyond the adiabatic approximation [15], but restricting the representation of the H-bond to a 3-D one,

because the cost to be paid, for working beyond the adiabatic approximation, was to multiply the dimension of the Hilbert subspaces characterizing each interacting oscillator in place of adding them. Besides, they have studied the influence of direct damping in situations where Davydov coupling and a single Fermi resonance are simultaneously occurring, within a 6-D representation [13]. All these works of Chamma et al. lead to conclude that Fermi resonances between the fast mode and some bending modes are strongly assisted by the anharmonic coupling between the fast mode and the H-bond bridge, so that Fermi resonances ought to be omnipresent in the area of IR spectra of the  $\nu_{X-H}$  mode. It must be underlined that the pure quantum theories quoted above are deeply interconnected: the complex theories are reducing, when the physical mechanisms they incorporate are removed, to the simpler ones which ignore these mechanisms (see Table 1).

If Davydov effect (4-D representation) and Fermi resonances (3-D, 4-D, 5-D... representations within the adiabatic approximation) have already been studied in the framework of the strong anharmonic coupling, it is not the case for

Table 1  
Quantum theories of the  $\nu(X-H)$  spectral density having used the SACT

Reference	Davydov coupling	Beyond 2-D description (Fermi resonance)	Tunneling effect		Direct damping	Indirect damping	Beyond adiabatic approximation	Slow mode anharmonicity	Beyond first order SACT
			Symmetric	Asymmetric					
[31]									
[31]	×						×		
[32]	×						×	×	
[10]		×							
[33]					×				
[34]	×	×							
[6]						×			
[21]			×			×			
[9]					×	×			
[11,12]		×			×				
[13,14]	×	×			×				
[5]					×		×		
[24]					×		×		×
[15]		×			×		×		
[35]					×		×	×	
[36]		×			×		×		
Present model			×	×	×		×		×

the intrinsic anharmonicity of the fast mode potential, for which there are only few papers working in different directions. For instance may be quoted the 1-D approach of Lawrence and Robertson [16], in which the strong anharmonic coupling is ignored. In an older important paper, Singh and Wood [17] have given a quantum 2-D approach of intermediate and strong symmetric H-bonds which incorporated a double minimum in the potential energy and an anharmonic coupling between the symmetric and antisymmetric stretching motions, as well as an electrical anharmonicity for the dipole moment. They ignored the possibility of Fermi resonances and did not take into account the possibility of dissociation in the symmetric coordinate. Using ranges of parameters appropriate to H-bond systems, they studied the combined effects of tunneling and vibrational interaction on tunnelling, far IR, normal IR transitions and also of combination bands. Unfortunately, their discussion was dealing with the Dirac delta peaks since their model ignored the surrounding. More recently, Romanowski and Sobczyk [18] have proposed for intermediate and strong symmetric H-bonds a model in which the influence of the surrounding is explicitly taken into account. But, the cost to be paid for that was the renouncing to a quantum treatment for the symmetric stretching motion. The stochastic model considered by these authors is very similar to that of Bratos: they considered for the quantum mechanical motion of the proton a symmetric double-minimum potential and supposed this potential to be modulated by the Gaussian-like statistical distribution of the symmetric stretching amplitude, i.e. of the H-bond bridge. They thus obtained an evolution of IR spectra from weak to strong H-bonds. The results they got must be considered keeping in mind that the slow mode is treated like a classical stochastic oscillator, as in the Bratos [19] and in the Robertson and Yarwood (RY) models [20] which, as we have seen, lead to broadening of the line shapes, at the opposite of the pure quantum theory of indirect damping of Boulil et al. [6]. Later, Abramczyk [21] has incorporated tunnelling involving symmetric double-well potential in the model of Boulil et al., working within the adiabatic approximation. However, in

the Abramczyk model, the strong anharmonic coupling between the slow and fast mode [6] and the symmetric double-well potential are assumed to be completely decoupled, assumption which is questionable. At last, must be quoted, even if not directly dealing with the SD, the important work of Röscher [22] who, thirty years ago, proposed a theoretical model in which were taken in an equal foot the strong anharmonic coupling of MW, the tunnelling involved in a double-well symmetric potential and the interaction with the surrounding.

It may be observed that, besides the above approaches, in which both the slow and fast modes are considered quantum mechanically, there have been some important semiclassical approaches lying also within the SACT, in which the slow mode is assumed to obey physical situations, where the non-commutativity of the position and of its conjugate momentum may be ignored. For instance, Bratos [19] has studied H-bonded complexes from a semiclassical point of view by considering within the LRT the influence of the H-bond bridge on the X–H dynamics, the physical idea being that in liquids, because the surrounding molecules are acting on the hydrogen bonds, the motion associated with the low frequency mode of the complex becomes stochastic. RY [20] have suggested that the slow modulation limit assumed by Bratos is not always realized and that the low frequency motion of the H-bonded complex in solution is not fully stochastic. Their major assumption was that the low frequency stretching mode is susceptible to be represented by a Brownian oscillator obeying to a Langevin equation.

It must be underlined that for strong H-bonds, the model of Singh and Wood [17] considers quantum mechanically both the slow and fast modes but ignored the surroundings, whereas that of Romanowski and Sobczyk [18], takes into account the surroundings but treats the H-bond bridge as classical. On the other hand, for weak non symmetric H-bonds, the model of MW [3] puts quantum mechanically the fast and slow modes in an equal foot, but neglects the influence of the medium, whereas that of Bratos [19] considers the stochastic influence of the neighborhood, but ignores the quantum properties of the

Table 2

Theories of IR line shapes of H-bond bridge (hemiquantal (semiclassical) and quantum theories using the strong anharmonic coupling theory)

Hemiquantal $[q, p] \neq 0$ $[Q, P] = 0$	Linear response theory	Complementary incorporated physical ideas					Quantum $[q, p] \neq 0$ $[Q, P] \neq 0$
		Beyond 2-D description Fermi resonances	Double-well tunnel effect	Double-well asymmetry	Dampings		
					Direct	Indirect	
[19]	×					×	
	×				×		[4]
	×					×	[6]
[19]	×	×				×	
	×	×			×		[11–15]
[18]	×		×			×	
			×				[17]
	×		×			×	[21] <sup>a</sup>
	×		×	×	×		This work

<sup>a</sup> Generalization of the Boulil et al. work [6] involving the approximation of a full decoupling in the equations between the physics of the double-well potential and that of the Boulil et al. work taking into account both the indirect damping and the strong anharmonic coupling theory.

H-bond bridge (see Table 2). As a consequence, for strong symmetric H-bonds, the Sing and Wood model plays with respect to that of Romanowski and Sobczyk [18] the same role, as for weak asymmetric H-bonds that of MW [3] with respect to that of Bratos [19].

The present paper is part II of our approach dealing with direct damping and intrinsic anharmonicity of the two important modes involved in the treatment of the IR  $\nu_{X-H}$  SD of H-bonded species. In part I [23] we treated the intrinsic anharmonicity of the slow mode by considering its potential as given by a Morse curve. In the present part II, we consider, always within the direct damping mechanism, the intrinsic anharmonicity of the fast mode by considering an asymmetric double well for the potential of this mode. More precisely, we shall consider a 2-D representation of the H-bond in which we shall treat quantum mechanically, in an equal foot, the intrinsic anharmonicity of the fast mode potential and the strong anharmonic coupling between the slow and fast modes. We shall work beyond the adiabatic approximation, by considering a general potential in which is incorporated the anharmonic coupling between the slow and fast modes, and the asymmetric double well describing the fast mode potential. This asymmetry would be weak, as for

crystal symmetric H-bonds, or large, as for asymmetric H-bonds in liquid or gas phases.

In this approach, we shall perform the following approximations:

- (i) We ignore Fermi resonances (requiring  $n$ -D representations with  $n > 2$ ) that we have considered in other papers [11,12] either for 3-D to 7-D situations (within the adiabatic and exchange approximations) or for 3-D situations (beyond the adiabatic and exchange approximations), by assuming both the slow and fast mode potentials to be harmonic, and neglecting the indirect damping [13–15].
- (ii) We ignore the intrinsic anharmonicity of the slow mode that we have considered explicitly in precedent papers [23,26], by working beyond the adiabatic approximation, describing the slow mode potential by a Morse curve, and neglecting the indirect damping.
- (iii) We assume that the damping parameter is the same throughout the spectrum including the transitions between the different vibrational states.
- (iv) We ignore the indirect damping of the fast mode through the slow mode to which it is coupled, that we have studied [6,9,27] for the simple 2-D situation of crude H-bond considered

within the adiabatic approximation (allowing to separate the low and high frequency motions) and within the harmonic approximation for both the fast and slow modes.

Owing to all these approximations, it would be objected that the present 2-D model is far from reality. But removing simultaneously all the approximations generally used up to day in the area of the SD of weak or intermediate H-bonds taking into account together the double-well nature of the fast mode potential, is a task which appears to be somewhat premature. We focus here our attention to a 2-D approach in order to elucidate the main consequences of the combination of the SACT and of the double-well nature of the high frequency mode on the general features of intermediate and strong H-bonds. For the same reasons, we shall not use any results from *ab initio* computations (dealing with force constants and harmonic coupling near the minima), which are special by definition.

Our present model must be considered with respect to our precedent approaches [1,5–9,11–15,23,25–27,30] as a new methodological step in our challenge to propose a complete description of the SD of the  $\nu_{X-H}$  (see Table 1) of the H-bond.

## 2. Theory

### 2.1. On the choice of the 2-D model

One may observe that in the present approach we shall consider the influence of the asymmetric double-well potential characterizing the fast mode on the  $\nu(X-H)$  IR line shapes induced within the SACT of Hofacker [2] and Witkowski [3] by the anharmonic coupling between the H-bond bridge and the fast X-H mode.

In these models it is well-known that the tunnelling splitting in vibrational spectra of non-rigid molecules is depending on several small amplitude vibrations more or less coupled with proton displacements. When one is focusing on the tunnelling splitting, it is possible to consider  $n$ -D representations with  $n = 3, 4, 5, 6, 7$ , because re-

markable perturbative instanton approach allows to successfully reproduce the splitting obtained directly by diagonalization using standard procedures. Besides, such splitting may be very well reproduced by the perturbative instanton approaches of Benderskii et al. [29]. As a matter of fact, all these results show that it is not possible to reduce the physics of intermediate or strong H-bonds to 2-D models. But, when one is dealing with the  $\nu(X-H)$  IR SD of H-bonds, it is difficult to accurately attain, within a  $n$ -D representation, all the  $n$ -D energy levels playing a role at room temperature in this IR SD. One must keep in mind that, in order to get, not the splitting of the line shapes, but the whole line shapes influenced by the anharmonic coupling, it is required to use for each oscillator truncated base of dimension around 25, so that for  $n$ -D representations of the H-bond, the dimensions of the matrices to be diagonalized are equal to  $25^n$  (i.e., respectively  $25^3 \simeq 1.5 \times 10^4$  for 3-D,  $25^4 \simeq 6 \times 10^5$  for 4-D and  $25^5 \simeq 10^7$  for 5-D).

However, the purpose of the present model is not to compute an exact SD susceptible to be compared to an experimental line shape, but to find how one is passing from weak to intermediate and strong H-bonds, i.e. to know how the fundamental MW model is progressively modified by the enhancement of the strength of the H-bond, that is how the SACT is perturbed by the progressive lowering of the double-well potential barrier. From this viewpoint, the cooperative physical effects between the anharmonic coupling and the double-well nature of the fast mode potential has no reason to do not conserve the same structure, when one is passing from one to several modes coupled to the high frequency oscillator. On the other hand, it may be observed that when the strength of a strong H-bond is weakened, the different anharmonic couplings between several small amplitude vibrations split progressively into two kinds, one of the same sort as that appearing in the SACT, and the other related to Fermi resonances. Now, we have shown [11–15,30] within the adiabatic approximation, that the main features of the line shapes of the IR  $\nu_{X-H}$  mode induced by Fermi resonances, remain wholly the same when one is passing from 3-D (1 Fermi resonances) to 4-D (2 Fermi resonances) and so on. As a consequence,

since the purpose of the present paper is only an investigation of the main features (broadening of the line shapes, low frequency shift of the first moment of the spectrum, existence of some fine structure, asymmetry, temperature and isotope effects), we prefer presently to work only within a 2-D description, which has the merit not only to simplify the description (matrices of dimension around  $5 \times 10^2$ ), but also to reduce the number of physical parameters involved in the model.

## 2.2. Basic parameters of the 2-D model

Now, define the basic parameters of the 2-D model of the H-bond.

- Position coordinate of the fast mode:  $q$  and conjugate momentum  $p$ ,
- position coordinate of the slow mode:  $Q$  and conjugate momentum  $P$ ,
- reduced mass of the fast mode:  $m^0$  and of the slow mode:  $M$ ,
- angular frequency of the slow mode:  $\omega^{00}$ ,
- angular frequency at the deepest minimum of the 1-D asymmetric double well describing the fast mode at the origin of  $Q$ :  $\omega^0$ ,
- anharmonic coupling parameter between  $q$  and  $Q$  coordinates:  $a$ ,
- distance between the two minima of the 1-D double-well potential:  $D$ ,
- barrier height of the 1-D double well with respect to the deepest well:  $V^0$ ,
- energy gap between the two minima of the 1-D double-well potential:  $\Delta$ ,
- direct damping parameter of the fast mode:  $\gamma^0$ ,
- absolute temperature of the medium:  $T$ .

The slow and fast modes coordinates will be considered in the following as both obeying quantum mechanics. It will also be of interest to define four other auxiliary parameters which will not appear in the model in its final suitable form, but will be useful in building this model. That are the adjustable parameters describing the 1-D asymmetric double-well potential, i.e.

- angular frequency of reference:  $\omega_B$  which will characterize the basis used for the quantum rep-

resentation of the full Hamiltonian describing the system,

- energetic pre-exponential factor  $A$  related to the barrier height of the double well,
- parameters related to the extension and the asymmetry of the double well:  $B$  (distance<sup>-1</sup>) and  $C$  (distance).

## 2.3. The full Hamiltonian

Now, consider the full Hamiltonian of the H-bond. It may be the sum of three Hamiltonians: that of the slow mode, that of the fast mode and that corresponding to the interaction between the fast and slow modes,

$$H_{\text{Tot}} = H_{\text{Slow}} + H_{\text{Fast}} + V_{\text{int}}.$$

The slow mode Hamiltonian is assumed to be that of a quantum harmonic oscillator:

$$H_{\text{Slow}} = \left[ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial Q^2} + \frac{1}{2} M \omega^{002} Q^2 \right].$$

On the other hand, the fast mode Hamiltonian is assumed to be that of a particle moving in an asymmetric double-well potential:

$$H_{\text{Fast}} = \left[ -\frac{\hbar^2}{2m^0} \frac{\partial^2}{\partial q^2} + U(q) \right]. \quad (1)$$

The double-well asymmetric potential may be in turn considered as an harmonic potential of pulsation  $\omega_B$  perturbed by an asymmetric Gaussian function according to:

$$U(q) = \frac{1}{2} m^0 \omega_B^2 q^2 + A \exp\{-B(q - C)^2\}. \quad (2)$$

Here  $A$ ,  $B$  and  $C$  are parameters characterizing the asymmetric Gaussian function, which will be related later to the parameters  $D$ ,  $V^0$  and  $\Delta$  defining the properties of the asymmetric double-well potential. Besides, working in the spirit of the main ideas of the SACT, the Hamiltonian coupling the slow and fast mode may be written:

$$V_{\text{int}} = a m^0 \omega^0 q^2 Q + \frac{1}{2} m^0 a^2 q^2 Q^2. \quad (3)$$

Owing to the above equations, the full Hamiltonian describing the X–H...YH-bond species becomes:



$$\begin{aligned}
H_{\text{Tot}} = & \left[ -\frac{\hbar^2}{2m^0} \frac{\partial^2}{\partial q^2} + \frac{1}{2} m^0 \omega_B^2 q^2 \right. \\
& \left. + A \exp \left\{ -B(q-C)^2 \right\} \right] \\
& + \left[ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial Q^2} + \frac{1}{2} M \omega^{002} Q^2 \right] \\
& + \left[ a m^0 \omega^0 q^2 Q + \frac{1}{2} m^0 a^2 q^2 Q^2 \right]. \quad (4)
\end{aligned}$$

One may observe that when one is passing to the X–D···Y species, the potential involved in the full Hamiltonian cannot be affected by the D-substitution. On the other hand, if the reduced mass of the slow mode is not affected by this substitution, at the opposite, the reduced mass of the fast mode is increased by a factor 2 by the same D-substitution and the corresponding angular frequency is decreased by a factor  $1/\sqrt{2}$ . As a consequence, the full Hamiltonian corresponding to the D isotopic substitution takes the same form as Eq. (4), except the presence of a factor 1/2 multiplying the kinetic energy of the fast mode.

Note that when  $A$  is vanishing, it is necessary to take  $\omega_B = \omega^0$ , since in this limit situation  $\omega_B$  must be the angular frequency of the harmonic fast mode. Then, the Hamiltonian (4) reduces to that which was assumed by MW in their pioneering work [3] (in which they ignored the relaxation) and recall that this limit Hamiltonian was at the basis of the RR [4] approach dealing with direct relaxation, and of that of the Boulil et al. dealing with indirect relaxation [6]. Besides, it must be remember that RY [20], in their semiclassical approach of the indirect damping, have assumed an Hamiltonian which is very similar to the limit Hamiltonian in which  $A$  is missing.

This full Hamiltonian may be partitioned into a diagonal and non-diagonal parts. The diagonal one is

$$\begin{aligned}
H_0 = & \left[ -\frac{\hbar^2}{2m^0} \frac{\partial^2}{\partial q^2} + \frac{1}{2} m^0 \omega_B^2 q^2 \right] \\
& + \left[ -\frac{\hbar^2}{2M} \frac{\partial^2}{\partial Q^2} + \frac{1}{2} M \omega^{002} Q^2 \right]. \quad (5)
\end{aligned}$$

The eigenvalue equation of the diagonal Hamiltonian is:

$$H_0 |\{k\}(n)\rangle \equiv (\hbar\omega_B[k + \frac{1}{2}] + \hbar\omega^{00}[n + \frac{1}{2}]) |\{k\}(n)\rangle. \quad (6)$$

Now, let us look at the corresponding  $(N^0 N^{00}) \times (N^0 N^{00})$  truncated matrix representation of the full Hamiltonian (1) in the basis defined by Eq. (6). Its eigenvalue equation is:

$$H_{\text{Tot}} |\Psi_l\rangle = \hbar\Omega_l |\Psi_l\rangle. \quad (7)$$

Here  $\Omega_l$  is the  $l$ th eigenvalue and  $|\Psi_l\rangle$  the corresponding eigenvector given by:

$$|\Psi_l\rangle = \sum_k \sum_m \{C_{l,\{k\}(m)}\} |\{k\}(m)\rangle. \quad (8)$$

It must be observed that for D-substitution, the perturbation appearing in the partition of the full Hamiltonian becomes more complex since, as we have seen above, because of the change in the reduced mass, the kinetic energy of the fast mode is divided by a factor 2 so that must appear in the non-diagonal part of the Hamiltonian a negative kinetic term the absolute value of which is equal to half the kinetic energy of the fast mode.

#### 2.4. Connection between physical parameters

Now, let us look at some redundancy between the parameters of the model, which is in relation with the auxiliary parameters describing the asymmetric double-well potential. In the full Hamiltonian (4), appear many parameters that are somewhat redundant. For instance,  $\omega^0$  which appears in the expression of  $V_{\text{int}}$ , is the angular frequency of the fast mode at the deepest minimum of the double-well fast mode potential, whereas  $\omega_B$  is an angular frequency which would be that of the harmonic oscillator characterized by the Gaussian part of the potential when  $A$  is vanishing (and thus leading to  $B$  and  $C$  inoperative). Recall that  $A$  is a measure of the potential barrier height,  $B$  is a measure of its width and  $C$  a measure of its asymmetry. On the other hand, the intuitive physical parameters governing the high frequency mode H-bond when one ignores its coupling with the H-bond bridge are: the barrier height  $V^0$ , the energy minima asymmetry  $\Delta$ , the distance between the two minima  $D$ , the angular frequency at the

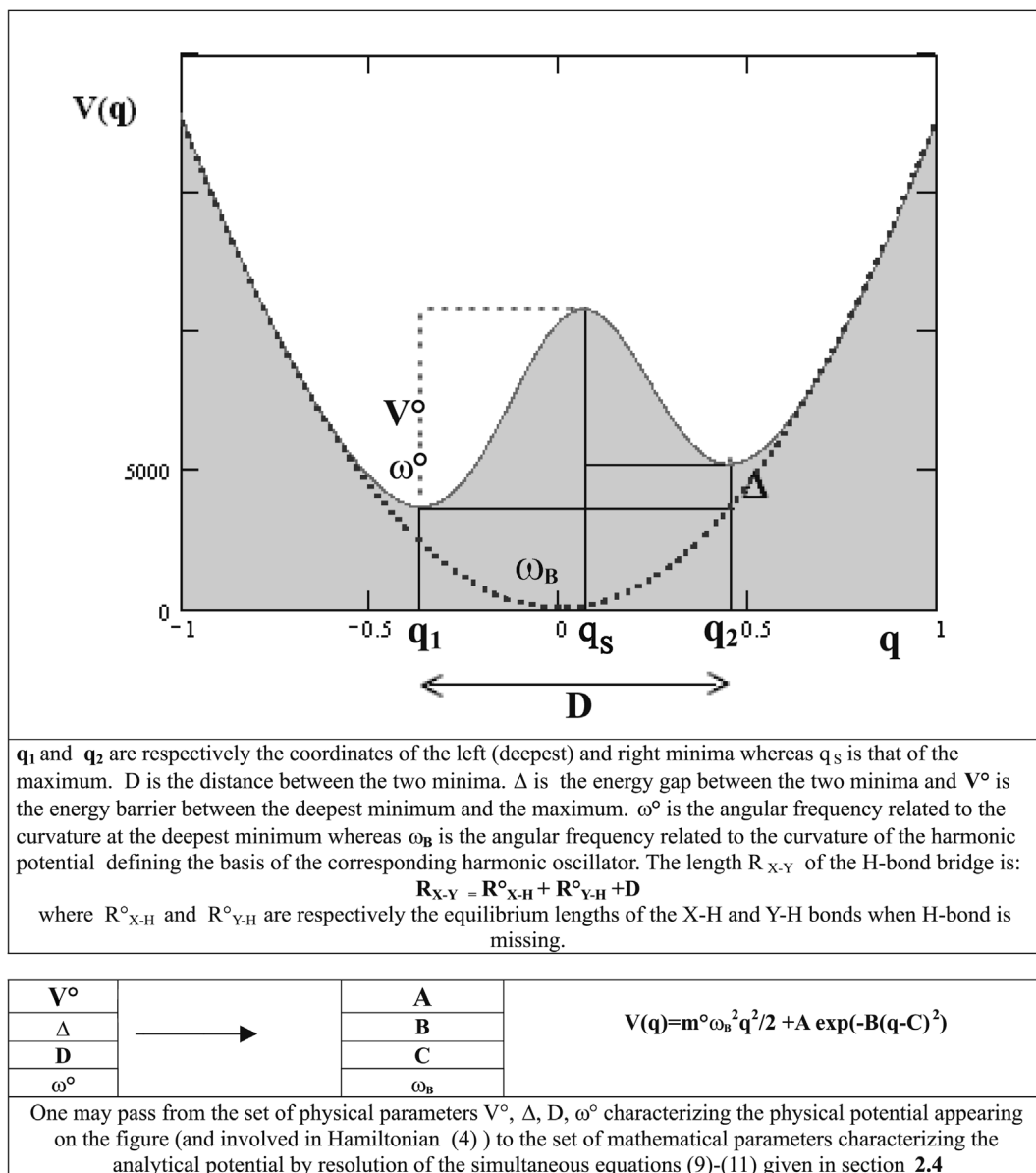


Fig. 1. Definition of the fundamental parameters of the 1-D double-well potential  $V(q)$ .

deepest energy minimum  $\omega^\circ$ . Fig. 1 depicts the connection between the  $A$ ,  $B$ ,  $C$  and  $\omega_B$  parameters of the Gaussian part of the potential defined by Eq. (2), and the more intuitive physical parameters describing usually the 1-D asymmetric double-minimum potential involved in the H-bond which are  $\omega^\circ$ ,  $V^\circ$ ,  $\Delta$  and  $D$ .

It must be underlined that, if  $\omega_B$  plays a fundamental role in the partition of the Hamiltonian since it characterizes together with  $\omega^\circ$  the angular frequency of the basis used for the representation of the Hamiltonian, it is not fundamental from a physical viewpoint since it is only one of the four ingredients of the double-well potential, the

deepest minimum of which being characterized by the angular frequency  $\omega^0$ . As a matter of fact, if  $\omega_B$  is fundamental from a numerical viewpoint, it remains an intermediate of calculus so that it must not play any role on the features of the line shapes. It is necessary to get the parameters involved in the Gaussian part of the potential, from those, more physical, which are governing the H-bond and which are therefore some of the basic parameters of the present model. That is to say, we have to compute the set  $\{A, B, C, \omega_B\}$  from that one  $\{\omega^0, V^0, \Delta, D\}$ .

For this purpose it may be suitable to use intermediate parameters, which are formally redundant but are facilitating the calculations that are the coordinates of the minima and of the maximum i.e.  $q_1$ ,  $q_2$  and  $q_S$  respectively. In a first place we may consider the three equations characterizing the three extrema:

$$m^0 \omega_B^2 q_i - 2AB(q_i - C) \exp[-B(q_i - C)^2] = 0, \quad (9)$$

where  $i$  stands for 1, 2 and  $S$  characterizing respectively the two minima and the saddle point.

Besides, there are the equation giving the barrier height from the lowest energy minimum, and that giving the distance  $D$  between the two minima.

$$\begin{aligned} V^0 &= U(q_S) - U(q_1), \\ D &= q_2 - q_1. \end{aligned} \quad (10)$$

At last, there are the equation giving the frequency in the lowest energy minimum which may be expressed as a function of the basis frequency  $\omega_B$  and that giving the energy asymmetry  $\Delta$  of the energy minima.

$$\begin{aligned} \omega^0 &= \omega_B \sqrt{\frac{k_1}{k_0}}, \\ \Delta &= U(q_2) - U(q_1), \end{aligned} \quad (11)$$

with the force constant at the deepest minimum given by:

$$\begin{aligned} k_1 &= \left( \frac{d^2 U}{dq^2} \right)_{q_1} = m^0 \omega_B^2 - 2AB[1 + 2B(q_1 - C)^2] \\ &\quad \times \exp[-B(q_1 - C)^2], \end{aligned}$$

whereas  $k_0$  is related to the angular frequency of basic harmonic oscillator appearing in the full Hamiltonian (4) through:

$$k_0 = m^0 \omega_B^2.$$

The system of simultaneous equations to be solved is then the set of Eqs. (9)–(11).

## 2.5. The autocorrelation function and the corresponding spectral density

Now, consider the dipole moment operator of the fast mode. If one neglects the electrical anharmonicity, the autocorrelation function (ACF) of the dipole moment operator of the H-bond is, in the absence of damping.

$$\begin{aligned} G^0(t) &\propto \text{tr} \left[ \exp\{-H_{\text{Tot}}/kT\} q \exp\left\{i \frac{H_{\text{Tot}} t}{\hbar}\right\} \right. \\ &\quad \left. \times q \exp\left\{-i \frac{H_{\text{Tot}} t}{\hbar}\right\} \right]. \end{aligned} \quad (12)$$

Performing the trace on the eigenstates of the total Hamiltonian and using the closeness relation on the eigenstates of the full Hamiltonian one obtains:

$$\begin{aligned} G^0(t) &\propto \sum_m \sum_n \exp\{-\hbar \Omega_m / kT\} |\langle \Psi_m | q | \Psi_n \rangle|^2 \\ &\quad \times \exp\{-i[\Omega_m - \Omega_n]t\}. \end{aligned}$$

Now, consider the situation of direct damping. In the spirit of the approach of RR, who worked within the adiabatic approximation, the quantum ACF may be written [24],

$$G(t) = G^0(t) \exp(-\gamma^0 t) \exp(i\delta\Omega t) \quad (13)$$

where  $\gamma^0$  is the direct damping parameter and  $\delta\Omega t$  is the angular frequency shift (cf. Lamb shift) resulting from the quantum approach of the direct damping. But we are working here beyond the adiabatic approximation, so that the damping parameter cannot be the same throughout the spectrum including the transitions between the different vibrational states. As a matter of fact, the evalu-

ation for the present model of the different effective damping parameters requires not only the knowledge of the reduced time evolution operator of the driven damped quantum harmonic oscillator we have obtained some years ago [6], but also their extraction from this reduced operator [27]. That is beyond the purpose of the present approach in which we focus attention on the main consequences of the combined influences of the SACT and of the double-well nature of the fast mode potential.

As a consequence, and owing to the above equations, the SD is:

$$I(\omega) \propto \sum_{m,n} \exp\{-\hbar\Omega_m/kT\} |\langle \Psi_m | q | \Psi_n \rangle|^2 \times \int \exp(-\gamma^0 t) \exp(i\delta\Omega t) \exp\{i[\Omega_n - \Omega_m]\} \times \exp(-i\omega t) dt. \quad (14)$$

## 2.6. The spectral density in the special situation where the asymmetric double-well potential becomes harmonic

Now look at the SD for the special situation where the asymmetric double-well potential becomes harmonic. Then, in the potential (2),  $A$  is vanishing, so that  $B$  and  $C$  do not play any role whereas the conventional angular frequency  $\omega_B$  must become equal to that of the fast mode  $\omega^0$ . Then, the full Hamiltonian becomes that used in the usual quantum approaches of the SACTs [25]. Recall that when the adiabatic approximation is performed, which allows to separate the high frequency motion from that of the H-bond bridge, it is possible to obtain different effective full Hamiltonians acting only on the space of the slow mode operator. Besides, the dipole moment operator  $q$  inducing the transition from the ground state to the first state of the fast mode, may be assumed in this harmonic approximation to be simply given by the transition operator built up from the ground state  $|\{0\}\rangle$  and the first excited state  $|\{1\}\rangle$  of the fast mode harmonic oscillator, i.e.  $q \propto |\{0\}\rangle\langle\{1\}|$ . Then, within the adiabatic approximation, the SD becomes [25]:

$$I(\omega) \propto \int \exp\{-\frac{1}{2}\alpha^2(1+2\tilde{n})\} \exp\{\frac{1}{2}\alpha^2(1+2\tilde{n})\} \times [2\cos(\omega^0 t) - 1] \exp\{i\alpha^2 \sin(\omega^0 t)\} \times \exp\{-i\alpha^2 \omega^0 t\} \exp\{i(\omega^0 - \alpha^2 \omega^0)t\} \times \exp\{-\gamma^0 t\} \exp\{-i\omega t\} dt, \quad (15)$$

where  $\tilde{n}$  is the mean occupation number of the quantum harmonic oscillator at a given temperature and  $\alpha$  a anharmonic dimensionless parameters given by

$$\alpha = \frac{a}{\omega^0} \sqrt{\frac{\hbar}{2M\omega^0}}. \quad (16)$$

This SD is that obtained by RR [4] within the direct damping mechanism. Besides, it reduces in turn to that obtained by MW in their pioneering work [3], when the direct damping  $\gamma^0$  is vanishing:

$$I(\omega)_{\gamma^0=0} \propto \sum_{n=0}^{N^0-1} \exp\{-\lambda n\} \sum_{m=0}^{N^0-1} |\Gamma_{m,n}(\alpha)|^2 \times \delta(\omega - [\omega^0 - 2\alpha^2 \omega^0 + (m-n)\omega^0]). \quad (17)$$

In this progression appear the well-known Franck–Condon factors  $\Gamma_{m,n}(\alpha)$ . When  $T = 0$  K, the SD (17) reduces to a Poisson distribution.

It must be observed that in this adiabatic approach the isotope effect resulting from the D-substitution of the proton of the H-bond bridge may be obtained directly by dividing both  $\omega^0$  and  $\alpha$  by  $\sqrt{2}$  because of the change in the reduced mass of the fast mode coordinate. That is different from the present non-adiabatic approach involving double-well potential, in which the isotope effect is only introduced by modifying the kinetic energy of the fast mode without changing, of course, the full anharmonic potential.

## 2.7. Basic physical parameters of the present model

Now, let us look at the basic physical parameters of the model. It may be first observed that the reduced mass  $m^0$  of the fast mode is, for many H-bonds, around unity in mass units. In the following we shall take in these units  $m^0 = 1$ . As a consequence, and owing to the above section, it appears that there are eight independent basic

physical parameters characterizing the present model.

- $\omega^0$  angular frequency of the fast mode at the deepest minimum of the one dimensional fast mode potential,
- $\omega^{00}$  angular frequency of the slow mode,
- $V^0$  barrier height with respect to the deepest minimum,
- $\Delta$  double-well asymmetry: difference between the two energy minima,
- $D$  distance between the two minima,
- $\alpha$  dimensionless anharmonic coupling parameter between the slow and fast mode defined by Eq. (16),
- $\gamma^0$  damping parameter dealing with the dephasing of the fast mode,
- $T$  absolute temperature.

Note that with respect to our precedent approaches of the SDs of weak H-bonds in which we neglected the possibility of tunnelling, there are only three new parameters, namely  $V^0$ ,  $\Delta$  and  $D$ , for which it is possible to perform reasonable assumptions. It must be underlined that  $\alpha$ , in the present situation, does not occur in the calculation. It is a dimensionless parameter reflecting the dimensional anharmonic coupling  $a$ , which is chosen only because its simplicity. Recall that the dimensional coupling parameter  $a$  is occurring in the full potential, which must be of course the same for the D and H species. This viewpoint is different from precedent approaches in which there were two parameters  $\alpha$ , one dealing with the H-species and the other one, with the D, that is not necessary in the present situation since it is  $a$  and not  $\alpha$  which is playing a role in the equations. Thus, in the present paper, since  $\alpha$  must be only considered as reflecting the strength of the anharmonic coupling, will be given only its value characterizing the H-species.

### 2.8. Discussion on the magnitude of the basic physical parameters

Now, let us look at the magnitude of the basic physical parameters that we shall use in the present paper. First consider the parameters which were

already appearing in our precedent approaches [26]. For the angular frequencies  $\omega^0$  and  $\omega^{00}$  of the fast mode, we take the values that we have yet used [26] for weak H-bonded systems, i.e.  $\omega^{00} = 150 \text{ cm}^{-1}$  and  $\omega^0 = 3000 \text{ cm}^{-1}$ . In the same way, for the dimensionless anharmonic coupling parameter, we take  $\alpha = 1$  as in precedent works [26], for reasons given there. At last, we select weak direct damping parameter  $\gamma^0$  around  $15 \text{ cm}^{-1}$  in order to preserve the fine structure of the SDs. Now, consider the parameters characterizing the intrinsic anharmonicity of the fast mode, i.e. the double-well potential. For the distance between the two minima, we choose values such as  $D$  plus twice the equilibrium X–H length will be around the X–H...Y length of the H-bonded species, which lies between  $2.9 \text{ \AA}$  for weak H-bonds to  $2.5 \text{ \AA}$  for strong H-bonds via  $2.75 \text{ \AA}$  for medium strength H-bonds. For the barrier height  $V^0$  of the double-minimum potential, we have considered values lying between 2 and  $3\omega^0$ . For the asymmetry  $\Delta$  of the double-well potential, we consider different situations in which  $\Delta$  starting from 0 increases progressively to attain the magnitude of  $\omega^0$ . At last, for the temperature we have generally considered two very different situations, i.e. zero temperature and “room temperature” ( $T = 300 \text{ K}$ ).

Now, consider the D-substitution of the proton involved in the H-bond bridge. One must keep in mind the fact the D-substitution does not modify any potential and thus does not affect the anharmonic coupling potential, but only introduce at the calculation level a new kinetic perturbative term in the partitioned Hamiltonian (5). It must be underlined that in the present model it is not necessary, as it was in the precedent ones [6,25], to reduce the angular frequency of the fast mode by the factor  $1/\sqrt{2}$ , since it is the new kinetic perturbative term which will reduce this angular frequency by an amount which will depend on the nature of the basic physical parameters characterizing the different potentials.

### 3. The IR line shapes

It must be underlined that all the computed energy levels and eigenfunction have been verified

to be stable with respect to an increase in the dimension of the used truncated basis. For practical situations considered in the present paper, the dimension of the basis is around 400, i.e.  $N^0 = N^{00} \simeq 20$ .

It has been shown in precedent papers [11–15], that Fermi resonances between harmonics of some bending modes and the first excited state of the fast mode are assisted by the anharmonic coupling between the slow and the fast mode: the line shape is deeply modified even for situations which are very far from resonance, i.e. where the energy gap between the harmonic and the fast mode excited state may be as larger as one order of magnitude than that of the Fermi coupling.

### 3.1. Special situations of high barriers: weak H-bonds

Now, let us look at the special situations involving high barriers of the double-well potential, i.e. weak H-bonds. It may be of interest to verify if, when the H-bond becomes very weak, i.e. when the barrier of the double-well potential is very high, the SDs obtained by the aid of the present model reduce to those which may be obtained from the fundamental model of the SACT, i.e. to those following from the present model in which an harmonic potential is used instead of the double-well potential (beyond the adiabatic approximation), keeping in mind that these non adiabatic SDs must reduce to those of the RR model when working within the adiabatic approximation, which, in turn, reduce to the MW SDs when the damping is missing (Poisson distribution of Dirac delta peaks at 0 K).

Fig. 2 gives an illustration of the good agreement between the approximate SDs obtained for weak H-bonds using for the fast mode the harmonic approximation and the more exact one obtained from the general equation (14). The left column gives line shapes at zero temperature and the right one at room temperature. The top line shapes have been computed from the general equations (14), for a situation involving a strongly asymmetric double-well potential  $A = 51413 \text{ cm}^{-1}$  for which the barrier is very high, i.e.  $V^0 = 297320 \text{ cm}^{-1}$  and the distance between the two wells

$D = 0.84 \text{ \AA}$  while the anharmonic coupling parameter is  $\alpha = 1$ . The middle SDs are those obtained within the harmonic approximation for the fast mode potential, but beyond the adiabatic approximation, i.e. by aid of the general equation (14) using the Hamiltonian (4) in which  $A = 0$  and  $m^0\omega_B^2 = m^0\omega^{02}$ . At last, the bottom SDs are the numerical expressions of the analytical equation (14). As a matter of fact, the two bottom SDs are the adiabatic approximations of the middle ones that are in turn the harmonic approximations of the bottom ones.

Inspection of the figure shows that for both zero and room temperatures, the three kinds of SDs are the same. This good agreement may be viewed as an a posteriori verification of the harmonic approximation for the fast mode within the adiabatic approximation and also of the adiabatic approximation. These results may also be considered as showing that our present model is “well behaved” in order to treat the limit situations of very asymmetric double-well potentials involving high barriers. Because of this good behavior, it is now possible to look at situations of greater interest, i.e. where the asymmetry and the barrier are lowered.

### 3.2. Spectral densities for low barriers: intermediate or strong H-bonds

Now, let us look at situations of greater interest for the present purpose, i.e. those of intermediate or strong H-bonds which are involving low barriers of the double-well potential. We shall consider in a first place H-bonds involving barriers around twice the angular frequency of the fast mode for which the asymmetry of the double well will be progressively increased from an initial symmetric potential.

Figs. 3–8 give an illustration of this purpose. On the right top of each figures is given a 1-D double-well potential with the eigenvalues and eigenfunctions (energy levels and associated wave functions) of the corresponding 1-D Hamiltonian. On the left top are depicted the dipolar transitions (at 0 and 300 K or in other situations only at 300 K) between the right top 1-D energy levels. At the bottom, are given some line shapes computed by the

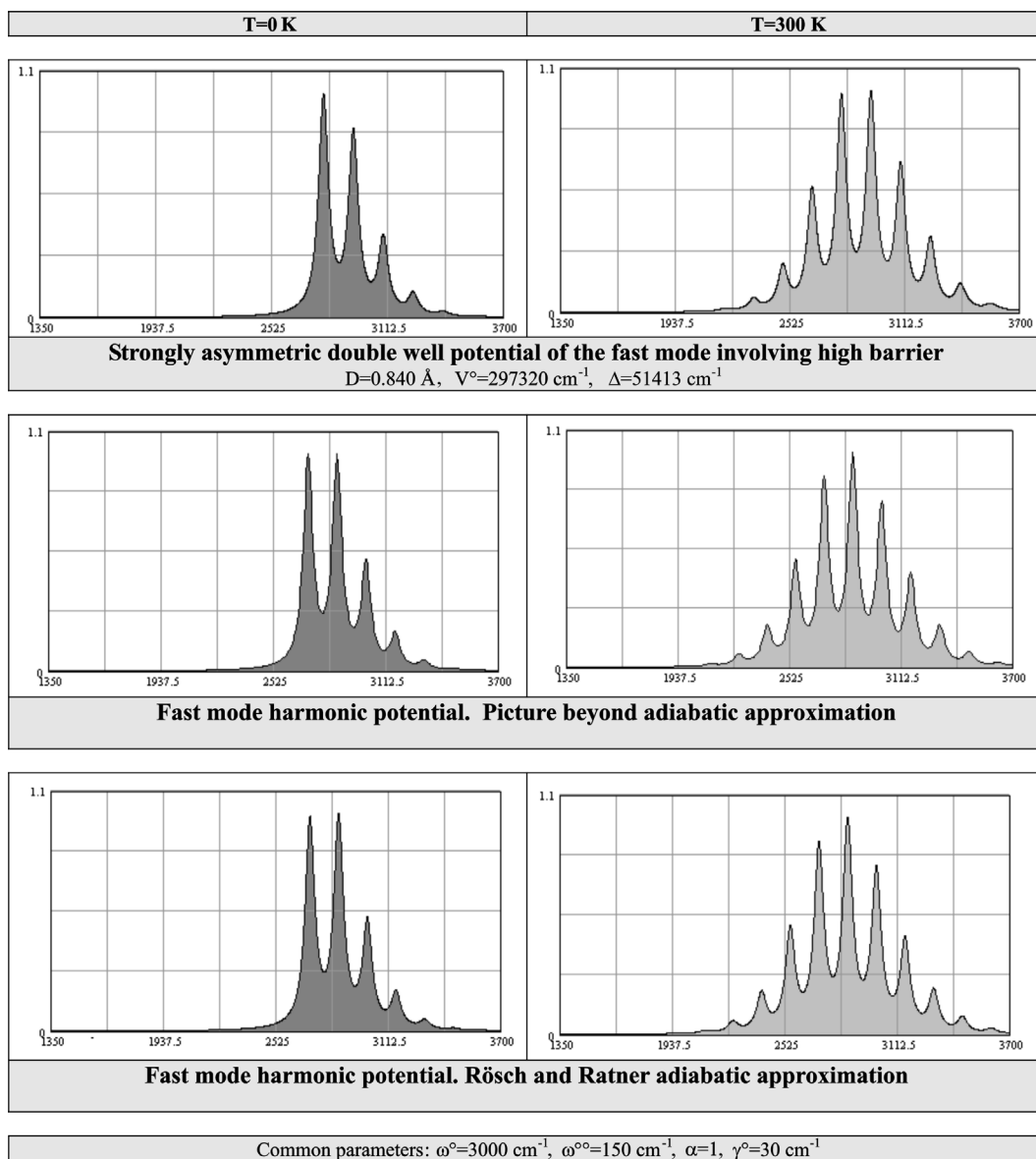
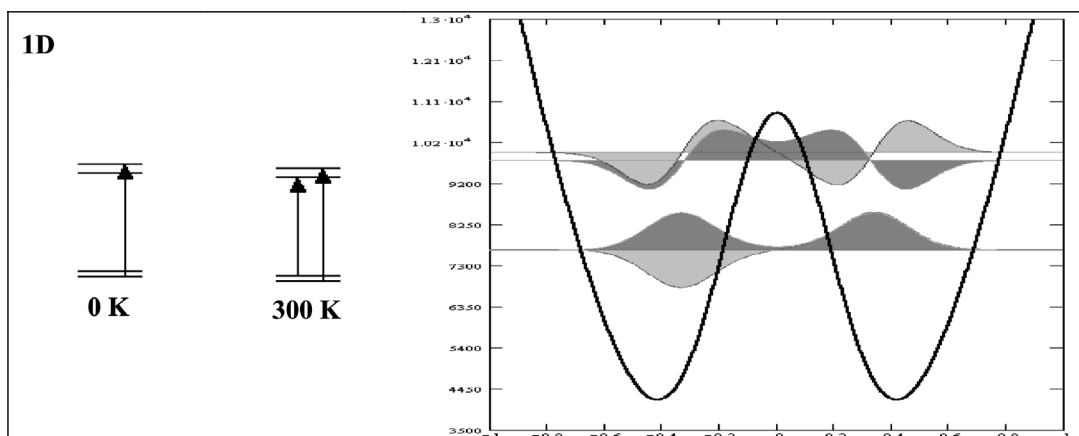


Fig. 2. SDs for limit situation where the double-well potential of the  $q$  mode is strongly asymmetric and involving high barrier. Comparison with SDs obtained within the harmonic approximation for the  $q$  mode within and beyond the adiabatic approximation.

aid of the general model, using the full 2-D Hamiltonian (4) with the right top 1 D-double-well potential describing the fast mode. For each figure, the set is starting from an uncoupled situation where the anharmonic coupling between the slow and fast mode is vanishing (up SD). Then the anharmonic coupling is progressively increased up

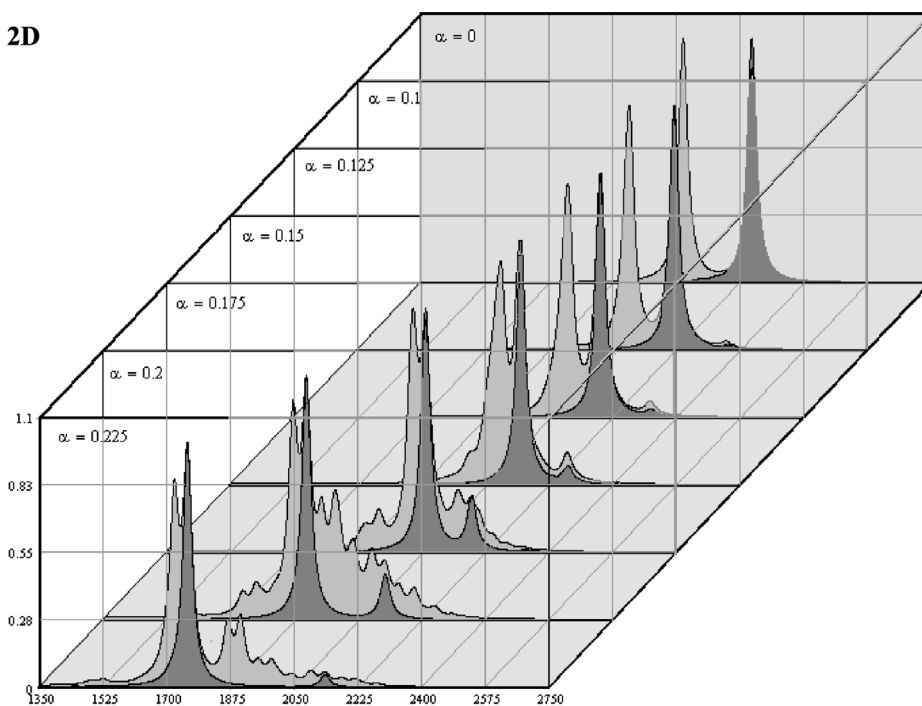
to down. As a matter of fact, the up uncoupled line shape computed by the aid of the 2-D Hamiltonian must reduce to that computed by the aid of the Hamiltonian involving the 1-D potential of the right top figure, so that this up line shape is the traduction of the transitions depicted on the left up figure. Fig. 3 illustrates the situation of a strictly



**(a) 1-D double well potential energy levels and corresponding wave functions.**

The right part of the first asymmetric wave function is occupied by the right part of the symmetric ground state. There is only one allowed dipolar transition at 0 K because at strict 0 K the upper level of the splitted ground state cannot be occupied. At higher temperatures, and therefore at 300 K, there are two allowed dipolar transitions.

**2D**



**(b) Evolution of the line shapes with an increase of the anharmonic coupling parameter  $\alpha$ , starting from an initial situation where for  $\alpha=0$ .**

Dark only : SDs at strict 0 K. Gray: hot bands at 300 K

Common parameters:  $\omega^o=3000 \text{ cm}^{-1}$ ,  $\omega^o=150 \text{ cm}^{-1}$ ,  $\gamma^o=15 \text{ cm}^{-1}$ ,  $V^o=6635 \text{ cm}^{-1}$ ,  $\Delta=0$ ,  $D=0.83 \text{ \AA}$ .

Fig. 3. SDs involving symmetrical double-well potential.



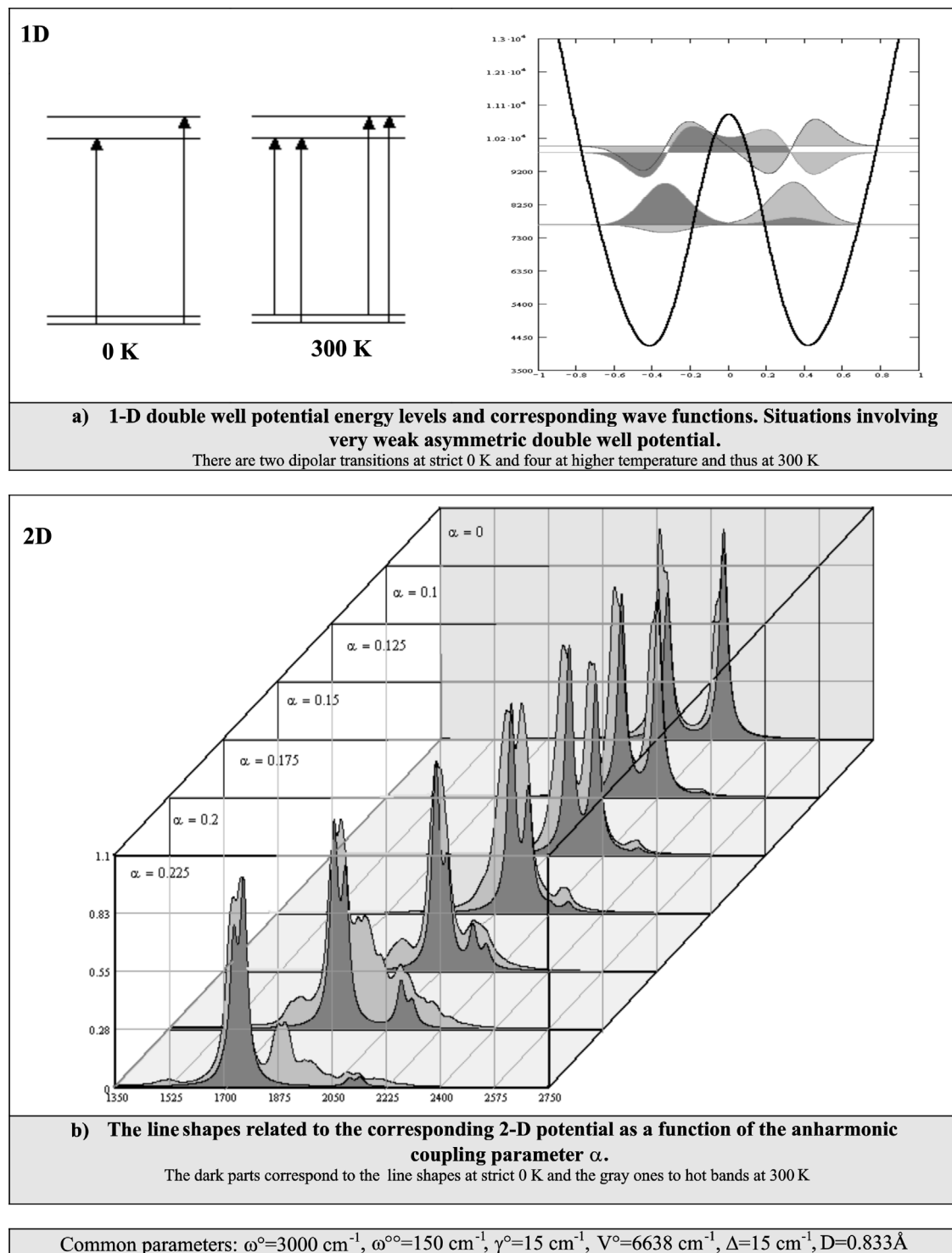


Fig. 4. SDs involving double-well potential near symmetry.

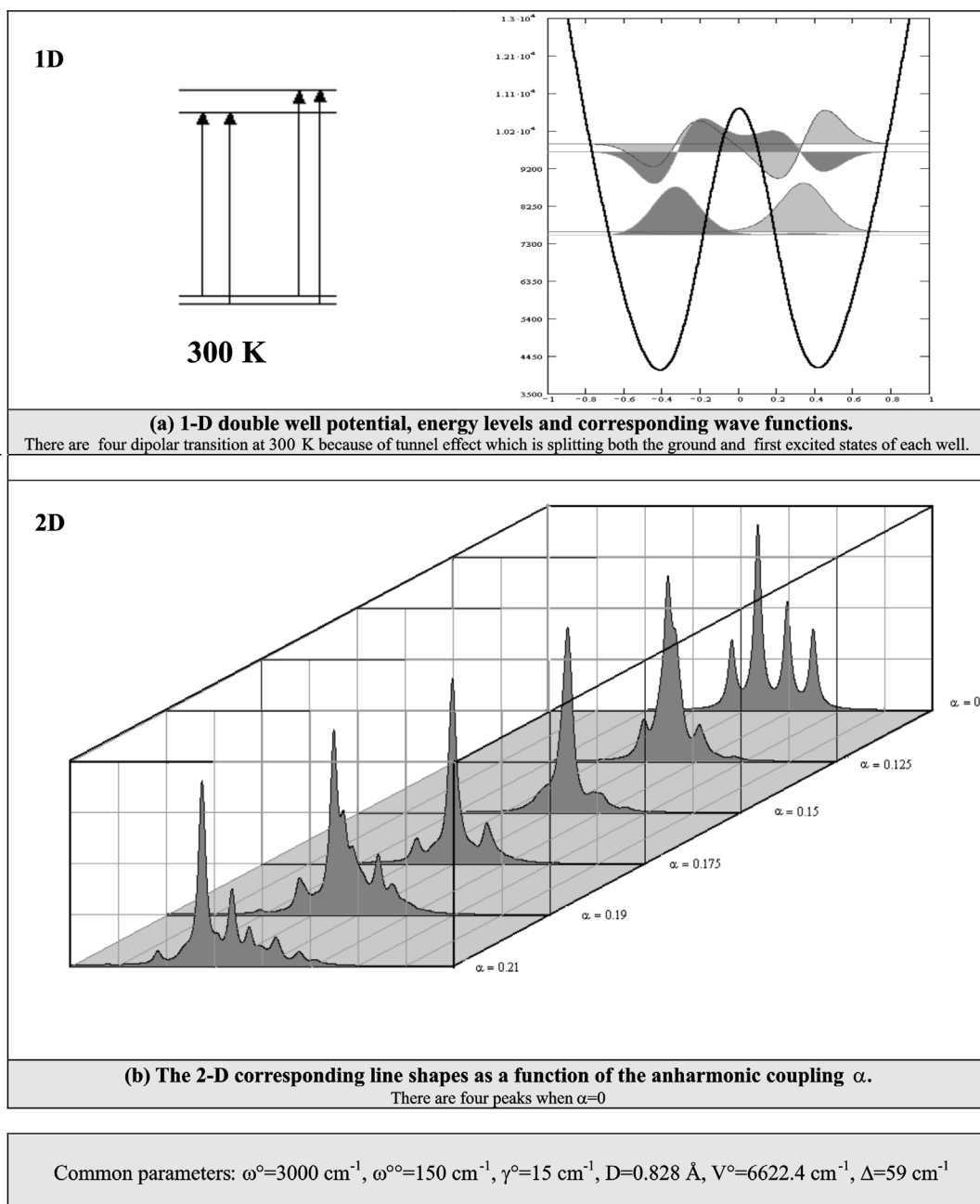


Fig. 5. SDs involving double-well potential near symmetry.

symmetric double-well potential. Figs. 4–6 are corresponding to double-well potentials which are very close to symmetry (gap between the double well around 1% of the barrier, and deepest well on

the left). Fig. 7 is dealing with a weak asymmetric double-well potential (gap less than 10% of the barrier) and Fig. 8 with an asymmetric double-well potential (gap around 1/3 of the barrier).

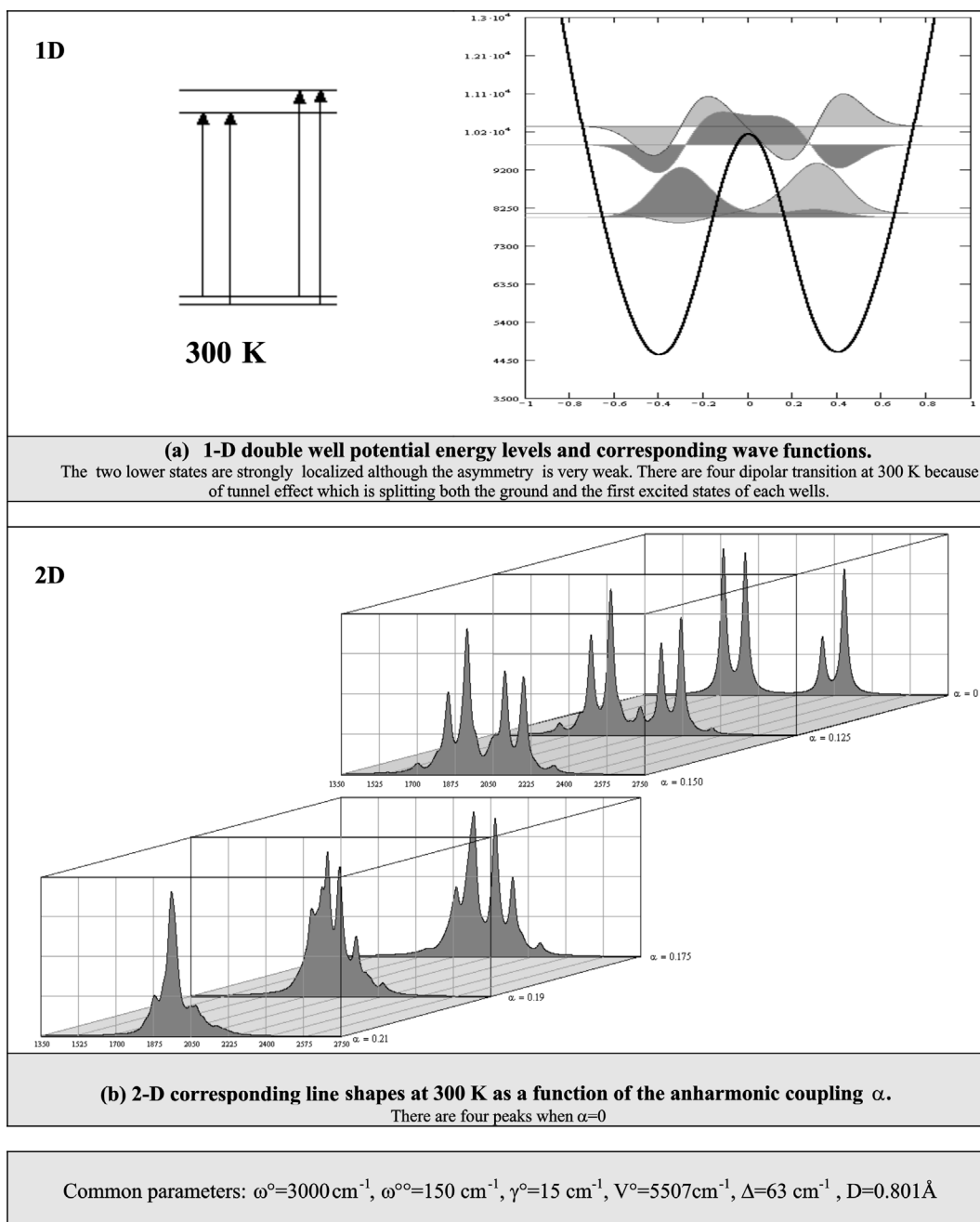


Fig. 6. SDs involving double-well potential near symmetry.

In a first place, one may interest at the simple SDs which may occur when the anharmonic coupling is missing ( $\alpha = 0$ ) i.e. to the top line shapes of

the figures. In the symmetrical situations of Fig. 3 there are, as required, two peaks, one corresponding to the dipolar allowed transitions at 0 K

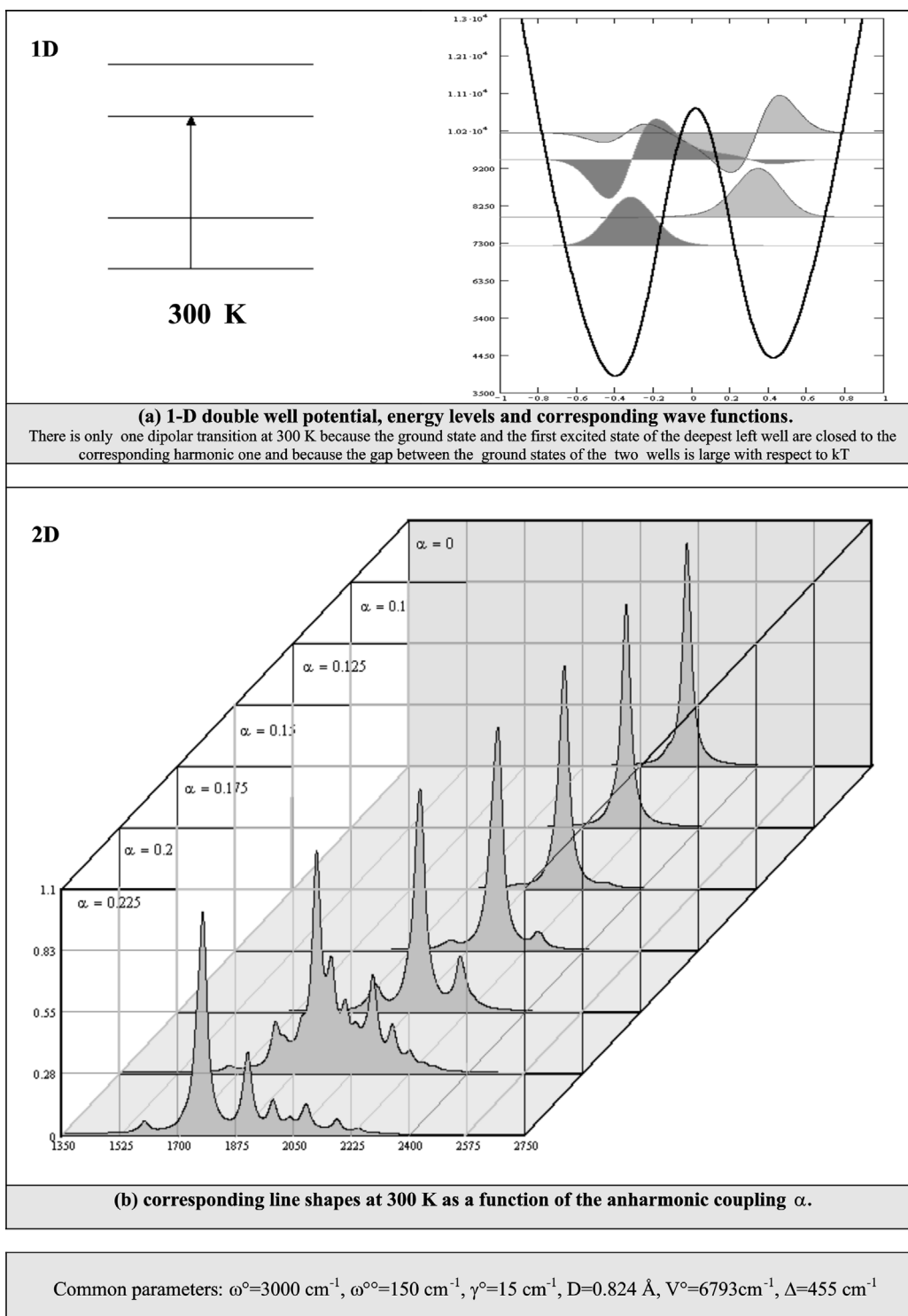


Fig. 7. SDs involving weak asymmetric double-well potential.

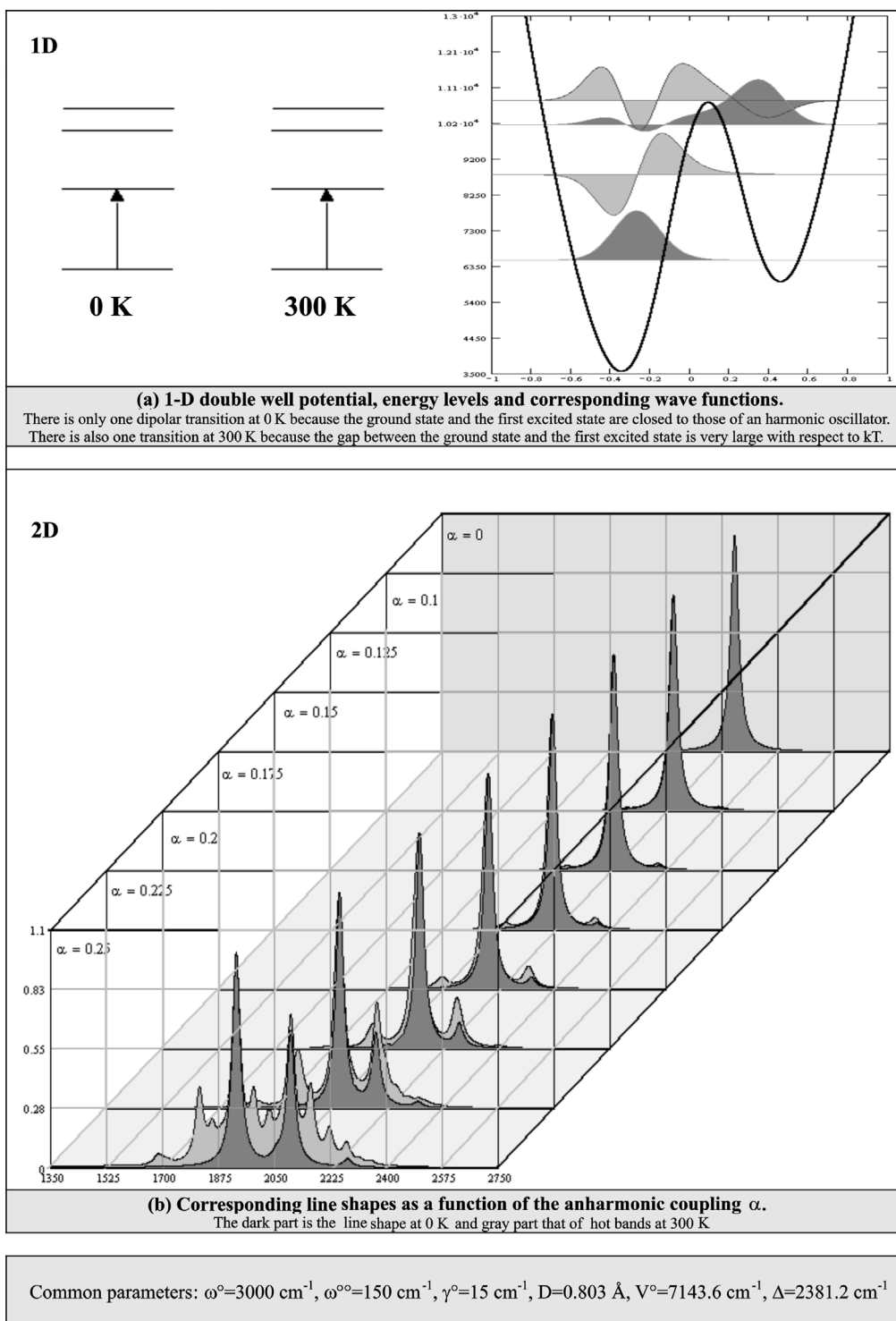


Fig. 8. SDs involving asymmetric double-well potential.

(high frequency peak) and the second one to the allowed dipolar hot band at 300 K (low frequency peak), the angular frequency gap being related to the splitting resulting from the tunnelling effect involving the first excited states of the right and left wells. Of course, since the tunnelling effect is very small for the ground states of the two wells, if at strict 0 K only the symmetrical delocalized ground state of the double-well system is occupied, at 300 K both the symmetrical and anti-symmetrical weakly split levels are thermally occupied with equal probabilities, so that the low frequency hot band (grayed SD) has the same intensity as the 0 K one (darkened SD). Now, when one is passing to asymmetric potential, the break of symmetry suppresses the selection rules even for very weak asymmetry: one observes, in Fig. 4, for which the asymmetry parameter is only 4/1000 of the barrier, two transitions occurring at strict 0 K in the place of one (the low frequency one being of less intensity because of the remanence of the symmetry selection rules) and four transitions at 300 K. In the situation of Fig. 4 the splitting at 300 K of each component of the 0 K doublet is very small because the asymmetry is very weak. Moreover, when the asymmetry is increased, passing from Figs. 4–6 through Fig. 5 by increasing weakly the asymmetry (4/1000 for Fig. 4 to around 1% for Figs. 5 and 6) the structure is deeply modified. At last, when the asymmetry is again increased, remains only one transition at 0 K as at 300 K: this is because the asymmetry of the potential introduces a localization of the lowest wave functions either on the right or on the left well, the 0 and 300 K transition involving only the left deepest well.

Now, consider what is occurring for the above situation when the anharmonic coupling between the slow and fast modes is introduced and then increased progressively. The SDs obtained in this way are given in the figures with which we were dealing above. In each figure the anharmonic coupling is progressively increased from  $\alpha = 0$  to  $\alpha = 0.225$ . In Figs. 3 and 4, for which the 1-D double-well potential is symmetric or very close to symmetry, the doublet appearing at 300 K when  $\alpha = 0$ , is progressively narrowing with an increase of  $\alpha$ , whereas is appearing an asymmetric tail in-

volving a fine structure. When passing to Fig. 5, dealing with line shapes at room temperature involving very weak asymmetric double-well potential, one may observe that the increase of the anharmonic coupling induces in a first step a narrowing of the quadruplet appearing for the 1-D situation, which is leading for  $\alpha = 0.15$  to a simple collapsing structure and then, after further increasing of the anharmonic coupling, to a subtle broadening of the line shapes, and at last for  $\alpha = 0.21$  to a wide asymmetric SD involving, as in Figs. 3 and 4, a high frequency asymmetric tail.

In Fig. 6, one may observe an evolution at room temperature in which is undergoing a collapse of the quadruplet characterizing the uncoupled initial situation. In Figs. 7 and 8, which are involving more asymmetric double-well potentials, and for which appears only a single peak for the initial uncoupled situation, it is possible to remark at room temperature a broadening of the line shapes with asymmetry and fine structure which is leading, in the case of Fig. 7 and for  $\alpha = 0.225$ , to a profile which is evoking that appearing in Fig. 5 for  $\alpha = 0.21$ . As a matter of fact, that is evoking a trend toward the Franck–Condon progression appearing for weak H-bonds when the fast mode is described by an harmonic potential. In Fig. 8, the broadening with an increase of the anharmonic coupling is more complex. Note in the puzzling structure the role played by hot bands when passing from  $\alpha = 0.225$  to  $\alpha = 0.250$ .

It may be of interest to verify how the tunnelling involved in the special situation of 2-D symmetrical double-well potential may affect the sub-bands induced by the anharmonic coupling. That is performed in Fig. 9 for  $\alpha = 0.2$  characterizing the sixth line shape appearing in Fig. 3, but with very weak damping ( $\gamma^0 = 1.5$  in place of  $15 \text{ cm}^{-1}$ ).

In this figure the temperature is increased up to down from  $T = 0$ –300 K passing by  $T = 5$  K. At 0 K, there are two peaks in this 2-D representation in place of one peak as waited in the 1-D representation (because of the symmetry rules and of the fact that only the *gerade* ground state is occupied). The appearance of the weak intensity peak is due to the existence of the anharmonic coupling ( $\alpha = 0.2$ ). At  $T = 5$  K, each peak of the

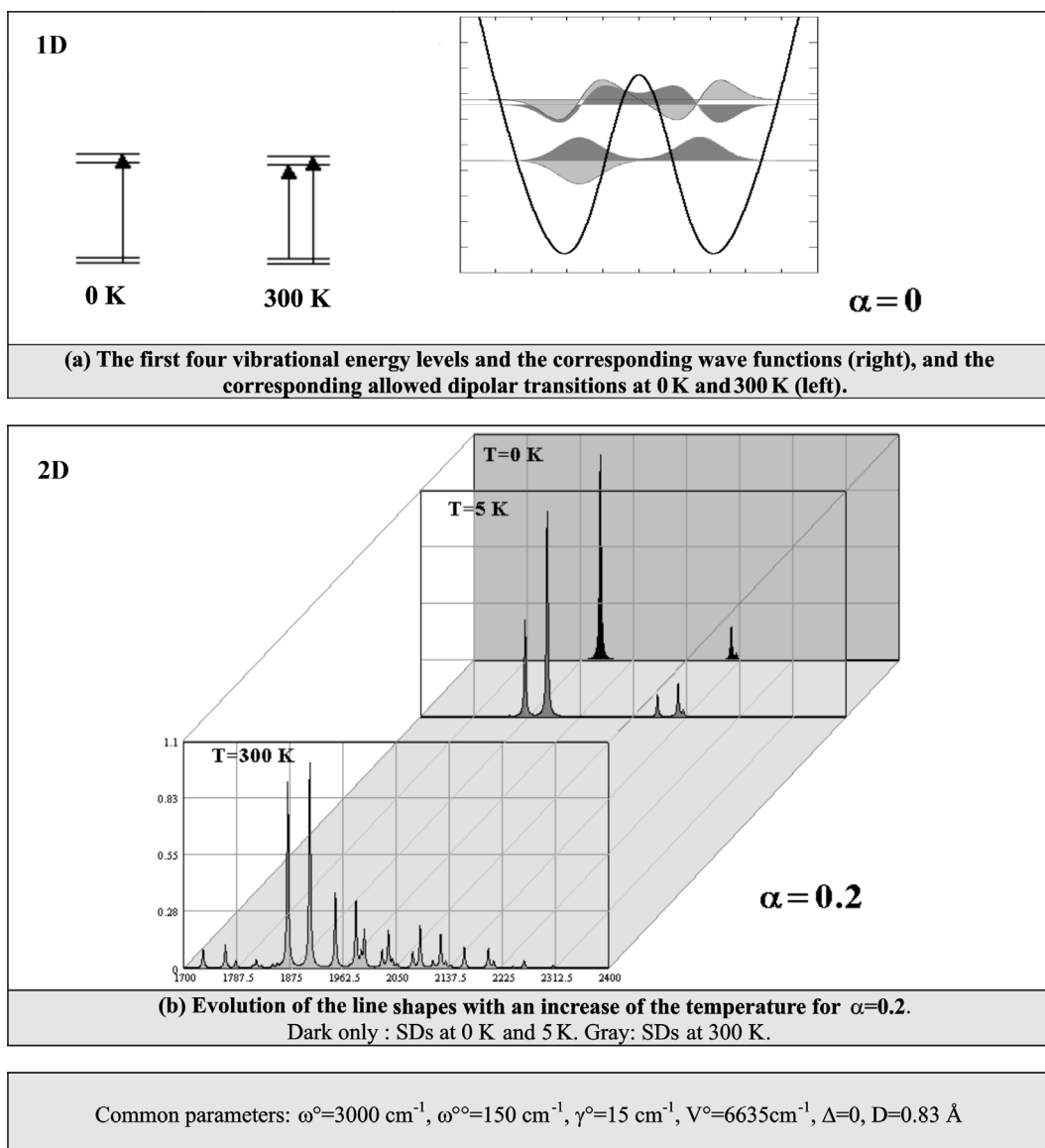


Fig. 9. SDs involving symmetrical double-well potential.

2-D 0 K situation is split into a doublet because of the thermal occupation of both the *gerade* and *ungerade* ground states, each doublet involving the same spacing. At 300 K, there are many doublets reflecting both the tunnelling due to the symmetric double-well potential and the anharmonic coupling which are both coupled through the 2-D potential.

Two main conclusions may be inferred from the inspection of Figs. 3–9. The first one is a trend for

the line shapes to evolve toward an asymmetric profile involving fine structure and evoking the blurred Franck–Condon progression appearing in the RR and MW models characterizing weak H-bonds in which the intrinsic fast mode potential is considered as harmonic. The second one is that when the fast mode potential is described by a double well, the magnitude required for the anharmonic coupling to induce a broadening of

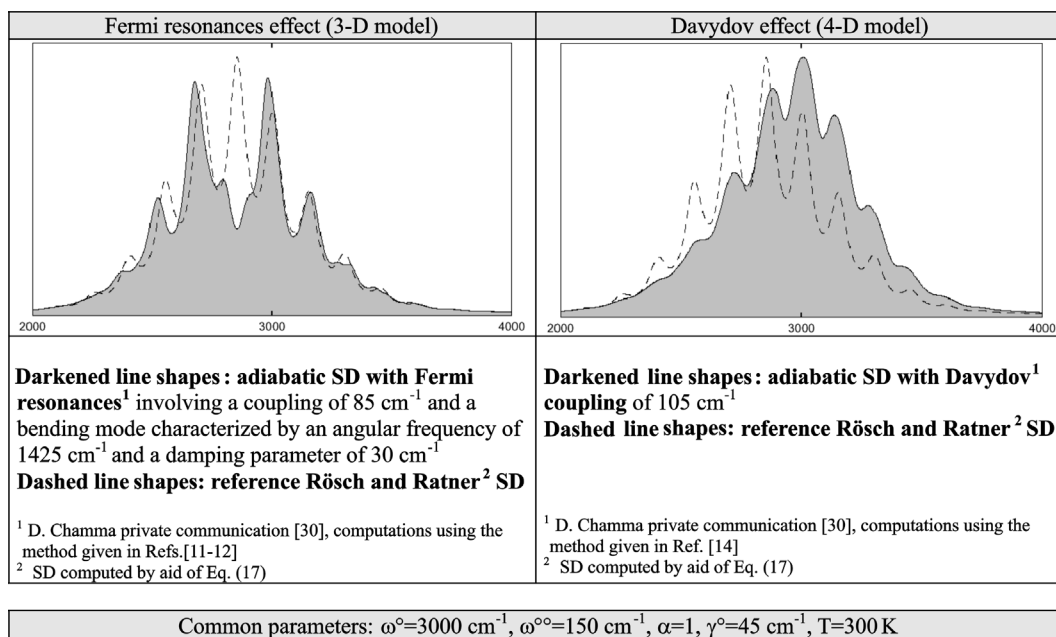


Fig. 10. Spectral densities involving Fermi resonances or Davydov coupling effects within the adiabatic approximation and assuming an harmonic fast mode potential.

some hundred of cm<sup>-1</sup>, is around 1/5 of that which is required within the SACT when the fast mode potential is approximated to be harmonic.

### 3.3. Comparison with 3-D and 4-D models

The above results may be compared to those we have obtained in earlier 3-D or 4-D studies performed, as here, within the SACT, but with an intrinsic potential of the fast mode assumed to be harmonic, and dealing (3-D model) with Fermi resonances (within the adiabatic and exchange approximations) or (4-D model) Davydov coupling (within the exchange approximation). An illustration of these line shapes computed by aid of the methods of the Refs. [13,14], is given in Fig. 10 [30].

Comparisons of the modifications induced in the Franck–Condon progression characterizing the line shape by passing for the fast mode from harmonic potential to double-well potential, to those induced by Fermi resonances or by Davydov coupling, show that the first ones are very much stronger because the Franck–Condon progression-

like structure is more conserved for Fermi resonances and Davydov coupling. As a consequence, it is possible that many features of the line shapes that are strongly escaping from the Franck–Condon profiles are due to the existence of the double-well potential, particularly when there are many irregularities in the intensities of the sub-bands, and in the frequency gap between them, or when the high frequency wing is more intense than the low frequency one.

### 3.4. Isotope effects

Now, consider the D-isotope effects resulting from the substitution of the proton of the H-bond by a deuterium. Fig. 11 illustrates the isotope effect at room temperature for three cases. The first one (top of the figure) is concerning a situation where the fast mode is described by an asymmetric double-well potential, but where the anharmonic coupling between the slow and fast modes is missing. The second case (middle of the figure) is dealing with both anharmonic coupling and double-well potential. The last case (bottom of the



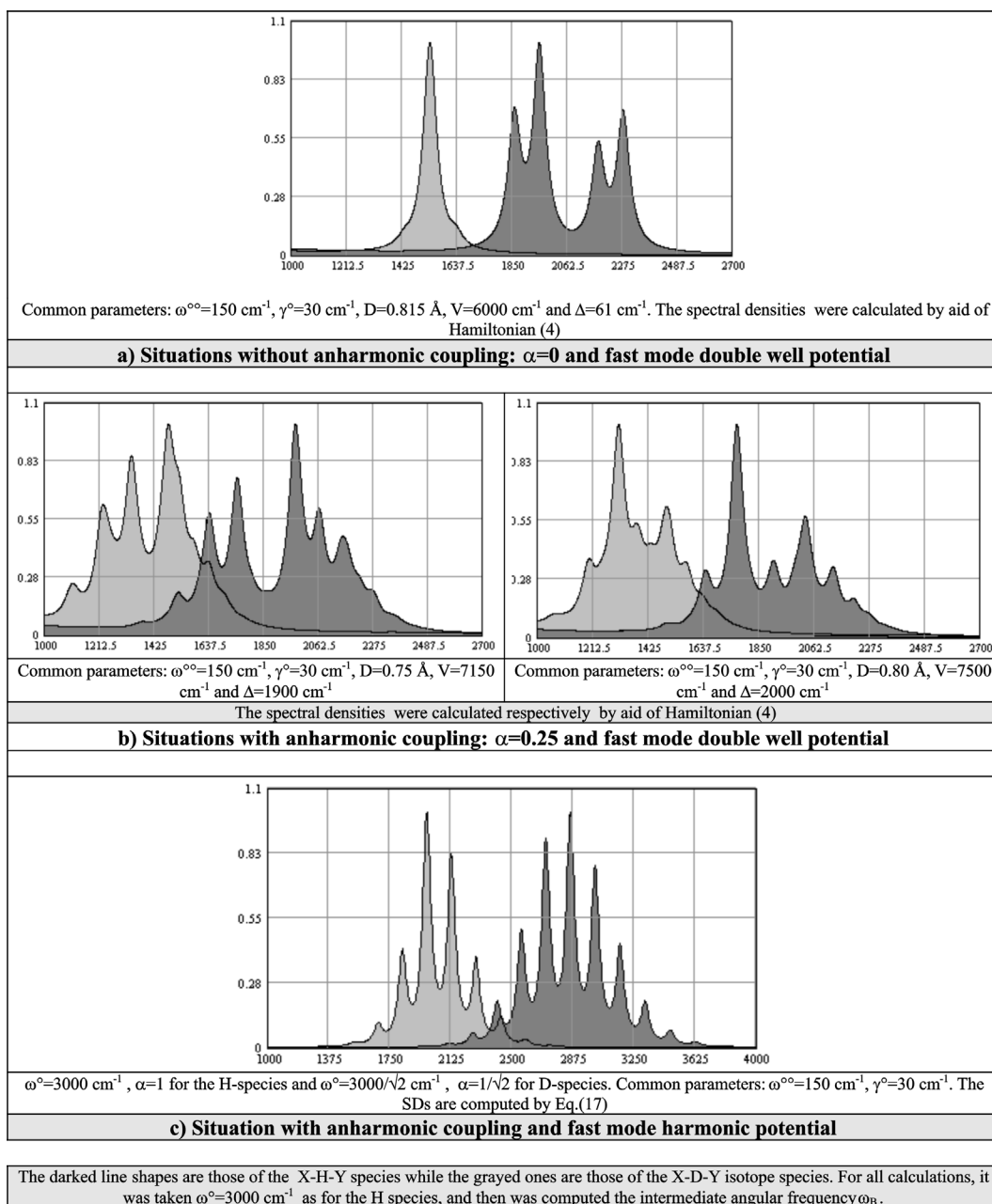


Fig. 11. Isotope effects on line shapes at 300 K.

figure) characterizes a situation in which the anharmonic coupling remains to hold but where the fast mode is described by an harmonic potential.

On this figure, all the grayed line shapes are characterizing H-bonded species and the darkened

ones, the corresponding D-substituted. Inspection of the figure shows in all situations a strong low frequency shift and a narrowing of the line shapes. This trend wholly agrees with experiment. Note that the general situation in which the potential of

the fast mode is of double-well nature and the anharmonic coupling is occurring, is that for which both the H and D line shapes contain subtle features. This result is of interest since the changes in the details are enough large to impose in the future drastic constraints in the attempts to interpret theoretically the experimental line shapes in order to avoid the possibility of obtaining fortuitously a good agreement (taking into account the details of the SDs) between theoretical and experimental spectra.

#### 4. Conclusion

The present approach deals with the quantum theory of the IR line shapes of intermediate or strong H-bonds, which may be symmetric or asymmetric. It is involving a 2-D model in which both the “slow” and “fast” modes are treated quantum mechanically, whereas in the Romanowski and Sobczyk model [18] the quantum treatment involves only the fast mode. As in the quantum theory of weak H-bond, a strong anharmonic coupling is assumed between the slow and fast modes. The repulsive potential generating the barrier has been assumed to be of Gaussian form in place of the inverted parabolic one used for instance by Romanowski and Sobczyk [18]. The theoretical SD is obtained, within the LRT by Fourier transform of the ACF of the dipole moment operator of the H-bond. The time dependence of the dipole moment operator is considered within the Heisenberg picture by the aid of the full Hamiltonian involving the 2-D potential. The ACF of the dipole moment is assumed to be damped in a simple way as in the RR model [4] of the direct damping. The present model involves the following approximations:

- the slow mode “Morse potential” curve is approximated by an harmonic potential,
- the electrical anharmonicity is neglected,
- the Fermi resonances are ignored, (i.e. 2-D model) is considered,
- the possibility of Davydov coupling (at least 4-D model) as appearing in the works of the Witkowski school, is not taken into account.

On the other hand, it is important to remark that the present approach is, by nature, beyond the adiabatic approximation as in our precedent works dealing with weak H-bonds [5,15,23].

The present model leads to line shapes that, when the barrier of the double-well potential becomes very high, are narrowing very satisfactorily those obtained within the RR model (involving the adiabatic approximation, and a potential describing the fast mode which is harmonic), which reduces in turn to the Franck–Condon progression of the MW model when the damping is ignored. On the other hand, when the barrier is low and symmetric, and if the anharmonic coupling between the slow and fast mode is vanishing, the model leads to line shapes that are those which may be met within the theory of tunnelling effect. The interest of the present model is to allow investigations on the line shapes when both the anharmonic coupling of the SACT and the anharmonicity following from an asymmetric double-well potential are taken in an equal foot. Our numerical investigations lead to the following conclusions:

- (i) The SD is shifted toward low frequencies by an amount (around  $1000\text{ cm}^{-1}$ ) for strong or intermediate H-bonds, which is greater than that obtained for weak H-bonds (around  $300\text{ cm}^{-1}$ ). That is in agreement with experiment.
- (ii) The SD is broadened as in theory of weak H-bond.
- (iii) The increase of the half width with temperature roughly agrees with experiment.
- (iv) It is not possible to separate in the features of the SD the influence of the anharmonic coupling and that of the double-well anharmonicity, except when the barrier is strictly symmetric.
- (v) Comparisons between the changes induced by the double-well anharmonicity and those induced by the Fermi resonance anharmonicity on the features of the  $\nu_{\text{X-H}}$  mode SD involving only the anharmonic coupling between the slow and fast modes (RR SDs), show that the perturbation of the Franck–Condon progression (which follows from the SACT) is weaker for Fermi resonances than for double-well anharmonicity.

(vi) If, when the fast mode potential is assumed to be harmonic the line shapes manifest more intense low frequency tails, which are not strongly modified by Fermi resonances ( $n$ -D model, with  $n = 3, 4 \dots$ ), Davydov coupling ( $2n$ -D model, with  $n = 2, 3 \dots$ ), indirect damping, etc., at the opposite, when the fast mode potential is considered as a double well one, there are many situations where opposite behavior, i.e. more intense high frequency tails, occur. That is of interest, since there are in the literature some examples of intense high frequency tails [28].

(vii) Isotope substitution of the proton of the H-bond bridge by deuterium leads to lower frequencies shifts and narrowing of the line shapes, as for situations where the intrinsic anharmonicity of the fast mode is ignored, but in a more complicated way. The Franck–Condon progression (appearing in the absence of double-well potential) is then broken: each X–H and X–D spectral density has its specific identity. It is therefore possible to verify an interpretation of experimental line shapes by systematic comparisons of the features of the X–H and X–D line shapes.

Now, consider the relative influence of the removing of the harmonic approximation for the fast mode potential (incorporation of the double-well potential of the fast mode) in the SACT with respect to the removal of other approximations (harmonic approximation for the fast mode, 2-D model, i.e. neglect of Fermi resonances). If one considers the above general trends in the light of those resulting from precedent studies [5,9,11–15,23–26,30], it appears that it is possible to propose a classification of the relative importance of the different anharmonicity mechanisms playing a physical role in the  $\nu_{X-H}$  line shapes of weak and medium H-bonds such as follows:

- (i) The crude first order anharmonic coupling between the slow and fast modes involved in the standard SACT, which induces general Franck–Condon features.
- (ii) The effect of the intrinsic anharmonicity of the fast mode through symmetric or asymmetric

double-well potentials which may strongly modify the Franck–Condon features.

- (iii) The anharmonic coupling between the fast mode and some bending modes leading to Fermi resonances (very sensitive even for situations which are very far from the Rabi conditions for resonance) which induces complex Evans windows destroying the Franck–Condon features.
- (iv) The intrinsic anharmonicity (Morse potential) of the slow mode.
- (v) The corrections to the crude first order anharmonic coupling.

On the other hand, all these influences have been considered within the direct damping of the fast mode by the medium, which is broadening in a standard way the fine structure resulting from the above anharmonicities. But it must be kept in mind that the indirect damping of the fast mode toward the medium through the slow mode must play a secondary role which is proved for simple situations to weakly modify the general features resulting from the anharmonicity [9].

If, in the present paper using 2-D representation of the H-bond, we have taken into account in an equal foot the anharmonicity of the double-well fast mode potential and the anharmonic coupling between the slow and fast modes, we have ignored the Morse-like anharmonicity of the slow mode and also the anharmonicity susceptible to lead to Fermi resonances.

As a consequence, the next step in our enterprise dealing with a general theory of the SD of  $\nu_{X-H}$  mode of H-bonded species, will be a  $n$ -D representation ( $n = 3, 4 \dots$ ) of the H-bond. Such a description will require to take into account all the following physical mechanisms:

- (i) the strong anharmonic coupling,
- (ii) the intrinsic anharmonicity of the slow mode by using a Morse potential,
- (iii) the intrinsic anharmonicity of the fast mode resulting from the asymmetric double-well potential,
- (iv) the anharmonicity linked to Fermi resonance requiring beyond 2-D representations,
- (v) Davydov coupling, requiring also beyond 2-D representations,

- (vi) electrical anharmonicity,
- (vii) direct damping, beyond the adiabatic approximation,
- (viii) indirect relaxation involving the H-bond bridge,
- (ix) damping of the low frequency mode other than that of the H-bond bridge,

and to know clearly what of these physical parameters may be neglected, approximated, separated, what of them must be taken explicitly into account or strongly correlated. Recall that we have already studied all these points in precedent papers, except the (vi), for somewhat separate situations in which we took only into account simultaneously two, three or four of these aspects.

## References

- [1] O. Henri-Rousseau, P. Blaise, in: D. Hadzi (Ed.), *Theoretical Treatment of Hydrogen Bonding*, Wiley, New York, 1997.
- [2] G. Hofacker, Y. Maréchal, M. Ratner, P. Schuster, G. Zundel, C. Sandorfy, *The Hydrogen Bond Theory*, North Holland, Amsterdam, 1976.
- [3] Y. Maréchal, A. Witkowski, *J. Chem. Phys.* 48 (1968) 2697.
- [4] N. Rösch, M. Ratner, *J. Chem. Phys.* 61 (1974) 3444.
- [5] P. Blaise, O. Henri-Rousseau, *Chem. Phys.* 243 (1999) 229.
- [6] B. Boulil, O. Henri-Rousseau, P. Blaise, *Chem. Phys.* 126 (1988) 263.
- [7] B. Boulil, J.-L. Déjardin, N. El-Ghandour, O. Henri-Rousseau, *J. Mol. Struct. Theochem* 314 (1994) 83.
- [8] B. Boulil, P. Blaise, O. Henri-Rousseau, *J. Mol. Struct. Theochem* 314 (1994) 101.
- [9] P. Blaise, O. Henri-Rousseau, A. Grandjean, *Chem. Phys.* 244 (1999) 405.
- [10] A. Witkowski, M. Wojcik, *Chem. Phys.* 1 (1973) 9.
- [11] O. Henri-Rousseau, D. Chamma, *Chem. Phys.* 229 (1998) 37.
- [12] D. Chamma, O. Henri-Rousseau, *Chem. Phys.* 229 (1998) 51.
- [13] D. Chamma, O. Henri-Rousseau, *Chem. Phys.* 248 (1999) 53.
- [14] D. Chamma, O. Henri-Rousseau, *Chem. Phys.* 248 (1999) 71.
- [15] D. Chamma, O. Henri-Rousseau, *Chem. Phys.* 248 (1999) 91.
- [16] G. Robertson, M. Lawrence, *Chem. Phys.* 62 (1981) 131.
- [17] J. Singh, J. Wood, *J. Chem. Phys.* 48 (1968) 4567.
- [18] H. Romanowski, L. Sobczyk, *Chem. Phys.* 19 (1977) 361.
- [19] S. Bratos, *J. Chem. Phys.* 63 (1975) 3499.
- [20] G. Robertson, J. Yarwood, *Chem. Phys.* 32 (1978) 267.
- [21] H. Abramczyk, *Chem. Phys.* 144 (1990) 305.
- [22] N. Rösch, *Chem. Phys.* 1 (1973) 220.
- [23] P. Blaise, O. Henri-Rousseau, *Chem. Phys.* 256 (2000) 85.
- [24] O. Henri-Rousseau, P. Blaise, *Chem. Phys.* 250 (1999) 249.
- [25] O. Henri-Rousseau, P. Blaise, *Adv. Chem. Phys.* 103 (1998) 1.
- [26] O. Henri-Rousseau, P. Blaise, D. Chamma, *Adv. Chem. Phys.*, in press.
- [27] P. Blaise, M. Giry, O. Henri-Rousseau, *Chem. Phys.* 159 (1992) 169.
- [28] M. Haurie, A. Novak, *J. Chim. Phys.* 62 (1965) 146.
- [29] V.A. Benderskii, E.V. Vetoshkin, H.P. Trommsdorff, *Chem. Phys.* 244 (1999) 299.
- [30] D. Chamma, private communication.
- [31] Y. Maréchal, A. Witkowski, *J. Chem. Phys.* 48 (1968) 3697.
- [32] J.L. Leviel, Y. Maréchal, *J. Chem. Phys.* 54 (1971) 1104.
- [33] N. Rösch, M. Ratner, *J. Chem. Phys.* 61 (1974) 3344.
- [34] M. Wojcik, *Mol. Phys.* 36 (1978) 1757.
- [35] O. Henri-Rousseau, P. Blaise, *Chem. Phys.* 256 (1999) 85.
- [36] D. Chamma, *J. Mol. Struct.* 552 (2000) 87.