The IR band shape theory of the stretching mode $\nu_s(XH\cdots Y)$ in H-bonded complexes is presented. The proton in the H-bond involves motion in the Born–Oppenheimer energy potential which is accompanied by the anharmonic coupling to the low-frequency hydrogen-bridge stretching motion $\nu_0$. Both the energy potential well and the anharmonic coupling are randomly modulated with time. The fluctuations of the energy potential arising from the direct coupling to the bath obey the stochastic Liouville equation. The time evolution of the anharmonic coupling constant is governed by the resonance energy exchange between the $\nu_s$ mode and the bath. The theory can be applied both to weak and strong H-bonds.

1. Introduction

One of the most striking aspects of H-bonds is found in their dynamical behaviour. From the experimental point of view, the most general method for studying these dynamical aspects is infrared spectroscopy. It appears, therefore, to be of great interest to construct a precise, quantitative IR band shape theory in H-bonds to understand the origin of most of the characteristic and unusual spectroscopic properties of H-bonds.

The various theoretical approaches used in the treatment of the vibrational dephasing relaxation and IR band broadening in H-bond complexes may be classified as weak-coupling limit [1-5] and strong-coupling limit theories [6-10]. The weak coupling of the system to the bath is treated through perturbation theory and it can be used only for weak hydrogen bonded complexes. For medium–strong and strong H-bonded complexes interactions are strong enough that the vibrational relaxation (dephasing) cannot generally be treated through perturbation theory. In the strong-coupling limit, the Hamiltonian in the excited vibrational state depends linearly (or nonlinearly) on the external coordinate $Q$ coupled to the internal vibrational mode $q$. This term is called the strong-coupling term. In this method, the Hamiltonian is diagonalized by performing a canonical transformation. For weak coupling of H-bonded system to a bath, the cumulant expansion approach is usually based assuming that the coupling is a purely classical, stochastic Gaussian process for which the cumulant expansion may be truncated beyond second order. Substantial progress has been made in answering what is the physical nature of this coupling.

Two main relaxation mechanisms have been proposed. One of these calculates broadening of the band due to the direct dipolar interaction of the dipole moment of the complex to the local fluctuating electric field produced by the solvent dipoles as proposed Zundel et al. [11] or of the dipole moment of the proton donor and the dipole moment produced by the H-bond as proposed Abramczyk [5,12] in the complex regarded as a non-rigid supermolecule. The other is an indirect relaxation mechanism caused by the anharmonic coupling of the high-frequency $\nu_s(X-H)$ stretching mode to the low-frequency hydrogen bridge motion $\nu_0(\tilde{X}-\tilde{H}\cdots \tilde{Y})$ [1-4,8-10]. The IR band shape of the $\nu_s$ mode is controlled by the dynamics of the bridge motion $\nu_0(\tilde{X}-\tilde{H}\cdots \tilde{Y})$.

Both weak and strong-coupling theories can be classified according to the level of approximation in treating the $\nu_0$ dynamics. Bratos [1] assumed that the time dependence of the coupling of the $\nu_0$ mode to the environment (bath) is suppressed (static limit). The X...H bridge is regarded as a Brownian oscillator obeying the Langevin equation in the model of Robertson and Yarwood [3] or generalized Langevin equation in the model...
of Sakun [4]. The interaction of the $\nu_0$ oscillator with the bath is ignored, so that the $X...Y$ length is allowed to oscillate without damping in the gas phase in the Maréchal–Witkowski model [8]. Recently, an approach of Boulil et al. [13] has been reported, which is fully quantum mechanical theory and the coupling to the bath is described as intermolecular resonance energy exchange with the molecules of the inert solvent (bath). This model is able to connect the Witkowski–Maréchal approach in the gas phase and the theories in the liquid phase. For medium–strong and strong H-bond complexes it is believed that additional IR band shaping mechanisms are efficient: Fermi resonances between $\nu_0$ and combinations and overtones involving other internal modes (for example the doubly excited in-plane hydrogen bending and the doubly excited out-of-plane hydrogen bending), mechanical and electrical anharmonicity of the $\nu_0$ mode itself, tunneling of the proton in a double-well potential.

The theoretical aspects of strong H-bonded complexes have been discussed in several papers [2,14,15]. The IR band shape theories of strong H-bond should explain not only the facts that the $\nu_0$ band is very broad, much more intense and shifted to lower wave numbers compared to the position of the free band but also a well-defined structure, especially Evans windows and A, B, C bands. Bratos and Ratajczak [2] have shown that Fermi resonances results in the A, B, C bands while Hofacker et al. [16] have pointed out that the theoretical intensities of this mechanism for carboxylic acids drastically deviate from the experimental intensity pattern. Fillaux [15] proposed that the A, B, C bands can be explained without supposing Fermi resonances. We feel that there is a gap between the theories for weak and strong H-bond IR band shape theories. It would be valuable to have a unified model, which takes into account the coupling of the $\nu_0$ mode to the low-frequency mode stretching mode of the bridge $\nu_o$, tunneling in the double-well potential, if it exist, the influence of the environment and fluctuations of the energy potential well in which the proton motion occurs.

Our study is intended to cover the gap between the weak and strong H-bond complex IR band shape theories by presenting the theory of the IR band shape of the $\nu_0$ mode in H-bond complex in which the proton motion in Born–Oppenheimer energy potential is accompanied by the anharmonic coupling to the low-frequency stretching mode $\nu_0$ of the bridge. Both the energy potential well as well as the strength of the coupling to the $\nu_0$ mode are randomly modulated with time. The anharmonic coupling between $\nu_0$ and $\nu_o$ is treated through the strong-coupling limit theory. The $\nu_0$ mode is coupled to the solvent undergoing resonant energy exchange with it. The fluctuations of the energy levels for the fixed energy potential arise from the direct, weak coupling to the solvent. The fluctuations of the energy potential shape arise from the change of the equilibrium geometry of the potential well other than the linear displacement with the low-frequency $Q$ mode of the bridge and the weak coupling to all of the other external vibrations of the bridge, which have not been taken explicit into account in the anharmonic coupling.

2. Theory of the band profile

2.1. Hamiltonian

In the linear response scheme, the absorption band shape $I(\omega)$ for proton motion in H-bond can be expressed as the Fourier transform of the dipole correlation function [17] of the vibrational dipole moment operator $\hat{M}$,

$$I(\omega) = \frac{1}{2 \pi} \omega \left[ 1 - \exp(-\hbar \omega/kT) \right] \int_{-\infty}^{\infty} dt \exp(i\omega t) \langle \hat{M}^{\ast}(t)\hat{M}(0) \rangle.$$  \hspace{1cm} (1)

To calculate $I(\omega)$ we have to know the time evolution of the dipole moment operator $\hat{M}(t)$ appearing in eq. (1). The symbol $\langle \rangle$ means averaging over the vibrational states of the $\nu_0$, $\nu_o$ modes and bath (solvent and the other external modes of the bridge).

Thus, let us first turn to a discussion of the Hamiltonian governing the time dependence $\hat{M}(t)$. We assume
that the proton motion involving in H-bond is coupled to the low-frequency stretching mode of the bridge. Thus, the Hamiltonian for the system can be written as

\[ H(q, Q) = h(q, Q) + p^2/2M \]  

and

\[ h(q, Q) = p^2/2m + U(q, Q), \]  

where \( m \) is the reduced mass of the \( \nu_s \) oscillator, \( M \) is the reduced mass of the \( \nu_a \) oscillator, \( q \) denotes the normal coordinate of the \( \nu_s \) mode, while \( Q \) is the normal coordinate of the \( \nu_a \) mode. We assume that only one external vibrational mode \( \nu_a \) is modified in the vibrational transition. Using Born–Oppenheimer approximation for the high \( q \) and low \( Q \) frequency vibrational motions we can write the eigenfunctions \( \psi(q, Q) \) of the Hamiltonian as a simple product

\[ \psi(q, Q) = \phi(q, Q) \chi(Q), \]  

where \( \phi(q, Q) \) is the proton eigenfunction of \( h(q, Q) \) and \( \chi(Q) \) is the vibrational eigenfunction for the \( Q \) mode.

The potential energy operator \( U(q, Q) \) consists of two contributions,

\[ U(q, Q) = V(q, Q) + U'(Q), \]  

where \( V(q, Q) \) is the potential energy of the \( q \) motion of the proton in the H-bond and \( U'(Q) \) is the vibrational potential energy operator for the \( Q \) mode. The potential \( V(q, Q) \) is taken in the form of the polynomial in \( q \) as proposed by Somorjai and Hornig [18],

\[ V(q, Q) = \sum \nu_n(Q) q^n. \]  

The coefficients \( \nu_n \) may be chosen in such a way, that they describe a single- or a double-well potential. The absorption and emission of the photons is considered instantaneous with respect to tunneling, if it exists, in the particular H-bond. Assuming that the \( Q \) mode is harmonic, one can write the total Hamiltonian (eqs. (2), (3)) in the form

\[ H(Q) = C_1(Q) + p^2/2M + \frac{\hbar^2}{\hbar\omega_0} Q^2, \]  

where \( \omega_0 \) is the frequency of the \( Q \) mode and the basis for the proton motion is defined as

\[ h(q, Q) = \sum_m E_m |m\rangle \langle m|, \]  

where \( E_m \) are the eigenenergies for the \( q \) mode in the potential well (eq. (6)) at fixed (equilibrium) vibrational displacement \( Q \).

Utilizing the second quantization representation, with the creation–annihilation operators \( a, a^* \) \( \{[a, a^*] = 1\),

\[ P = i(M\hbar/\omega_0)^{1/2} (a^* - a), \quad Q = (\hbar/2M\omega_0)^{1/2} (a^* + a), \]  

we obtain for the ground and the first excited state of the \( q \) mode

\[ H_0 = \hbar\omega_0 [a^* a + \frac{1}{2} - \frac{1}{2} \alpha_0 (a^* + a)] + E_0^G(Q), \quad H_0' = \hbar\omega_0 [a^* a + \frac{1}{2} - \frac{3}{2} \alpha_0 (a^* + a)] + \hbar\omega_0' + E_0^G(Q), \]  

where \( E_0^G(Q) \) is the value of the \( E_0(Q) \) for the equilibrium displacement \( Q \). \( \alpha_0 \) is the dimensionless anharmonic coupling constant and reflects the strength of the coupling between the \( q \) and \( Q \) mode,

\[ \alpha_0 = -2^{-1/2} \left( \frac{\partial E_0}{\partial Q} \right)_{Q_0} \left( \frac{\hbar^2}{2M}\omega_0 \right)^{1/2} \frac{2}{\hbar\omega_0}, \]  

(11)
where the index \( m \) at the proton frequencies \( \omega^m_q \) goes over all the vibrational transitions between the ground and the first excited state of the \( q \) mode.

The anharmonic coupling between the \( q \) and \( Q \) mode can be treated in terms of the strong-coupling theory. In this method, the coupling term is treated in an exact, nonperturbative way, on which a canonical transformation is performed as is common in polaron theory. The transformed Hamiltonian describes the dynamic effects of the \( Q \) motion on the \( q \) motion of proton as it moves between its Born–Oppenheimer eigenstates. Performing the phase transformation on \( H_0 \) and \( H^m_q \),

\[
H_0 = A^+(\frac{1}{2} \alpha_0)H_0A(\frac{1}{2} \alpha_0), \quad H^m_q = A^+(\frac{1}{2} \alpha_0)H^m_q A(\frac{1}{2} \alpha_0),
\]

with the operator

\[
A(\frac{1}{2} \alpha_0) = \exp[\frac{1}{4} \alpha_0 (a^+ - a)]
\]

and changing the origin of the energy level we obtain

\[
H_0 = \hbar \omega_0 a^+ a, \quad H^m_q = \hbar \omega_0 a^+ a - \alpha_0 (a^+ + a) \hbar \omega_0 - \alpha_0^2 \hbar \omega_0 + \hbar \omega^m_q.
\]

The \( Q \) mode basis corresponding to the Hamiltonian (14) is denoted as \( |\hat{\alpha}\rangle \). It is convenient to pass to a new representation, in which the Hamiltonian governing the \( Q \) mode is diagonal in its first excited state.

Using once again the phase transformation, which is in this case the displacement operator of the normal coordinates \( a^+ \) and \( a \),

\[
A(\alpha_0) = \exp[\frac{1}{4} \alpha_0 (a^+ - a)],
\]

we can write finally

\[
H^m_q = \hbar \omega_0 (a^+ a - 2 \alpha_0^2) + \hbar \omega^m_q
\]

with the \( Q \) mode basis \( |\hat{\alpha}\rangle \).

### 2.2. Calculation of the dipole correlation function

As we can see from eq. (1) in order to calculate the absorption band shape, we have to know the time evolution of the dipole correlation function \( \langle M^+(t)M(0) \rangle \). The dipole correlation function can be expressed as

\[
G(t) = \text{Tr} \langle \rho_q(0)\rho^*_B(0)M^+(t)M(0) \rangle
\]

where, following the adiabatic approximation, we may write the total density operator of the system \( \rho(0) \) at time \( t=0 \) as a product of the vibrational density operators for the \( q \) and \( Q \) motions,

\[
\rho(0) = \rho_q(0)\rho^*_B(0) \cdot \rho(0). \quad (18)
\]

The index 0 at \( \rho^*_B(0) \) denotes, that the proton is in its ground vibrational state. The symbol \( \langle \rangle \) here means averaging over the bath. First, we average over the states for the \( q \) motion. Using a representation of the eigenstates of \( q \) motion in the adiabatic basis (eq. (8)) we may write

\[
G(t) = \text{Tr} \left\langle \rho^*_B(0) \sum_{m,n,n'} \langle \rho_q(0) \rangle_{mn} M^*_m(t)M_{n'n}(0) \right\rangle, \quad (19)
\]

where the sum over \( m, n, n' \), is restricted to \( 0^+, 0^-, 1^+, 1^- \) states (fig. 1) of the ground and first vibrational state splitted by tunneling. If there is no tunneling in the protonic motion, \( m, n, n' \) are simply limited to 0 and 1 for one transition.

The density operator governing the vibrational motion \( q \) corresponds to an equilibrium

\[
\rho^b_{0^+0^+} = \exp(-E_{0^+}/kT)/\text{Tr} \rho_q, \quad \rho^b_{0^-0^-} = \exp(-E_{0^-}/kT)/\text{Tr} \rho_q. \quad (20)
\]
Fig. 1. Double-well potential $V(q, Q)$ of the ground $|0\rangle$ and first excited $|1\rangle$ vibrational state and characteristic parameters $V_{\text{max}}$ and $\Delta V$. The equilibrium value of the vibrational coordinate $q$ for the proton in the $|1\rangle$ state is displaced from that for the proton in the $|0\rangle$ state by $2\alpha_0$.

Using eq. (20) we obtain

$$
G(t) = \text{Tr} \langle \rho_0^{\text{g}}(0) \{ \exp\left(-E_0^{+}/kT\right) \text{Tr}^{-1} \rho_q \{ M_{q+1}^{+} + M_{q-1}^{-} \} \{ M_{q+1}^{+} M_{q-1}^{-} \} \} \rangle 
$$

where $\omega_0$ is the tunneling frequency in the vibrational ground state. In the strong coupling limit theory the transition dipole moment for the $q$ vibrational motion becomes

$$
M_{mn}(0) = A(\alpha_0) \left( \frac{\partial M}{\partial q} \right)_0 q_{mn}(0), \quad M_{mn}^{+}(t) = A^+(t) \left( \frac{\partial M}{\partial q} \right)_0 q_{mn}(t),
$$

where $m$ and $n$ go over $n = 0^+, 0^-$ and $m = 1^+, 1^-$. The operator $A(\alpha_0)$ and $A^+(t)$ represent the displacement operators at time $t=0$ (eq. (15)) and at time $t$, respectively. The time evolution of $q_{mn}(t)$ is governed by the Heisenberg equation

$$
-i\hbar \frac{\partial q}{\partial t} = [H, q],
$$

where $H$ is the strong coupling Hamiltonian given by eq. (16). Using the Heisenberg equation we obtain (let us take the transition $0^+ \rightarrow 1^-$)

$$
-i\hbar \frac{\partial q_{0+1+}}{\partial t} = \langle 0^+ | H | 0^+ \rangle \langle 0^+ | q_1^- \rangle - \langle 0^+ | q_1^+ \rangle \langle 1^+ | H | 1^- \rangle + \langle 0^+ | H | 0^- \rangle \langle 0^- | q_1^- \rangle - \langle 0^+ | q_1^- \rangle \langle 1^- | H | 1^- \rangle.
$$

Because $H$ is acting only on the subspace corresponding to the first excited state, eq. (24) is simplified to the form

$$
i\hbar \frac{\partial q_{0+1+}}{\partial t} = (\hbar \omega_0^{+1-} - 2\alpha_0^2 \hbar \omega_0) q_{0+1-}.
$$

Thus, the dipole correlation function (eq. (21)) is written as

$$
G(t) = \left( \frac{\partial M}{\partial q} \right)_0^2 \text{Tr} \langle \rho_0^{\text{g}} A^+(t) A(0) \{ q_{0+1-} \} \{ \exp\left(-i(\omega_0^{+1-} - 2\alpha_0^2 \omega_0)t\right) \}} \right) 
$$

$$
+ q_{0+1+} \exp\left(-i(\omega_0^{+1-} - 2\alpha_0^2 \omega_0)t\right) + \exp(-\hbar \omega_0/kT) \{ q_{0+1-} \} \{ \exp\left(-i(\omega_0^{+1-} - 2\alpha_0^2 \omega_0)t\right) \}
$$

$$
+ q_{0+1+} \exp\left(-i(\omega_0^{+1-} - 2\alpha_0^2 \omega_0)t\right) \} \rangle ,
$$

(26)
where
\[ \epsilon = \exp \left( -\frac{E_0}{kT} \right) / \text{Tr} \rho_a \]  
(27)

2.3. The time evolution of the displacement operator \( A(t) \)

Now, we will perform the averaging over the vibrational motion of the mode \( Q \), which is coupled to the proton motion. The density operator \( \rho_Q^0(0) \) governing the vibrational mode \( Q \) corresponds to Boltzmann equilibrium, when the \( Q \) oscillator is in its ground state

\[ \rho_Q^0(0) = \epsilon_1 \exp \left( -\hbar a^+ a / kT \right) , \]
(28)

where the trace \( \text{Tr} \rho_Q^0 \) is equal to \( \epsilon_1^{-1} \),

\[ \epsilon_1 = 1 - \exp \left( -\hbar \omega_{00} / kT \right) . \]
(29)

If we take a representation of the displacement operator \( A \) in terms of the basis of the Hamiltonian (14) of the \( Q \) mode,

\[ A = \sum_{\alpha \beta} A_{\alpha \beta} | \alpha \rangle \langle \beta | \]
(30)

we obtain from eq. (26)

\[ G(t) = \left( \frac{\partial M}{\partial q} \right)_0 \left( \sum_{\alpha \gamma} \epsilon_1(\gamma) \exp \left( -\hbar \omega_{00} / kT \right) \langle \alpha | A^+ (t) | \gamma \rangle \langle \gamma | A(0) | \alpha \rangle \right. \]

\[ \times \left[ q_0^+ q_{0-} \exp \left[ -i(\omega_0^{0+1} - 2\alpha_0^0 \omega_{00}) t \right] + q_{0+}^+ q_{0-}^+ \exp \left[ -i(\omega_0^{0+1} - 2\alpha_0^0 \omega_{00}) t \right] \right] \]

\[ + \exp \left( -\hbar \omega_{00} / kT \right) \left[ q_0^+ q_{0-} \exp \left[ -i(\omega_0^{0+1} - 2\alpha_0^0 \omega_{00}) t \right] + q_{0+}^+ q_{0-}^+ \exp \left[ -i(\omega_0^{0+1} - 2\alpha_0^0 \omega_{00}) t \right] \right] \]
(31)

The matrix elements appearing in eq. (26) are Franck-Condon factors. According to Koide [19], we have for

\[ \langle \gamma | A(0) | \alpha \rangle = \exp \left( -\alpha_0^0 / 2 \right) (\alpha! \gamma!)^{1/2} \sum_{k=0}^\gamma (-1)^k \alpha_0^0^{2k+\gamma-k} (\gamma-k)! k! (\gamma-\alpha+k)!^{-1} . \]
(32)

In order to find the time dependent matrix elements \( \langle \alpha | A^+ (t) | \gamma \rangle \) we must know the time evolution of the total density operator \( \rho(t) \). Let us assume that the vibrational mode \( Q \) is relaxing to a bath (i.e. the external modes other than the mode \( \nu_a \) coupled with the proton, reorientational and translational degrees of freedom), when the proton has jumped abruptly to its first vibrational excited state. Thus, the total density operator \( \rho(0) \) may be written as

\[ \rho(0) = \rho_Q^0(0) \rho_{\text{bath}}(0) , \]
(33)

where \( \rho_Q^0 \) is the vibrational \( Q \) density operator at time \( t=0 \) when the proton is in its first vibrational \( q \) excited state. The Liouville equation governing the time dependence of the density operator \( \rho(t) \) can be solved using the method of Louise11 and Walker [20] as recently was shown by Boulil et al. [13]. They have shown that \( A(t) \) may be expressed as

\[ A^+ (t) = \exp \left[ \alpha^a(t) a^+ - \alpha(t) a \right] , \]
(34)

where
\( \alpha(t) = a_0 \exp(-i \omega_{00} t) \exp(-\Gamma t/2). \) (35)

Here, \( \Gamma \) is the damping parameter given by
\[
\Gamma = 2\pi \sum_j |k_j|^2 \delta(\omega_j - \omega_{00}).
\] (36)

When there is no coupling to the bath (the coupling constants \( k_j = 0 \)), the expression for \( \alpha(t) \) takes the form
\[
\alpha(t) = a_0 \exp(-i \omega_{00} t).
\] (37)

Using eq. (34), we can calculate \( \langle \alpha | A^+ (t) | \gamma \rangle \).
\[
\langle \alpha | A^+ (t) | \gamma \rangle = \exp\left[ -\alpha^2(t)/2 \right] (\alpha! \gamma!)^{1/2} \sum_{j=0}^\alpha (-1)^j (\alpha(t) | 2^j | (\alpha - j)! (\gamma - j)!)^{-1}.
\] (38)

Substituting (32) and (38) into (31) we obtain
\[
G(t) = \left( \frac{\partial M}{\partial q} \right)^2_0 \left\langle \epsilon_1 \sum_{\gamma_0=0}^\infty \epsilon_2(\gamma) \sum_{\alpha=0}^4 \sum_{j=0}^\alpha \sum_{k=0}^\alpha \sum_{l=0}^\alpha \sum_{q=0}^l A_{\gamma_0\gamma}(B_{\alpha\alpha}^m C_{kj\alpha} F_{\gamma_0q}) + \sum_{\alpha=\gamma+1}^\infty \sum_{j=0}^\alpha \sum_{k=0}^\alpha \sum_{l=0}^\alpha \sum_{q=0}^l A_{\gamma_0\gamma}(B_{\alpha\alpha}^m C_{kj\alpha} F_{\gamma_0q}) \right\rangle,
\] (39)

with
\[
A_{\gamma_0\gamma} = \left( \frac{1}{q} \right) \frac{\gamma! \alpha! (-1)^{k+j+l}}{(k-j)! (k-j)! (\gamma-k)! (\gamma-k)!}.
\] (40)

\[
B_{\alpha\alpha}^m = f_m \exp\left\{ -i[\omega_{00}^m - 2\alpha^2_{00} \omega_{00} + (\gamma - \alpha) \omega_{00}]t \right\},
\] (41)

\[
C_{kj\alpha} = \alpha^2_{00} \left( k-j+1 \right) + \alpha - \gamma ,
\] (42)

\[
F_{\gamma_0q} = \exp\left\{ -(\gamma - \alpha + 2q + 2j)\Gamma t/2 \right\}.
\] (43)

where
\[
f_1 = q_0^1 \alpha^- , \quad f_2 = q_0^2 \alpha^- , \quad f_3 = q_0^3 \alpha^- \exp\left\{ -\hbar \omega_0^1/kT \right\} , \quad f_4 = q_0^4 \alpha^- \exp\left\{ -\hbar \omega_0^1/kT \right\} ,
\]
\[
\omega_0^0 = \omega_0^0 \alpha^- , \quad \omega_0^2 = \omega_0^2 \alpha^- , \quad \omega_0^3 = \omega_0^3 \alpha^- , \quad \omega_0^4 = \omega_0^4 \alpha^- ,
\]
\[
\epsilon_2 = \exp\left\{ -\gamma \hbar \omega_{00}/kT \right\}.
\] (44)

As we can see from eqs. (39)–(44) the IR absorption band of the H-bonded complex consists potentially of the four lines shifted by the tunneling in the ground and/or first excited states. Each vibrational transition line consists of many lines peaked at \( \omega_{00}^m - 2\alpha^2_{00} \omega_{00} + (\gamma - \alpha) \omega_{00} \).

Each line consists of a number of Lorentzians differing by their intensities, which depend on the products of the form \( A_{\gamma_0\gamma} \), \( \epsilon_2(\gamma) \) and \( C_{kj\alpha} \) with the half-width
\[
\Gamma_{\gamma_0q} = \left( \gamma - \alpha \right) + 2q + 2j \Gamma.
\] (45)

2.4. Fluctuations of the energy levels and the Born–Oppenheimer energy potential

So far, we have taken into account indirect influence of the bath on the \( q \) oscillator involved in H-bond through the coupling of it with the \( Q \) mode relaxing to the solvent. However, the solvent acts also directly through creating a fluctuating electric field, which perturbs the energy levels of the ground and excited vibrational states.
of proton motion as well as change the potentials of the H-bond protons and destroy their symmetry. All these
effects are very important for the IR spectra of H-bonds of the type \((BH...B)^+\) and \((BH...B)^-\) because the high
polarizability of the H-bond causes strong induction effects of such H-bonds by ions and dipoles of the molecular
environment. We have assumed that the stretching mode \(\nu_s\) is coupled only to \(\nu_o\). In fact, it is also coupled,
however weakly, to all of the other external vibrations of the bridge. It does not seem to be reasonable to treat
them explicitly (too much parameters). It is much better to consider them as a cause of fluctuations of the Born–
Oppenheimer potential.

The influence of these factors on the IR absorption band shape is formally included by averaging over bath in
eq. (39). In this section we will concentrate on the averaging of the dipole correlation function \(G(t)\) over the
bath. Using the static double well potential (fig. 1) that is, a double well in the case of Born–Oppenheimer \(q\)
and \(Q\) modes separation and working in the basis given by eq. (8) one can write the following Hamiltonian for
the isolated system,

\[
\hat{h}_0 = \begin{pmatrix}
E_{0+} & 0 \\
0 & E_{0-}
\end{pmatrix},
\]

where \(E_{0+}\) and \(E_{0-}\) are the energy of the \(0^+\) and \(0^-\) levels when the \(q\) mode is in its ground state. Let us simulate
the effect of the bath by assuming that the matrix elements of the Hamiltonian undergo fluctuations

\[
\hat{h}_0 = \begin{pmatrix}
E_{0+} + \varepsilon_{0+}(t) & \theta(t) \\
\theta(t) & E_{0-} + \varepsilon_{0-}(t)
\end{pmatrix}.
\]

The same expression one can write for the \(q\) mode in its first excited state.

In order to calculate the time evolution of the energy matrix elements one has to solve a Liouville equation
with stochastic matrix elements. We have used the method proposed recently by Lami and Villani [21] with

\[
\frac{\partial \rho}{\partial t} = A \rho,
\]

where

\[
\rho = \begin{pmatrix}
\rho_{++}(t) \\
\rho_{+-}(t) \\
\rho_{-+}(t) \\
\rho_{--}(t)
\end{pmatrix},
\]

and the stochastic vector

\[
r(t) = \begin{pmatrix}
\varepsilon_{0+}(t) \\
\varepsilon_{0-}(t) \\
\theta(t)
\end{pmatrix}.
\]

The matrix \(A\) is given in our case by the expression

\[
A = -\frac{i}{\hbar} \begin{pmatrix}
0 & 0 & -\theta(t) & \theta(t) \\
0 & 0 & \theta(t) & -\theta(t) \\
-\theta(t) & \theta(t) & [E_{0+} + \varepsilon_{0+}(t)] - [(E_{0-} + \varepsilon_{0-}(t)] \\
\theta(t) & -\theta(t) & 0 & [E_{0+} + \varepsilon_{0+}(t)] - [(E_{0-} + \varepsilon_{0-}(t)]
\end{pmatrix}.
\]

If the stochastic vector \(r(t)\) is a Markov process, then it has been shown [22] that the joint process \((\rho, r)\) is also
Markovian and its probability density \(P(\rho, r, t)\) (i.e. the probability density that at time \(t\) the density matrix
will be that specified by the vector \(\rho\) for the realization of \(r\) indicated by \(r\)) satisfies the equation
where \( \partial P(\rho, r, t) / \partial t = - \sum \frac{A_{\mu \nu}(r)}{\partial \rho_{\nu}} P(\rho, r, t) + \dot{W} P(\rho, r, t) \),

\[ (52) \]

where \( \dot{W} \) is the operator which appears in the master equation for the transition probability density of \( r \), i.e.

\[ \dot{H}(r, t/r_0, 0) = \dot{W} II(r, t/r_0, 0) \].

\[ (53) \]

Let us return to the special situation considered in our model. The values of vibrational frequencies appearing in eq. (44) fluctuate with time according to the fluctuations of the energy levels governed by the Hamiltonian (47). Thus, we may write

\[ \omega_0^m(t) = \langle \omega_0^m \rangle + \Delta \omega^m(t) \],

\[ (54) \]

where

\[ \Delta \omega^m(t) = \omega_0^m(t) - \langle \omega_0^m \rangle \].

Returning to eq. (39) we can perform the averaging over the environment. We can see that environment averaging over the bath has to be performed on the term \( B^m_{\mu} \) (eq. (41)). Thus, we have

\[ \langle B^m_{\mu} \rangle = f_m \exp \left\{ -i [ -2 \alpha^2 \omega_0 + (\gamma - \alpha) \omega_0 ] t \right\} \exp (-i \omega_0^m t) \].

\[ (55) \]

The average of the exponential in eq. (55) is now expressed as the exponential of an average (central limit theorem - cumulant expansion [23])

\[ \langle B^m_{\mu} \rangle = f_m \exp \left\{ -i [ -2 \alpha^2 \omega_0 + (\gamma - \alpha) \omega_0 ] t \right\} \exp \left( -i \langle \omega_0^m \rangle t - \int_0^t dt_1 \int_0^{t_1} dt_2 \langle \Delta \omega^m(t_1) \Delta \omega^m(t_2) \rangle \right) \].

\[ (56) \]

It is convenient to express the vibrational transitions \( \omega_0^m \) in the following way

\[ \omega_0^m(t) = \langle \omega_0^m \rangle + \Delta \omega^m(t) + \Delta \omega^m(t) \],

where

\[ \langle \omega^{1t} \rangle = 0, \quad \Delta \omega^{1t}(t) = 0, \]

\[ \langle \omega^{2t} \rangle = - \langle \omega_1^t \rangle, \quad \Delta \omega^{2t}(t) = - \Delta \omega_1^t(t), \]

\[ \langle \omega^{3t} \rangle = - \langle \omega_0^t \rangle, \quad \Delta \omega^{3t}(t) = - \Delta \omega_0^t(t), \]

\[ \langle \omega^{4t} \rangle = - \langle \omega_0^t + \omega_1^t \rangle, \quad \Delta \omega^{4t}(t) = - [ \Delta \omega_0^t(t) + \Delta \omega_1^t(t) ] \].

(57)

Substituting (56) into (55), the average \( \langle B^m_{\mu} \rangle \) will take the form

\[ \langle B^m_{\mu} \rangle = f_m \exp \left\{ -i [ -2 \alpha^2 \omega_0 + (\gamma - \alpha) \omega_0 ] t \right\} \]

\[ \times \exp \left( -i \langle \omega_0^m \rangle t - \int_0^t dt_1 \int_0^{t_1} dt_2 \left\{ \langle \Delta \omega^m(t_1) \Delta \omega^m(t_2) \rangle \right\} \right), \]

\[ (58) \]

where \( \omega_0 \) and \( \omega_1 \) are the tunneling frequencies of the ground and first excited vibrational states.

Two different processes govern the time dependence of the correlation functions \( \langle \Delta \omega_0^m(t_1) \Delta \omega_0^m(t_2) \rangle \) and \( \langle \Delta \omega^m(t_1) \Delta \omega^m(t_2) \rangle \). The tunneling frequency correlation function \( \langle \Delta \omega_0^m(t_1) \Delta \omega_0^m(t_2) \rangle \) reflects the fluctuations of the energy levels of the ground or first excited vibrational state for the fixed Born-Oppenheimer potential. In the frequency correlation function \( \langle \Delta \omega^m(t_1) \Delta \omega^m(t_2) \rangle \) both vibrational states are involved and the transition from the ground to first excited state occurring between different Born-Oppenheimer potential
(as an effect of the coupling to all of the other external vibrations) can be treated as a transition in the potential fluctuating with time.

Because vibrational transitions are instantaneous with respect to tunneling we can assume that there is no “cross” correlations $\langle \Delta \omega^{(1)} \Delta \omega^{(2)} \rangle$ in eq. (58).

Now, let us concentrate on the tunneling frequency correlation function. The energy level fluctuations are created by the solvent molecular motions and we can model this situation by assuming that only the diagonal matrix elements of $\hat{H}_0$ and $\hat{H}_1$ (eq. (47)) are stochastic. According to eq. (47) we can write

$$\Delta \omega_0(t) = \omega_0(t) - \langle \omega_0 \rangle = [e_{0-}(t) - e_{0+}(t)]/\hbar,$$

$$\Delta \omega_1(t) = \omega_1(t) - \langle \omega_1 \rangle = [e_{1-}(t) - e_{1+}(t)]/\hbar.$$  

From eqs. (59) and (60) results that the stochastic vector $r$ (eq. (50)) fluctuates between four realizations:

$$r_1 = \begin{pmatrix} a \\ a \end{pmatrix}, \quad r_2 = \begin{pmatrix} a \\ -a \end{pmatrix}, \quad r_3 = \begin{pmatrix} -a \\ a \end{pmatrix}, \quad r_4 = \begin{pmatrix} -a \\ -a \end{pmatrix}$$

with the probability

$$w = \frac{f_a}{4} \begin{pmatrix} -3 & 1 & 1 & 1 \\ 1 & -3 & 1 & 1 \\ 1 & 1 & -3 & 1 \\ 1 & 1 & 1 & -3 \end{pmatrix},$$

where $a$ is the tunneling frequency jump due to the fluctuations of energy levels caused by the solvent, $f_a$ is the probability per unit time of making the jump. As is shown in appendix A, the tunneling frequency correlation function is given by

$$\langle \Delta \omega^{(1)}(t_1) \Delta \omega^{(2)}(t_2) \rangle = 2a^2 \exp\left[-f_a(t_1 - t_2)\right],$$

where $f_a$ can be characterized by the correlation time,

$$\tau_a = 1/f_a.$$  

Let us concentrate on the correlation function $\langle \Delta \omega^{(1)}(t_1) \Delta \omega^{(2)}(t_2) \rangle$. The vibrational frequency fluctuations $\Delta \omega$ due to the change of the energy potential going from the ground to first vibrational state can be simulated by a two-level problem, in which the nondiagonal matrix element $\delta(t)$ (eq. (47)) takes a nonzero value. Thus, the stochastic vector $r$ (eq. (50)) fluctuates between two realizations,

$$r_1 = (b), \quad r_2 = (-b).$$

As we show in appendix B, the correlation function $\langle \Delta \omega^{(1)}(t_1) \Delta \omega^{(2)}(t_2) \rangle$ is given by

$$\langle \Delta \omega^{(1)}(t_1) \Delta \omega^{(2)}(t_2) \rangle = -b^2 \exp\left[-f_b(t_1 - t_2)\right].$$

Substituting (63) and (66) into (58) we obtain

$$\langle B_{m(\nu)} \rangle = f_m \exp\left[-i\langle \omega_0 \rangle + \langle \omega^{\text{vib}} \rangle - 2\alpha_0 \omega_0 + (\gamma - \alpha) \omega_0 \right] t \times \exp\left[-2a^2 [\tau_2 (e^{-i\omega_0 t} - 1) + \tau_3 f] \right] \exp\left[-b^2 [\tau_2^2 (e^{-i\omega_0 t} - 1) + \tau_3 f] \right].$$  

Finally, substituting (67) into (39), the dipole correlation function takes the form
$$G(t) = \left( \frac{\partial M}{\partial q} \right)^2 \sum_{\gamma=0}^{\infty} \epsilon_{2}(\gamma) \sum_{m=1}^{A} \left[ \sum_{\alpha=0}^{\gamma} \sum_{\beta=0}^{\gamma} \sum_{\delta=0}^{\gamma} \sum_{\epsilon=0}^{\gamma} A_{\alpha\beta\gamma\delta} \langle B_{\alpha\beta\gamma\delta} \rangle C_{\alpha\beta\gamma\delta} \right.$$  
$$+ \sum_{\alpha=\gamma+1}^{\infty} \sum_{\beta=0}^{\gamma} \sum_{\delta=0}^{\gamma} \sum_{\epsilon=0}^{\gamma} A_{\alpha\beta\gamma\delta} \langle B_{\alpha\beta\gamma\delta} \rangle C_{\alpha\beta\gamma\delta} \right) \), \quad (68)$$

where $A_{\alpha\beta\gamma\delta}$, $\epsilon_{\alpha}$, $\epsilon_{\beta}$, $f_{m}$, $C_{\alpha\beta\gamma\delta}$ have the same meaning as in eqs. (39)-(41), whereas $\langle B_{\alpha\beta\gamma\delta} \rangle$ is given by eq. (67).

Substituting the time correlation function $G(t)$ (eq. (68)) into eq. (1) we can calculate the IR absorption band profile.

We would like to stress that eq. (68) is general and it can be used both for a single- and a double-well potential. If there is no tunneling in the proton motion, all of the $f_{m}$ (except $f_{1}$) and $\langle \omega^{m} \rangle$ vanish and we obtain the expression for the single minimum potential.

3. Conclusions

The basic result of this paper for the IR absorption spectrum of H-bonded complexes is contained in eq. (68). The present development, in comparison with other treatments which are currently in the literature, is more general as opposed to developments based on specific models which treat only one aspect of the problem. Specific important points are:

(i) Inclusion by the stochastic Liouville equation of inhomogeneous broadening effects which arise naturally due to fluctuations of the potential well, in which proton motion occurs and molecular motions of the solvent species.

(ii) Combining into one treatment of the quantum mechanical models based on the idea of the anharmonic coupling between vibrational modes and the models based on the assumption of the statistical variety of the potential wells for proton in disordered media.

(iii) The introduction of nonlocalized terms due to tunneling which may be responsible at least partially for the asymmetry of $I(\omega)$ for strong H-bonds.

Due to the symmetry reasons some of them may be negligible or weaker than the others [18]. Each of the vibrational band consists of a great number of lines peaked according to the rule

$$\omega_{\alpha\gamma} = \langle \omega_{\alpha} \rangle + \langle \omega^{m} \rangle - 2\alpha\beta\gamma\delta\omega_{0\alpha} + (\gamma - \alpha)\omega_{0\alpha}, \quad (69)$$

with its own half-width

$$\Gamma_{\alpha\gamma} = [(\gamma - \alpha) + 2q + 2j]\Gamma, \quad (70)$$

due to the coupling "$q$ mode--$Q$ mode--bath". Thus, in the cases when the proton tunneling is not effective and the fluctuations from the environment play no role, the total band intensity is the superposition of many Lorentzian bands as was shown recently by Bouil et al. [13]. Generally however, the band width is modified by the fluctuations of the energy levels and as a result of the fluctuations in the vibrational frequency due to the different Born–Oppenheimer potential in the ground and the first excited vibrational state.

These effects are given by the correlation functions (eq. (67))

$$G_{m}(t) = \exp\{-2\alpha^{2}[\tau_{a}^{2}(e^{-\tau_{a}^{2}} - 1) + \tau_{a}t]\}, \quad G_{b}(t) = \exp\{-b^{2}[\tau_{b}^{2}(e^{-\tau_{b}^{2}} - 1) + \tau_{b}t]\}. \quad (71)$$

Two limiting situations can then be written down, namely, that the correlation times $\tau_{a}$ and $\tau_{b}$ decay much slower or much faster than the amplitude coherence, i.e.

$$\langle \Delta \omega^{2} \rangle_{a}^{1/2} \tau_{a} \gg 1, \quad \langle \Delta \omega^{2} \rangle_{b}^{1/2} \tau_{b} \gg 1, \quad \text{slow limit},$$

$$\langle \Delta \omega^{2} \rangle_{a}^{1/2} \ll 1, \quad \langle \Delta \omega^{2} \rangle_{b}^{1/2} \tau_{b} \ll 1, \quad \text{fast limit}. \quad (72)$$
In our case, the amplitudes are given by the tunneling frequency jump \(a\) and the vibrational transition frequency jump \(b\),

\[
\langle \Delta \omega^2 \rangle_a^{1/2} = 2^{1/2}a, \quad \langle \Delta \omega^2 \rangle_b^{1/2} = b.
\]

(73)

In the slow limit, eqs. (71) simplify to

\[
G_m(t) = \exp(-2a^2t^2/2), \quad G_0(t) = \exp(-b^2t^2/2)
\]

(74)

with an associated Gaussian profile. Eqs. (74) describe static situations, that is to say, a time independent distribution \(\langle \Delta \omega^2 \rangle_a^{1/2}\) and \(\langle \Delta \omega^2 \rangle_b^{1/2}\) of the line shifts around the unperturbed vibrational transition frequency. The fast limiting situation predicts Lorentzian band profiles

\[
G_m(t) = \exp(-2a^2\tau_a t), \quad G_0(t) = \exp(-b^2\tau_b t)
\]

(75)

with the half-widths

\[
\Delta \tau_a = 4a^2, \quad \Delta \tau_b = 2b^2.
\]

(76)

Numerical calculations based on the theory presented in this paper will be shown in our further paper [24].

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Appendix A

Here, we will derive eq. (63) for the tunneling correlation function \(\langle \Delta \omega^m(\tau_1)\Delta \omega^m(\tau_2) \rangle\). The correlation function can be calculated if we know the initial distribution \(P_0\) of the frequencies and the conditional transition probabilities \(P(j/k)\) at time \(t = \tau_1 - \tau_2\), since \(\langle \Delta \omega^m(\tau_1)\Delta \omega^m(\tau_2) \rangle = \langle \Delta \omega^m(0)\Delta \omega^m(t) \rangle\). Thus, one may write

\[
\langle \Delta \omega^m(\tau_1)\Delta \omega^m(\tau_2) \rangle = \sum_{j,k} \Pi(j/k)\Delta \omega^m(j)\Delta \omega^m(k)P_0(\Delta \omega^m(k)),
\]

(A.1)

where \(\Pi(j/k)\) is governed by the master equation (53) with \(\dot{W}\) given by eq. (62). \(P_0(\Delta \omega^m(k))\) is equal to 1/4 since each from the four realizations of the stochastic vector (eq. (61)) has the same probability at time \(t=0\). Solving the master equation by matrix diagonalization

\[
\frac{\partial \Pi(j/k)}{\partial t} = \sum_l W(j/l)\Pi(l/k)
\]

(A.2)

we have

\[
\Pi(l/k) = \sum_m c_{lm} \exp(\epsilon_{mm}t)\tilde{c}_{mk},
\]

(A.3)

where

\[
\begin{pmatrix}
0 & 0 & 0 & 0 \\
0 & -f & 0 & 0 \\
0 & 0 & -f & 0 \\
0 & 0 & 0 & -f \\
\end{pmatrix}
\]  \hspace{1cm} \text{(A.4)}

and

\[
\begin{pmatrix}
1 & 1 & 1 & 1 \\
1 & 1 & -1 & -1 \\
1 & -1 & -1 & 1 \\
1 & -1 & 1 & -1 \\
\end{pmatrix}
\frac{1}{\sqrt{2}}
\]

\hspace{1cm} \text{(A.5)}

Substituting (A.3) into (A.1) we obtain

\[
\langle \Delta \omega^{m1}(\tau_1) \Delta \omega^{m1}(\tau_2) \rangle = 2a^2 \exp \left[ -f_a(\tau_1 - \tau_2) \right].
\]  \hspace{1cm} \text{(A.6)}

**Appendix B**

Here, we will derive eq. (66) for the frequency correlation function $\langle \Delta \omega^0_1(\tau_1) \Delta \omega^0_1(\tau_2) \rangle$. We consider here the problem of vibrational transition between the ground and first excited states characterized by different potentials. Thus, the stochastic vector $r$ (eq. (50)) fluctuates between two realizations,

\[
r_1 = (b), \quad r_2 = (-b),
\]  \hspace{1cm} \text{(B.1)}

with the probability

\[
W = \frac{f_b}{2} \begin{pmatrix}
-1 & 1 \\
1 & -1 \\
\end{pmatrix}
\]  \hspace{1cm} \text{(B.2)}

and with the matrix $A$ (eq. (51))

\[
A = \frac{i}{\hbar} \begin{pmatrix}
0 & 0 & -\theta(t) & \theta(t) \\
0 & 0 & \theta(t) & -\theta(t) \\
-\theta(t) & \theta(t) & 0 & 0 \\
\theta(t) & -\theta(t) & 0 & 0 \\
\end{pmatrix}
\]  \hspace{1cm} \text{(B.3)}

The parameter $b$ in (B.1) is the jump of the vibrational frequency, when the $q$ mode of proton motion jumps from the ground to first excited state with the probability per unit time $f_b$. Thus, one can write

\[
\langle \Delta \omega^0_1(\tau_1) \Delta \omega^0_1(\tau_2) \rangle = \sum_{j,k} \Pi(j/k) \Delta \omega^0_1(i) \Delta \omega^0_1(k) P_0(\Delta \omega^0_1(k)),
\]  \hspace{1cm} \text{(B.4)}

where $P_0(\Delta \omega^0_1(k))$ is the initial distribution of the frequency $\Delta \omega^0_1$. The initial distribution is taken as

\[
P_0(\Delta \omega^0_1(k)) = \delta(\Delta \omega^0_1(k) - b)
\]  \hspace{1cm} \text{(B.5)}

and

\[
\langle \Delta \omega^0_1(\tau_1) \Delta \omega^0_1(\tau_2) \rangle = \Pi(2/1) \Delta \omega^0_1(2) \Delta \omega^0_1(1) + \Pi(1/1) \Delta \omega^0_1(1) \Delta \omega^0_1(1),
\]  \hspace{1cm} \text{(B.6)}

where $\Pi(2/1)$ is the conditional probability that at time $t = \tau_2 - \tau_1$ the $q$ mode jumps from ground to its first excited state. The conditional probability $\Pi(j/k)$ is governed by (B.2). Solving the master equation, we have

\[
\Pi(j/k) = \sum_m c_{lm} \exp(W_{mm}t) c_{mk},
\]  \hspace{1cm} \text{(B.7)}
where

\[ w = \mathbb{W} \mathbb{C} = \begin{pmatrix} -f_b & 0 \\ 0 & 0 \end{pmatrix} \quad \text{(B.8)} \]

and

\[ c = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ -1 & -1 \end{pmatrix} \quad \text{(B.9)} \]

Then, substituting (B.7) into (B.6) we obtain

\[ \langle \Delta \omega_b(r_1) \Delta \omega_b(r_2) \rangle = b^2 \exp \left[ -f_b(r_1 - r_2) \right] \quad \text{(B.10)} \]

References