A level-crossing model for infrared pump-probe spectroscopy of water

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Abstract.   The level-crossing model is applied to pump-probe spectroscopy of the intramolecular vibration of hydrogen-bonded HDO molecules dissolved in H_2O. The parameters of the model are extracted from experimental data. It is shown that within the linear approximation for the dependence of the vibrational transition frequency on the hydrogen-bridge length, the pumping light saturates not only the $v = 0 \rightarrow v = 1$, but also the $v = 1 \rightarrow v = 2$ transition, resulting in the suppression of superabsorption in transmission spectra. The non-linearity of the transition frequency may be introduced through either anharmonic corrections to the vibrational energy levels, or different curvatures of parabolic levels. As the result, the $1 \rightarrow 2$ transition shifts out of resonance with the pumping field, no population of the $v = 2$ level appears, and the transmission spectra fit better to experimental observations.

1. Introduction

It has been known for a long time that intramolecular vibrational transitions are strongly broadened in the presence of the intermolecular hydrogen bond. With new powerful experimental techniques, such as coherent pump-probe spectroscopy, it became possible to observe non-stationary infrared spectra with extremely high resolution in both frequency and time domains. This provides a unique opportunity for direct experimental time-resolved investigation of liquid structure and molecular dynamics on the subpicosecond timescale [1–3]. One of the characteristic features of the transmission spectra obtained in such experiments is the existence of *superabsorption* in the low-frequency wing, i.e. the absorption of the probe light in that spectral region is stronger after pumping than before it. This effect is conventionally explained by absorption from the first excited vibrational level, $v = 1$, populated by pumping, to the next one, $v = 2$ (see [1–3] and references therein).

According to a widely recognized model [4–6], the dominant broadening mechanism is based on the coupling of the intramolecular stretch vibration v_s with the intermolecular low-frequency hydrogen-bridge stretching mode v_σ. Thus, the frequency migration over the inhomogeneous spectral structure of the intramolecular mode v_s bears important information on the dynamics of intermolecular hydrogen bonds. The modulation of the intramolecular vibrational frequency, Ω, by the slow hydrogen-bridge coordinate (length), q, is often considered as a classical Gaussian random process [4–7]. Recently, such a model was employed in quantum mechanical calculations of the third-order optical susceptibility to describe pump-probe experiments [3, 8]. The problem then becomes in fact very similar to that of Doppler

broadening. In both cases the spectral frequency is proportional to a random variable (either the particle velocity or the H-bond length).

However, such a simple framework is not well verified in the case of non-linear spectroscopy. The population of the upper level during and after pumping is not negligible. It is natural to assume that both the lower and the upper vibrational levels are coupled to the H-bond coordinate, q, though in general differently. The thermal relaxation of hydrogen-bridge lengths for species in the vibrational ground and excited states constitutes then *two* random processes. Moreover, under the action of the strong pumping field, the population distributions in both levels are strongly distorted and are not Gaussian any longer.

Recently, we proposed an alternative model [9], in which these effects are dealt with explicitly. We assume the hydrogen-bridge oscillator coordinate to be overdamped, since otherwise the inhomogeneous spectrum of the vibrational transition should have had regular spiking structure reflecting the underlying oscillations of the H-bond length [7]. Next, we assume the random process, $q(t)$, to be strongly correlated and describe it by the usual Fokker–Planck equations. Since the transverse relaxation time of the ν_s-transition is the shortest timescale in the problem, the off-diagonal components of the density matrix can be neglected and the evolution equations reduce to the set of 'rate' equations for population distributions only. They are coupled by the light-induced transitions, which occur only at the point q_L of exact resonance of the laser frequency, Ω_L, with the ν_s-vibrational transition frequency, $\Omega(q)$. Thus, we consider the saturation of the absorption spectrum as a classical level-crossing problem with diffusional motion along the levels $U_i(q)$. The vertical distance between the levels, $U_1(0) - U_0(0)$, is given by the average frequency of ν_s-vibration, while the horizontal shift between their minima (in terms of the coordinate q) is determined by the coupling of the ν_s-vibration with the H-bond oscillator.

In previous works we investigated a model problem with linear coupling and parabolic energy levels $U_i(q)$. Such assumptions result in simple linear dependence of the transition frequencies on the coordinate (the 'linear model' hereafter):

$$\Omega_i(q) = U_{i+1}(q) - U_i(q) = Fq.$$

It is well known, however, that this dependence is more complex (see, e.g., [10]). In this work we use parameters for the level-crossing model which correspond to real experiments carried out on HDO species dissolved in water. We show that within the linear model the absorption of the pumping light occurs not only from the ground state, but also from the first excited level, $v = 1$ (to the next one). This results in saturation of the $1 \to 2$ transition as well as the $0 \to 1$ transition, and suppression of the superabsorption of the probe light, especially at the pumping frequency adjusted to the red wing of the inhomogeneous spectrum. To resolve the contradiction with experimental observations, we model a non-linear $\Omega_i(q)$ dependence considering the third-order corrections to the energy levels $U_i(q)$. We show, however, that the necessary correction is small and that the main effect comes not from modification of level distributions, but from the non-linearity of the $\Omega_i(q)$ dependence. Hence, similar results should be obtained, e.g., for parabolic levels, $U_i(q)$, but with different curvatures, since this results in the same quadratic $\Omega_i(q)$ dependence. When the non-linearity of $\Omega_i(q)$ is taken into account, the $1 \to 2$ transition shifts out of resonance with the pumping field. As a result, the situation surprisingly becomes qualitatively similar to that of the strong hydrogen bond, extensively studied in our previous works. In the latter case, the successive horizontal shifts of energy levels, $U_i(q)$, are so large due to the strong coupling with the ν_σ-mode that the pumping light is out of resonance with the $1 \to 2$ transition even within the parabolic level approximation.

2. The theoretical model

We consider the energies of the intramolecular vibrational states as functions of the fluctuating hydrogen-bridge coordinate, q. They may be taken in the form

$$U_i(q)/\hbar = \frac{\beta(q - q_i)^2}{2} + \alpha(q - q_i)^3 + \Delta G_i \tag{1}$$

where β is the force constant of the hydrogen-bridge oscillator, α is the third-order expansion coefficient accounting for the anharmonicity, and q_i is the (local) minimum of the potential. It is convenient to choose the origin at $q_0 = 0$, $\Delta G_0 = 0$. The expression (1) can be viewed as the two-lowest-term expansion near the minimum of a general intermolecular potential, e.g. a Morse potential or that obtained from *ab initio* calculations. The potential curves (1) result in a 'quadratic approximation' for the transition frequencies:

$$\Omega_i(q) = [U_{i+1}(q) - U_i(q)]/\hbar = \Omega_i(0) + Fq + \epsilon q^2 \tag{2}$$

where, within the model (1),

$$\Omega_i(0) = \Delta G_{i+1} - \Delta G_i + \beta(q_{i+1}^2 - q_i^2)/2 + \alpha(q_i^3 - q_{i+1}^3)$$

$$F = \beta(q_i - q_{i+1}) + 3\alpha(q_{i+1}^2 - q_i^2)$$

$$\epsilon = 3\alpha(q_i - q_{i+1}).$$

The quantities of interest are the statistical distributions of the level populations in the subensembles of species in the ground and excited vibrational states, $n_i(q)$. Their evolution in potential (1) can be described by the system of equations

$$\frac{\partial n_0(x, \tau)}{\partial \tau} = \hat{L}_0 n_0(x, \tau) - w_{01}(x)[n_0(x, \tau) - n_1(x, \tau)] + \frac{n_1(x, \tau)}{\tau_1} \tag{3}$$

$$\frac{\partial n_1(x, \tau)}{\partial \tau} = \hat{L}_1 n_1(x, \tau) + w_{01}(x)[n_0(x, \tau) - n_1(x, \tau)]$$
$$- w_{12}(x)[n_1(x, \tau) - n_2(x, \tau)] - \frac{n_1(x, \tau) - n_2(x, \tau)}{\tau_1} \tag{4}$$

$$\frac{\partial n_2(x, \tau)}{\partial \tau} = \hat{L}_2 n_2(x, \tau) + w_{12}(x)[n_1(x, \tau) - n_2(x, \tau)] - \frac{n_2(x, \tau)}{\tau_1}. \tag{5}$$

Under the assumption of overdamped oscillator motion, the evolution operators become the operators of the diffusion in the one-dimensional space of the H-bond length q:

$$\hat{L}_i n_i = \frac{\partial}{\partial x} e^{-U_i(x)} \frac{\partial}{\partial x} e^{U_i(x)} n_i.$$

The dimensionless variables in (3), (4) are defined as

$$\tau_1 = \nu_0 T_1 \qquad \tau = \nu_0 t \qquad x = q\sqrt{\beta/T^*}$$

where T_1 is the lifetime of the vibrational excitation, $T^* = k_B T/\hbar$ is the temperature in frequency units, and ν_0 is the diffusion coefficient. For simplicity we assume in (3)–(5) the same excitation lifetime, T_1, for both excited levels, $v = 1, 2$.

The field-induced transitions between adjacent levels $i, i + 1$ are assumed to occur at a single point $x_Q^{(i)}$, at which the field of frequency Ω_L is in resonance with the vibrational transition frequency (2), so

$$w_{01}(x) = w_0\delta(x - x_Q^{(0)}) \qquad w_{12}(x) = Dw_0\delta(x - x_Q^{(1)}) \qquad w_0 = \frac{u_0}{\nu_0}\sqrt{\frac{\beta}{T^*}}. \tag{6}$$

Here, $u_0 = 2\pi |V_{01}|^2/\beta q_1$, and $|V_{01}| = |d_{01}E_0|/\hbar$ is the Rabi frequency which is proportional to the dipole interaction with the light wave, $E = E_0(t)\exp(-i\Omega_L t)$. The factor $D = |d_{12}|^2/|d_{01}|^2$ in (6) takes into account the difference between the $0 \to 1$ and $1 \to 2$ transition probabilities (if the H-bond oscillator were harmonic, we would have $D = 2$). Since the $\Omega_i(x)$ dependence is quadratic, there are, generally speaking, *two* resonances with laser frequency Ω_L. However, with the parameters chosen for water, the second one appears far away from the equilibrium points q_i, in the region where the populations $n_i(q)$ are zero. Moreover, the expansion (1) is valid only near the bottom of the potential well and the second resonance point would be an artifact.

In the previous works [9] we considered the reduced system of diffusional equations (for $v = 0, 1$ levels only), setting $w_{12}(x) \equiv 0$, $n_2(x, \tau) \equiv 0$. Here, with the parameters corresponding to the spectroscopy of water, the field-induced $1 \to 2$ transition will be investigated as well. We will show that only within the quadratic model, $\epsilon \neq 0$, can the whole system be reduced to two equations, (3), (4), since $w_{12}(x)$ is then negligibly small, with the result that $n_2(x) \simeq 0$.

We assume that the diffusional modulation is slow, that is $v_0 \ll \Delta = \beta |q_1|\langle q \rangle$, where Δ is the width of the inhomogeneous spectrum, which is Gaussian within the linear model, $\epsilon = 0$. For water, $\Delta \sim 200$ cm^{-1}, and the characteristic diffusional time $1/v_0 \sim 1$ ps. Hence, no motional narrowing arises and the quasistatic limit can be safely used, i.e. the shape of the optical absorption is solely determined by the instantaneous difference of level populations.

For the absorption of the weak probe beam with a frequency Ω, we have

$$I(\Omega, \tau) = \hbar\Omega v_0 w_0 \left\{ n_0(x(\Omega), \tau) - n_1(x(\Omega), \tau) + D[n_1(x'(\Omega), \tau) - n_2(x'(\Omega), \tau)] \right\} \qquad (7)$$

where $n_i(x, \tau)$ are the solutions of the system (3)–(5). The solution of the same equations without pumping gives the linear absorption spectrum, $I_0(\Omega)$. There are contributions in (7) from absorption/emission on $0 \to 1$ and $1 \to 2$ transitions, and the points $x(\Omega)$ and $x'(\Omega)$ are those at which the probe field is in resonance with these transitions, respectively.

In this work we restrict our consideration to the stationary level distributions and spectra under the action of steady pumping. In addition, we follow conventional presentation of experimental data and plot not the absorption, $I(\Omega)$, but transparency:

$$S(\Omega, \tau) = I_0(\Omega) - I(\Omega, \tau).$$

3. Results

To start with, we adjust the coefficient α in (1). It was found that the $\Omega_0(q)$ dependence fits well to the experimental curve for water [10] in the relevant region $-3 < x < 3$ at dimensionless anharmonicity coefficient

$$\alpha' = \alpha\sqrt{T^*}/\beta^{3/2} = -0.03.$$

For simplicity we use the same anharmonicity coefficient for the excited levels. The difference q_1 between the potential minima in the ground and the first excited vibrational states is directly related to the width of the inhomogeneous linear absorption spectrum of the v_s-transition. In the linear model, $\epsilon = 0$, the static spectrum reproduces the shape of the Gaussian equilibrium distribution $n_0(q)$ in the ground vibrational state. The width of this Gaussian spectrum is

$$\Delta = \sqrt{\beta T^*}|q_1| = T^*|x_1|.$$

With the measured full width at half-maximum (FWHM) of the spectrum of 260 cm^{-1}, the shift in the linear model is $x_1 = -0.54$ at room temperature (it is negative, since the intermolecular hydrogen bond is known to be stronger for the excited vibrational state).

In the anharmonic case, $\alpha \neq 0$, we find numerically the equilibrium distribution $n_0(x)$, which is the stationary solution of (3) with the pumping intensity and excited-state population both set to zero. The linear absorption spectrum is simply

$$I_0(\Omega) = n_0(x(\Omega)) \frac{dx}{d\Omega}. \tag{8}$$

The linear spectrum $I_0(\Omega)$ was found to have the required FWHM at $x_1 = -0.57$.

Note, that the Jacobian $dx/d\Omega$ of the coordinate–frequency transformation is a constant in the linear model ($\epsilon = 0$), and only guarantees the proper normalization of $I_0(\Omega)$. However, at $\epsilon \neq 0$, the non-linear frequency dependence $\Omega_i(x)$ has a maximum at some point (figure 1(b)) and the Jacobian becomes singular. This behaviour is clearly unphysical, and indicates that the spectral diffusion is important and the static limit cannot be used in the vicinity of an extremum of $\Omega_i(x)$. With the chosen anharmonicity coefficient of -0.03, however, the extremum points appear far enough from the origin, within the depopulated region, where $n_i(x) = 0$.
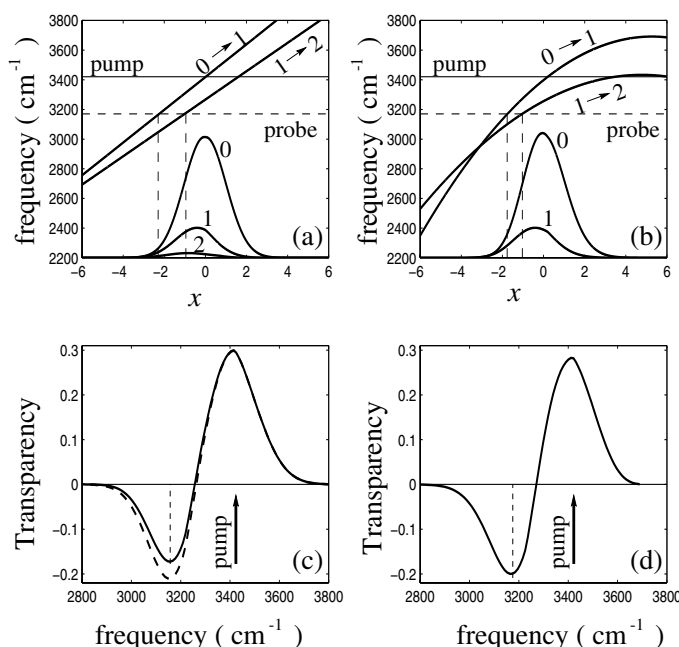

Figure 1. The $\Omega_0(x)$ and $\Omega_1(x)$ transition energies ($0 \rightarrow 1$ and $1 \rightarrow 2$, respectively) and stationary level populations $n_i(x)$ as functions of the dimensionless intermolecular hydrogen-bridge length, x, for the linear, $\epsilon = 0$ (a), and quadratic, $\epsilon \neq 0$, frequency modulation (b); (c) the transmission spectrum within the linear model with saturation of the $1 \rightarrow 2$ transition taken into account (solid line) and neglected (dashed line); (d) the transmission spectrum within the quadratic model.

The energy separation, ΔG_1, between the ground and the first excited states is fitted to give the experimental value (3420 cm^{-1}) of the central frequency of the inhomogeneous contour $I_0(\Omega)$. We found $\Delta G_1 = 16.45T^* = 3389$ cm^{-1} for the parabolic levels and $\Delta G_1 = 16.34T^* = 3366$ cm^{-1} with the anharmonicity included.

The parameters ΔG_2 and x_2 for the second excited level cannot be extracted from the linear spectrum. They become of importance under strong pumping, when the excited levels are overpopulated. At long relaxation time, $T_1 > 1/\nu_0$, the superabsorption develops in the red wing of the inhomogeneous spectrum solely due to the appearance of strong probe-field

absorption on the $1 \rightarrow 2$ transition. The position and width of the superabsorption spectral wing are determined by ΔG_2 and x_2, respectively. However, it is difficult to unambiguously identify these parameters, since the choice of all other parameters (diffusion rate, relaxation time, pumping intensity) also influences the result. We found that reasonable values are $x_2 = -1$ for the linear model and $x_2 = -0.99$ for the quadratic one, and $\Delta G_2 = 15.5T^* = 3193$ cm^{-1} for both cases.

It is interesting to note that until now the two models have seemed very similar and the parameters practically identical. The equilibrium distribution $n_0(x)$ in the lowest level is very close to the Gaussian one at the small anharmonicity chosen. All the difference comes from the modification of the dependence of the transition frequency on the coordinate, $\Omega_i(x)$. First, in the quadratic model, the growth of $\Omega_i(x)$ slows down at $x > 0$ compared to the linear model (compare figures 1(a) and 1(b)). As a result, the right-hand wing of the $n_0(x)$ distribution falls into a narrow spectral region and the corresponding linear spectrum $I_0(\Omega)$ becomes asymmetric—sharp at high frequencies and more extended towards lower ones—which is in accordance with experimental observations. This is a trivial consequence of the presence of the Jacobian $\mathrm{d}x/\mathrm{d}\Omega$ in the transformation (8). Much more interesting consequences arise in the non-equilibrium situation, under strong pumping. In the figures 1(a), 1(b) the stationary level distributions, $n_i(x)$, are shown for rather strong pumping, $w_0 = 1$. We chose the representative case of pumping at the centre of the inhomogeneous linear spectrum, $\Omega_L = 3420$ cm^{-1}. One can see that within the linear model, $\epsilon = 0$ (figure 1(a)), the pumping light is in resonance with the $1 \rightarrow 2$ transition at $x \sim 2$. Though the excited level distribution, $n_1(x)$, is small at this point, the pumping intensity is large enough to create a non-negligible population in the next excited level (marked '2' in the figure). Within the quadratic model, $\epsilon \neq 0$ (figure 1(b)), the resonance of the pumping light with the $1 \rightarrow 2$ transition occurs now at $x \sim 4$, where $n_1(x)$ is negligible, and the $v = 2$ level stays unpopulated.

Let us discuss now the absorption of the probe light. The horizontal dashed lines in the figures correspond to the probe-field frequency adjusted to the centre of the superabsorption spectral component. The resonance with the $0 \rightarrow 1$ transition occurs in the tail of the level distributions, at $x \sim -2.3$ in the linear model and $x \sim -1.8$ in the quadratic one. The bleaching appears there due to the saturation, as the populations of the $v = 0$ and $v = 1$ levels are almost equalized at that point. However, the resonance of the probe field with the $1 \rightarrow 2$ transition occurs closer to the centre of the $n_1(x)$ distribution, giving rise to a strong absorption which is absent in equilibrium ($n_1(x) \simeq 0$). Thus, the superabsorption (negative-transmission) spectral component develops. When the $v = 2$ level is populated by pumping, the $1 \rightarrow 2$ transition also becomes saturated and the superabsorption decreases (the solid line in figure 1(c)).

It can be seen from figure 1(a) that within the linear model, if the pumping frequency becomes larger, the resonance with the $1 \rightarrow 2$ transition occurs at larger H-bond lengths, x, at which the stationary level population $n_1(x)$ is negligibly small. Hence, for the pumping into the blue wing of the inhomogeneous spectrum, the absorption of the strong light from the $v = 1$ level can be neglected. For the pumping into the red wing, the situation is the opposite. The $1 \rightarrow 2$ resonance appears then closer to the maximum of $n_1(x)$, the population of the $v = 2$ level becomes larger, and the superabsorption becomes strongly suppressed. This is in contradiction to experimental observations, which show similar superabsorption components in transmission spectra regardless of the pumping frequency. This can be explained only if the non-linearity of $\Omega_i(x)$ is taken into account. Within the quadratic model, the $v = 2$ level is not populated at all pumping frequencies used in experiments (see, e.g., [2, 3]) and the resulting transmission spectra are similar, with a well developed superabsorption component (as in figure 1(d)).

Note that, with the very weak anharmonicity chosen, the stationary level distributions are practically unaffected, and the effect comes mainly from the non-linear $\Omega(x)$ dependence. Thus, our results should be valid not only for anharmonic energy levels, but also e.g. for harmonic levels, $U_i/\hbar = \beta_i(q - q_i)^2/2 + \Delta G_i$, but with different force constants $\beta_1 \neq \beta_2$. An additional advantage of the latter model is that one can use the analytical solution of reduced system (3), (4) obtained earlier [9].

To summarize, we have studied the infrared pump-probe spectroscopy of water within the framework of the level-crossing model. We have shown that the weakness of the hydrogen bond (smallness of x_i) makes the linear approximation for the ν_s-transition frequency inapplicable, as the $1 \rightarrow 2$ transition is also saturated by the pumping light in this case. As a result, the superabsorption is strongly suppressed for pumping into the red wing of the inhomogeneous spectrum. The non-linearity of $\Omega(q)$ shifts the $1 \rightarrow 2$ transition out of resonance with the pumping field. The situation then becomes similar to the previously studied case of the strong hydrogen bond [9]. In the latter case, the pumping light is out of resonance with the $1 \rightarrow 2$ transition even within the linear model due to large shifts x_i between the levels.

Acknowledgments

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