



UvA-DARE (Digital Academic Repository)

Simultaneous photon absorption as a probe of molecular interaction and hydrogen-bond cooperativity in liquids

Woutersen, S.

Publication date
2007

Published in
Journal of Chemical Physics

[Link to publication](#)

Citation for published version (APA):

Woutersen, S. (2007). Simultaneous photon absorption as a probe of molecular interaction and hydrogen-bond cooperativity in liquids. *Journal of Chemical Physics*, 127(15), 154517/1-154517/5.

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, P.O. Box 19185, 1000 GD Amsterdam, The Netherlands. You will be contacted as soon as possible.

Simultaneous photon absorption as a probe of molecular interaction and hydrogen-bond correlation in liquids

Sander Woutersen

*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam,
Nieuwe Achtergracht 127-129, 1018 WV Amsterdam, The Netherlands*

(Dated: February 6, 2008)

We have investigated the simultaneous absorption of near-infrared photons by pairs of neighboring molecules in liquid methanol. Simultaneous absorption by two OH-stretching modes is found to occur at an energy higher than the sum of the two absorbing modes. This frequency shift arises from interaction between the modes, and its value has been used to determine the average coupling between neighboring methanol molecules. We find a rms coupling strength of $46 \pm 1 \text{ cm}^{-1}$, much larger than can be explained from transition-dipole coupling, suggesting that hydrogen-bond mediated interactions between neighboring molecules play an important role in liquid methanol. The most important aspect of simultaneous vibrational absorption is that it allows for a quantitative investigation of hydrogen-bond cooperativity. We derive the extent to which the hydrogen-bond strengths of neighboring molecules are correlated by comparing the line shape of the absorption band caused by simultaneous absorption with that of the fundamental transition. Surprisingly, neighboring hydrogen bonds in methanol are found to be strongly correlated, and from the data we obtain a hydrogen-bond correlation coefficient of 0.69 ± 0.12 .

When two molecules are in close proximity, there is a finite probability for them to simultaneously absorb a single photon and 'share' its energy. For vibrational transitions, this effect was first observed more than fifty years ago in the near-infrared absorption spectra of gas mixtures [1], and later in crystalline hydrogen chloride [2] and other condensed-phase systems [3, 4]. Simultaneous absorption is observed as an absorption peak at the sum frequency of the two vibrational modes, and arises from a process in which one near-infrared photon is absorbed, and both of the molecules involved become vibrationally excited. It is obvious that simultaneous photon absorption can occur only if the two molecules involved 'sense' each other's presence, that is, if they interact [5]. Here, we show that simultaneous vibrational absorption in fact provides a unique probe of intermolecular interactions in liquids. It can be used to determine the vibrational interactions between neighboring molecules, and more importantly, it can be used to determine quantitatively the correlation between the strengths of neighboring hydrogen bonds. This hydrogen-bond correlation (or cooperativity) is believed to be a key property of hydrogen-bonded liquids [6, 7, 8], but has as yet been difficult to investigate experimentally.

We have investigated the simultaneous absorption by neighboring CD_3OH molecules in liquid $\text{CD}_3\text{OH}/\text{CD}_3\text{OD}$ mixtures. By measuring on isotopically diluted solutions of CD_3OH in CD_3OD , the concentration of $\text{OH}\cdots\text{OH}$ pairs can be varied continuously without any change in the structural properties of the liquid. The absorption spectra were measured using a Fourier-transform infrared spectrometer (Bruker Vertex 70) with a spectral resolution of 0.5 cm^{-1} . Samples were prepared by mixing appropriate amounts of CD_3OH and CD_3OD (Euriso-Top SA, >99.80%D, HDO/ D_2O content <0.03%). The weak background absorption caused by overtones and combination modes of CD-stretching vibrations [3] was eliminated by subtracting the spectrum of pure CD_3OD measured in the same sample cell as used for the mix-

tures. Samples were kept between CaF_2 windows separated by either a 2.2 or 10.0 mm thick spacer.

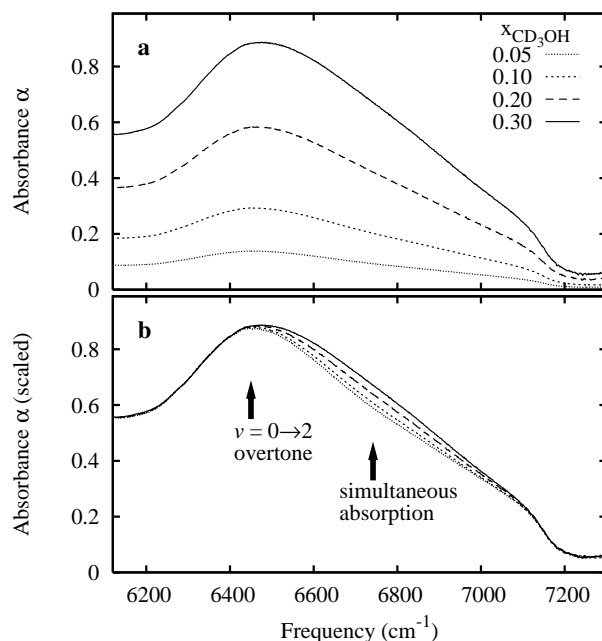


FIG. 1: (a) Absorption spectra of $\text{CD}_3\text{OH}/\text{CD}_3\text{OD}$ mixtures with increasing molar fractions $x_{\text{CD}_3\text{OH}}$ (sample-cell thickness 10.0 mm, CD_3OD absorption subtracted). (b) Same spectra, scaled to the OH-stretch overtone ($\nu = 0 \rightarrow 2$) intensity at 6300 cm^{-1} .

Figure 1a shows the near-infrared absorption spectrum of a series of $\text{CD}_3\text{OH}/\text{CD}_3\text{OD}$ mixtures with increasing molar fraction $x_{\text{CD}_3\text{OH}}$ (CD_3OD background subtracted). The most prominent feature of these spectra is the band centered at $\sim 6450 \text{ cm}^{-1}$, which is caused by $\nu = 0 \rightarrow 2$ overtone absorption of the OH-stretch mode of CD_3OH [3]. The intensity of this band increases linearly with the OH-stretch concentration $x_{\text{CD}_3\text{OH}}$. Closer inspection shows that as the concentration of

OH groups increases, a second absorption feature appears at higher frequency. This can most clearly be seen when the spectra are scaled to the overtone absorption and overlaid, see Figure 1b. As the feature appears and grows with increasing CD_3OH concentration, it can be assigned to simultaneous absorption by more than one CD_3OH molecule [3, 4].

By subtracting the absorption spectrum at low CD_3OH concentration (where the simultaneous absorption is relatively smaller) from the spectra at higher $x_{\text{CD}_3\text{OH}}$, the simultaneous absorption peak can be observed separately from the more intense overtone band. The simultaneous absorption spectrum obtained in this way is shown in Figure 2 (solid curve). Identical simultaneous absorption spectra (apart from an overall scaling factor) are obtained for all values of $x_{\text{CD}_3\text{OH}}$ up to 0.3. As the center frequency of the simultaneous absorption band ($\sim 6700 \text{ cm}^{-1}$) is close to twice the fundamental OH-stretch frequency of CD_3OH , it seems logical to assign the peak to simultaneous absorption of one photon by the OH-stretch modes of two CD_3OH molecules in close proximity [4]. To verify that indeed two, and not more, CD_3OH molecules are involved, we have determined the concentration dependence of the simultaneous absorption (Figure 3). Whereas the overtone absorption (solid points) varies linearly with $x_{\text{CD}_3\text{OH}}$ confirming that it is due to “one-molecule absorption”, the simultaneous absorption intensity (open points) varies quadratically with $x_{\text{CD}_3\text{OH}}$, which proves that the simultaneous absorption involves pairs of CD_3OH molecules (“two-molecule absorption”). It may be noted that the quadratic $x_{\text{CD}_3\text{OH}}$ dependence can already be seen directly from the *linear* dependence of the simultaneous absorption feature in the *scaled* data of Fig. 1b. We conclude that the observed simultaneous absorption peak must be due to the absorption of photons by the OH-stretching modes of pairs of CD_3OH molecules, since all other normal modes of CD_3OH have frequencies too low to give a sum frequency of $\sim 6700 \text{ cm}^{-1}$ [9].

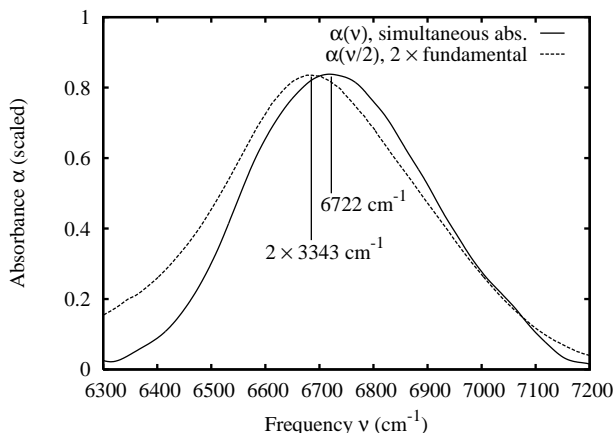


FIG. 2: Solid curve: simultaneous absorption band, obtained by subtracting the absorption with $x_{\text{CD}_3\text{OH}} = 0.05$ (scaled to overtone absorption) from that with $x_{\text{CD}_3\text{OH}} = 0.2$. Dashed curve: $\nu = 0 \rightarrow 1$ absorption spectrum, multiplied horizontally by a factor of 2. The simultaneous absorption occurs at a frequency 36 cm^{-1} higher than twice the fundamental frequency.

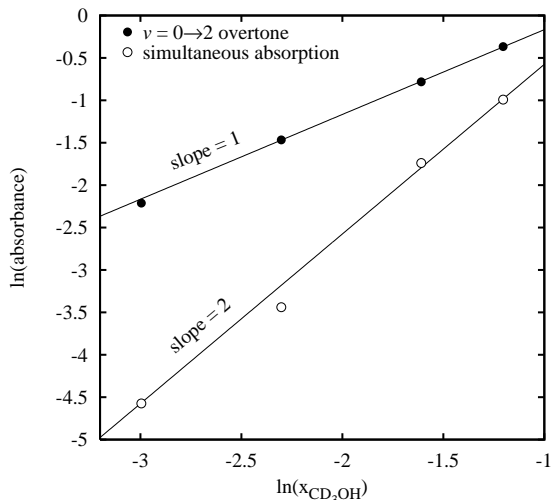


FIG. 3: Log-log plot of the intensities of the $\nu = 0 \rightarrow 2$ overtone band and of the simultaneous absorption band vs. $x_{\text{CD}_3\text{OH}}$ (the simultaneous absorption points have been vertically shifted by 1 unit for better comparison). Also shown are lines with slopes of 1 and 2, corresponding to linear and quadratic concentration dependence, respectively.

As already stated, simultaneous absorption can arise only if there is interaction between the vibrational modes involved. In the present case, the interaction required is between the OH groups of two methanol molecules, which should therefore be in sufficiently close proximity. It is easily demonstrated that only pairs of OH groups that are direct neighbors can contribute significantly to the observed simultaneous absorption band. The intensity of simultaneous absorption is proportional to the square of the interaction between the oscillators [5]. As a consequence, the simultaneous-absorption intensity due to dipolar interaction (the dominant interaction mechanism [10]) between two OH groups decays with their distance as r^{-6} ; and the non-dipolar contributions to the interaction (occurring for instance through the $\text{OH} \cdots \text{OH}$ hydrogen bonds [11, 12]) decay even faster with distance. Hence, the contribution of OH pairs that are next-nearest neighbors (or even farther apart) is negligible, and the simultaneous absorption is caused by neighboring OH groups only.

Interestingly, the simultaneous absorption occurs not at exactly twice the OH-stretch frequency ($2 \times 3343 = 6686 \text{ cm}^{-1}$), but at a frequency which is higher (6722 cm^{-1}). This can be seen clearly in Figure 2, where the simultaneous band is compared with the fundamental absorption band multiplied horizontally by 2 (dashed curve). This dashed curve corresponds to the hypothetical case of simultaneous absorption by two non-interacting CD_3OH molecules (note that because of the low $x_{\text{CD}_3\text{OH}}$, the fundamental and overtone bands are due to absorption by isolated CD_3OH molecules, the concentration of which is much higher than that of paired ones). Apparently, the interaction between the paired OH groups is large enough to change the energy of the simultaneously excited state significantly. From the position of the simultane-

ous absorption band with respect to the doubled fundamental frequency (which corresponds to the situation in absence of coupling), we can derive the (average) magnitude of the coupling between the OH-stretching modes. This coupling is dominated by the contribution lowest-order in the two OH-stretch displacements [9], and we can write it as $V = \beta q_1 q_2$, where q_1 and q_2 are the normal-coordinate displacement operators of the neighboring OH-stretch modes, and β the coupling strength. We treat the coupling as a perturbation, denoting by $|ij\rangle$ the unperturbed state having the OH-stretch mode of molecule A in the $\nu = i$ vibrational level, and the OH-stretch mode of neighboring molecule B in the $\nu = j$ vibrational level. Using harmonic approximations for the wave functions [13, 14], we have $\langle 11|q_1 q_2|11\rangle = 0$, so that the first-order correction to the energy of the simultaneously excited state $|11\rangle$ vanishes [14]. The second-order energy correction with respect to the situation without coupling is given by [15]

$$\Delta E_{11}^{(2)} = \sum_{i,j} \frac{|\langle ij|V|11\rangle|^2}{E_{11}^{(0)} - E_{ij}^{(0)}}, \quad (1)$$

where $E_{ij}^{(0)}$ is the unperturbed energy of state $|ij\rangle$. Because of the $i \rightarrow i \pm 1$ selection rule for the q_i operator, the V matrix element in the numerator is nonzero for only a few states. Of these, the only ones sufficiently close in energy to contribute significantly to the above sum are the $|02\rangle$ and $|20\rangle$ overtone states, see Figure 4. Hence, we have

$$\langle \Delta E_{11}^{(2)} \rangle = \frac{4 \langle \beta^2 \rangle}{E_{11}^{(0)} - E_{02}^{(0)}}, \quad (2)$$

where we have used harmonic vibrational wave functions to calculate the matrix element [15], and where $\langle \dots \rangle$ denotes ensemble averaging over all OH pairs contributing to the simultaneous absorption band. Since only nearest neighbors contribute significantly, this averaging is essentially over the relative orientation distribution of two neighboring OH groups. Setting $\langle \Delta E_{11}^{(2)} \rangle$ in the above expression equal to the observed shift of $36 \pm 2 \text{ cm}^{-1}$, and substituting the unperturbed values $E_{11}^{(0)}$ and $E_{02}^{(0)}$ (see Fig. 4), we obtain the root-mean-square coupling constant $\langle \beta^2 \rangle^{1/2} = 46 \pm 1 \text{ cm}^{-1}$ [16].

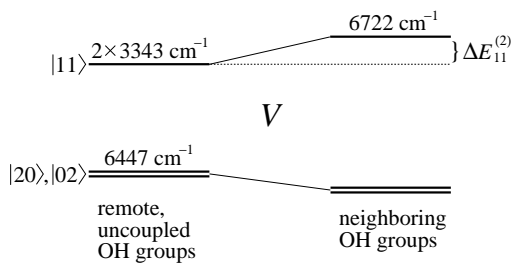


FIG. 4: Energy-level diagram (not to scale) for the OH-stretch two-exciton states. On the left the energy levels in absence of interaction between the two OH groups (isolated OH groups), on the right the energy levels when the molecules are neighbors.

This experimentally determined OH-OH interaction may be compared to the transition-dipole coupling between the two OH groups, which is in general the dominant contribution to intermolecular vibrational couplings [10, 17]. The transition-dipole coupling strength between two OH groups A and B is [17]

$$\beta_{\text{dipole}} = \frac{1}{4\pi\epsilon_0} \left[\frac{\boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_B}{r_{AB}^3} - 3 \frac{(\mathbf{r}_{AB} \cdot \boldsymbol{\mu}_A)(\mathbf{r}_{AB} \cdot \boldsymbol{\mu}_B)}{r_{AB}^5} \right], \quad (3)$$

where \mathbf{r}_{AB} is the distance vector between the transition dipoles $\boldsymbol{\mu}_A$ and $\boldsymbol{\mu}_B$. The values of $\mu_A = \mu_B = 0.264 \text{ D}$ and $r_{AB} = 2.84 \text{ \AA}$ are known [18], but the angle between the transition dipoles of the two CD_3OH molecules will vary from pair to pair. To obtain an upper limit for the transition-dipole coupling, we calculate β_{dipole} for the case of parallel transition dipoles, for which we find $\beta_{\text{dipole}} = -30 \text{ cm}^{-1}$. This upper limit has a magnitude much smaller than the observed rms value of 46 cm^{-1} . Hence, the coupling between two neighboring OH-groups is much larger than can be explained from transition-dipole coupling alone, and apparently other coupling mechanisms, like hydrogen-bond mediated coupling [11, 12, 17], contribute strongly to the molecular interaction in methanol.

Perhaps the most important and surprising aspect of simultaneous vibrational absorption is that it can be used to study correlation among hydrogen bonds. There is strong evidence [6, 7, 8] that in hydrogen-bonded liquids, hydrogen bonding occurs in a cooperative way: an OH group acting as an acceptor in a strong hydrogen bond in turn tends to form strong hydrogen bonds as a donor, and *vice versa*. It is well known that the OH-stretch frequency of a hydrogen-bonded OH group is proportional with the strength of the hydrogen bond (low OH-stretch frequency corresponding to short $\text{OH} \cdots \text{O}$ hydrogen-bond distance) [19, 20]. In hydrogen-bonded liquids, there generally exists a distribution of hydrogen-bond strengths, leading to an OH-stretch absorption band that is inhomogeneously broadened [20, 21], its width reflecting the width of the distribution of hydrogen-bond lengths. Because of the proportionality between hydrogen-bond length and OH-stretch frequency, a correlation between neighboring hydrogen bonds should give rise to an identical correlation between the OH-stretch frequencies of neighboring OH groups. Hence, by determining the correlation between the OH-stretch frequencies ν_A and ν_B of two neighboring OH groups, we can directly determine the correlation between their hydrogen bonds. To what extent two frequencies ν_A and ν_B are correlated can be quantitatively determined by comparing the width of the distribution of the sum $\nu_A + \nu_B$ with that of the fundamental distributions of ν_A and ν_B [22], that is, by comparing the widths of the simultaneous and fundamental absorption bands. We define the correlation coefficient between the frequencies ν_A and ν_B in the usual manner as

$$r = \frac{\langle (\nu_A - \langle \nu \rangle) (\nu_B - \langle \nu \rangle) \rangle}{\sigma_\nu^2}, \quad (4)$$

where $\langle \dots \rangle$ denotes ensemble averaging, and where we have

defined $\langle v \rangle = \langle v_A \rangle = \langle v_B \rangle$ and $\sigma_v = \sigma_{v_A} = \sigma_{v_B}$ (note that this is possible because the probability distributions of v_A and v_B are identical). It is easily shown that the correlation coefficient is related to the ratio of the widths of the fundamental and simultaneous absorption bands by [22]

$$\frac{\sigma_{v_A+v_B}}{\sigma_v} = \sqrt{2+2r}, \quad (5)$$

a result that is independent of the functional form of the $v_{A,B}$ probability distribution. The familiar limiting cases of this equation are: completely independent frequencies ($r = 0$), where $\sigma_{v_A+v_B}^2 = \sigma_{v_A}^2 + \sigma_{v_B}^2 = 2\sigma_v^2$ so that $\sigma_{v_A+v_B} = \sqrt{2}\sigma_v$, and completely correlated frequencies ($r = 1$), where $v_A = v_B$ so that $\sigma_{v_A+v_B} = \sigma_{2v_A} = 2\sigma_v$. The simultaneous absorption bands predicted for these two limiting r values are drawn as dotted curves in Figure 5. The observed simultaneous absorption band lies between these limiting cases, which implies that the OH-stretching frequencies of neighboring methanol molecules are partially, but not completely correlated. From the observed ratio $\sigma_{v_A+v_B}/\sigma_v$ of the widths of the simultaneous and fundamental absorption bands we can determine r by means of Eq. (5). We observe $\sigma_{v_A+v_B}/\sigma_v = 1.84 \pm 0.06$, from which a correlation coefficient $r = 0.69 \pm 0.12$ is obtained. To our knowledge, this constitutes the first experimental determination of the correlation coefficient between neighboring hydrogen bonds in a liquid, a fundamental parameter that characterizes hydrogen-bond cooperativity in a quantitative way. As yet, no theoretical prediction is available for this number, and we hope the results presented here will stimulate work in this direction.

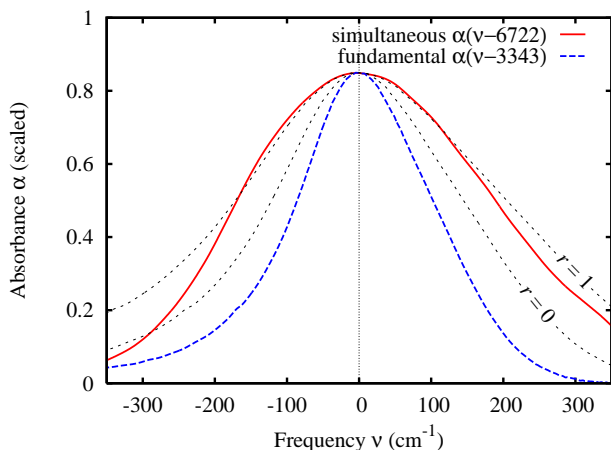


FIG. 5: Solid curve: simultaneous absorption band. Dashed curve: fundamental absorption band. Both bands have been centered at the origin. Dotted curves: fundamental absorption band, horizontally multiplied by a factor of $\sqrt{2}$ and by a factor 2. These two curves are the simultaneous absorption bands expected if the two coupled OH-oscillators are completely uncorrelated ($r = 0$), and completely correlated ($r = 1$), respectively. The experimental simultaneous absorption band is between the $r = 0$ and $r = 1$ curves, indicating that the OH-frequencies are partially correlated.

The author gratefully acknowledges Huib Bakker, Jennifer Herek and Wybren Jan Buma for critically reading the

manuscript, and Wietze Buster for technical support.

-
- [1] J. Fahrenfort and J. A. A. Ketelaar, *J. Chem. Phys.* **22**, 1631 (1954).
 - [2] A. Ron and D. F. Hornig, *J. Chem. Phys.* **39**, 1129 (1963).
 - [3] C. Bourdéron and C. Sandorfy, *J. Chem. Phys.* **59**, 2527 (1973).
 - [4] W. A. P. Luck and M. Fritzsche, *J. Mol. Struct.* **295**, 47 (1993).
 - [5] S. P. Velsko and D. W. Oxtoby, *J. Chem. Phys.* **73**, 4883 (1980).
 - [6] R. Lamanna, G. Floridi, and S. Cannistraro, *Phys. Rev. E* **52**, 4529 (1995).
 - [7] F. N. Keutsch and R. J. Saykally, *Proc. Natl. Acad. Sci. USA* **98**, 10533 (2001).
 - [8] P. Raiteri, A. Laio, and M. Parrinello, *Phys. Rev. Lett.* **93**, 087801 (2004).
 - [9] G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules* (Van Nostrand Reinhold, New York, 1945).
 - [10] H. Torii, *J. Phys. Chem. A* **110**, 9469 (2006).
 - [11] A. C. Belch and S. A. Rice, *J. Chem. Phys.* **78**, 4817 (1983).
 - [12] S. Woutersen and H. J. Bakker, *Nature* **403**, 507 (1999).
 - [13] P. Hamm, M. Lim, W. F. DeGrado, and R. M. Hochstrasser, *Proc. Natl. Acad. Sci. USA* **96**, 2036 (1999).
 - [14] We have also calculated the first-order correction when using anharmonic vibrational wavefunctions. Using a Morse potential with parameters determined from the $v = 0, 1, 2$ levels (and the expressions given in Ref. [23]), we obtain $\langle 11|q_1q_2|11 \rangle = 0.0097$. Hence, the more precise first-order correction $\langle 11|\beta q_1q_2|11 \rangle$ is not exactly zero, but still only 1% of the second-order correction.
 - [15] L. D. Landau and E. M. Lifschitz, *Quantum Mechanics, Non-relativistic Theory* (Butterworth-Heinemann, Oxford, 1999).
 - [16] The information obtained from the simultaneous absorption spectrum is to some extent comparable to that derived from two-dimensional optical spectroscopy methods [24, 25], which can also be used to determine couplings between vibrations [13, 26, 27] and even correlations between vibrational frequencies [28]. However, since two-dimensional vibrational spectroscopy requires that the coupled vibrations have different center frequencies, it cannot be used to reveal the molecular interaction and hydrogen-bond correlation observed here.
 - [17] A. Moran and S. Mukamel, *Proc. Natl. Acad. Sci. USA* **101**, 506 (2004).
 - [18] J. E. Bertie and S. L. Zhang, *J. Mol. Struct.* **413**, 333 (1997).
 - [19] C. P. Lawrence and J. L. Skinner, *J. Chem. Phys.* **118**, 264 (2003).
 - [20] C. J. Fecko, J. D. Eaves, J. J. Loparo, A. Tokmakoff, and P. L. Geissler, *Science* **301**, 1698 (2003).
 - [21] M. L. Cowan, B. D. Bruner, N. Huse, J. R. Dwyer, B. Chugh, E. T. J. Nibbering, T. Elsaesser, and R. J. D. Miller, *Nature* **434**, 199 (2005).
 - [22] W. Feller, *An Introduction to Probability Theory and Its Applications*, vol. I (Wiley, New York, 1968).
 - [23] R. H. Tipping and J. F. Ogilvie, *J. Chem. Phys.* **79**, 2537 (1983).
 - [24] S. Mukamel, *Annu. Rev. Phys. Chem.* **51**, 691 (2000).
 - [25] A. Stolow and D. M. Jonas, *Science* **305**, 1575 (2004).
 - [26] O. Golonzka, M. Khalil, N. Demirdöven, and A. Tokmakoff, *Phys. Rev. Lett.* **86**, 2154 (2001).
 - [27] A. T. Krummel and M. T. Zanni, *J. Phys. Chem. B* **110**, 13991 (2006).
 - [28] N. Demirdöven, M. Khalil, and A. Tokmakoff, *Phys. Rev. Lett.*

89, 237401 (2002).