Accidental vibrational degeneracy in vibrational excited states observed with ultrafast two-dimensional IR vibrational echo spectroscopy

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The coupling between the OD stretch $v=2$ level and benzene-ring modes in 2-methoxyphenol-OD (hydroxyl H replaced by D) is observed with ultrafast two-dimensional (2D) IR vibrational echo spectroscopy. Because of this coupling, the 1-2 transition peak in the 2D spectrum is split into a doublet with peaks of approximately equal amplitudes. Several molecules and solvents were used to study this phenomenon. Near-IR (NIR) spectroscopy measurements and density-functional theory calculations (B3LYP/6-31+G(d,p) level) were also applied. Experimental results and calculations show that the OD stretch 1-2 transition is coupled to a combination band related to the benzene-ring motions. A simple quantum-mechanical model indicates that the combination band has a frequency of 5172 and 5176.5 cm^{-1} in CCl$_4$ and hexane, respectively. The transition between this combination band and the ground state is too weak to detect by NIR. The transition between this band and the OD stretch first excited state is also so weak that most of the intensity of the doublet comes from the oscillator strength produced by coupling to the OD stretch. The model gives the coupling strengths as 6.5 and 7 cm^{-1} in CCl$_4$ and hexane, respectively. © *2005 American Institute of Physics.*
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I. INTRODUCTION

Accidental degeneracy frequently occurs in vibrational spectra of complex molecules.[1] A nonlinear polyatomic molecules has $3n-6$ vibrational normal modes, where n is the number of atoms. Each mode has a vast number of excited states, the number only limited by the dissociation threshold. For IR active modes, transitions between states, give rise to absorption bands in the IR spectrum. Transitions can involve a single mode or they can be combination bands involving a change in quantum number of more than one mode. As the energy is increased above the ground state, the possibility that two or more vibrations will have approximately the same frequency is very high; that is, an accidental degeneracy or near degeneracy will occur. Two energy levels involved in an accidental degeneracy can have a resonant interaction if it is not forbidden by symmetry. For degenerate levels, the interaction will break the degeneracy and produce two levels. For nearly degenerate levels, the interaction will shift the levels provided the interaction is comparable to the level separation that would occur in the absence of coupling.[1] Because of accidental degeneracy, in some systems it can be difficult to assign certain peaks in linear vibrational spectra.

Here we report for the first time the influence of accidental degeneracy in an excited vibrational level ($v=2$) on the ultrafast infrared two-dimensional (2D) vibrational echo-correlation spectrum.[2] The 2D IR vibrational echo spectrum is akin to a 2D NMR spectrum.[3] In the vibrational echo-correlation spectrum, peaks involving the 0-1 transition and

peaks involving the 1-2 transition appear with approximately equal amplitude. The OD stretch of 2-methoxyphenol-OD (hydroxyl H replaced by D) is studied. The 2D IR spectrum of the OD stretch would be expected to be composed of one peak on the diagonal (0-1 transition) and one peak off-diagonal arising from the 1-2 transition and shifted by the vibrational anharmonicity. In the results presented below, one peak appears on the diagonal as expected, but the off-diagonal peak involving the 1-2 transition is split into a doublet. Examination of a variety of compounds similar to the 2-methoxyphenol-OD (2MP) establishes that the doublet arises from near-accidental degeneracy of the $v=2$ level of the OD stretch with a combination band involving benzene-ring modes. A simple quantum-mechanical model is used to extract the state frequencies in the absence of coupling between the levels and the strength of the coupling in two solvents.

II. EXPERIMENTAL PROCEDURES

2D IR vibrational echo spectroscopy measures the population and vibrational dephasing dynamics in two frequency dimensions, ω_τ and ω_m (in NMR, ω_τ and ω_m are called ω_1 and ω_3, respectively[4]). The ω_m axis is similar to the frequency axis in frequency-resolved pump-probe spectroscopy. The ω_τ axis does not have an analog in the pump-probe experiment; it provides an additional dimension of information that is contained only in the 2D IR spectrum. The positions and signs of peaks in the correlation spectra contain the history of the various vibrational transitions involved in the experiment. This technique has been applied to the study of

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ultrafast chemical exchanges,[5] hydrogen-bond dynamics,[6] intramolecular coupling of vibrational modes,[7] and dynamics of proteins.[8]

The ultrashort IR pulses employed in the experiments are generated using a Ti:sapphire regeneratively amplified laser optical parametric analyzer (OPA) system. The output of the regen is ~40 fs transform-limited 2/3 mJ pulses at 1 kHz repetition rate. These are used to pump an IR OPA. The output of the OPA is compressed to produce 51 fs transform-limited IR pulses as measured by nonresonant three-pulse nonlinear experiments in the sample cell.

The IR beam is split into five beams. Three IR pulses impinge on the sample and stimulate the emission of the vibrational echo, the fourth pulse that leaves the sample in a unique direction. A fifth pulse, the local oscillator, is overlapped with the vibrational echo pulse to phase-resolve the signal. The frequency and phase-resolved, stimulated vibrational echo was measured as a function of one frequency variable, ω_m, and two time variables, τ and T_w, the time between the first and second and the second and third IR pulses, respectively. The vibrational echo signal is frequency resolved by a spectrograph and a 32-element array detector, providing the frequency axis ω_m. The spectral resolution is ~1.5 cm^{-1}. The data are taken in several 32-frequency blocks. By numerical Fourier transformation, the τ scan data are converted into the frequency variable ω_τ, providing the ω_τ axis of the 2D IR vibrational echo spectrum. By properly controlling the phase relationships across the entire spectrum and using the dual-scan technique, all of the 2D vibrational echo spectra in this paper are purely absorptive.[9] Experimental details are discussed elsewhere.[9]

The hydroxyl groups of the phenol derivatives were deuterated by deuterium exchange with methanol-OD. Names and structures of the chemicals used in the experiments are shown in Fig. 1. Samples for 2D IR measurements, 1 mol % phenol derivatives in CCl$_4$ and 1.8 mol % in hexane, were held in a sample cell of CaF$_2$ flats with a spacing of 0.2 mm. Samples for NIR measurements are 2 mol % solutions in a cell with a spacing of 1 mm. The experiments were conducted at room temperature.

III. RESULTS AND DISCUSSION

A. FTIR and 2D IR spectra

Figure 2 shows the Fourier transform infrared (FTIR) spectra of the OD stretch of 2MP (solid curve) and 2MPD4 (the four H's on the ring replaced with D's; dashed curve) in CCl$_4$ (a) and hexane (b). In both solvents, 2MP and 2MPD4 form an intramolecular hydrogen bond as indicated in Fig. 1.[10] The spectra in CCl$_4$ are broader than those in hexane and shifted somewhat to lower frequency. 2MPD4 has a higher OD stretch frequency than 2MP by ~1.5 cm^{-1} in CCl$_4$ and ~0.5 cm^{-1} in hexane. Other than the small shifts, the undeuterated and deuterated spectra in each solvent are virtually identical.

Figure 3 displays the 2D IR vibrational echo spectra for 2MP [(a) and (b)] and 2MPD4 (c) in CCl$_4$ as contour plots. The data have been normalized to the largest peak in each plot. The positive-going contours (+) represent the vibra-
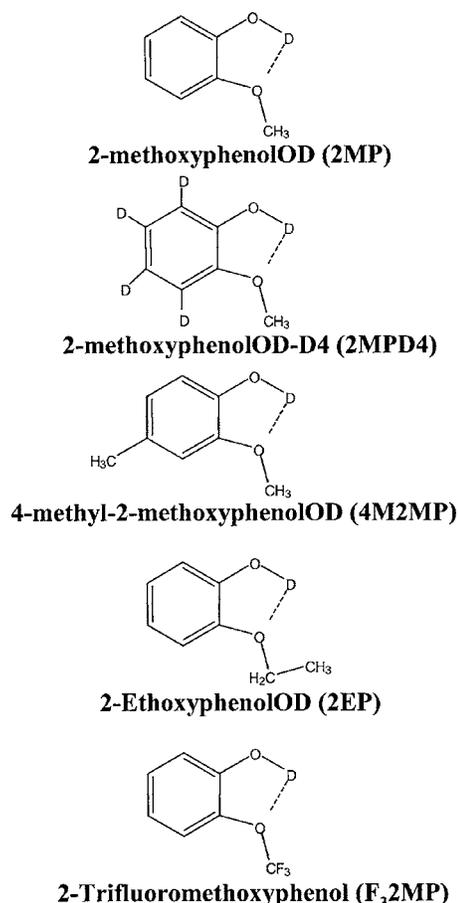
FIG. 1. Structures, names, and abbreviations for the five phenol-OD (hydroxyl H replaced by D) derivatives used in the experiments.

tional echo emitted by the 0-1 transition and the negative-going contours (−) represent the vibrational echo emitted by the 1-2 transition. In the 2D IR vibrational echo spectrum, the frequency at which the first pulse excites a mode is the mode frequency on the ω_τ axis (horizontal axis). The third pulse stimulates a mode to emit the vibrational echo pulse. The frequency of the stimulated emission is the frequency on the ω_m axis (the vertical axis). For their 0-1 vibrational transitions, because the ω_τ frequency equals the ω_m frequency there will be a peak on the diagonal ($\omega_\tau = \omega_m$). This is what is seen in each panel of Fig. 3, where there is one peak on the diagonal. If the frequency of stimulated emission (ω_m, third pulse) is different from the frequency of initial excitation (ω_τ, first pulse), peaks will appear off-diagonal. For a single mode (OD stretch) giving rise to a single diagonal peak, it would be expected that there would be a single off-diagonal peak shifted by the vibrational anharmonicity because the mode is initially excited at its 0-1 frequency (ω_τ), but the stimulated emission is at its 1-2 frequencies (ω_m).[3,11] A single off-diagonal peak is seen in Fig. 3(c), but doublets occur in Figs. 3(a) and 3(b).

Figure 3(a) is a spectrum for 2MP at a very short T_w [200 fs, (a)] and a long T_w [5 ps, (b)]. At $T_w = 200$ fs, the peaks are elongated along the diagonal. By 5 ps, the peaks are round. The change in shape is caused by spectral diffusion.[6,12,13] At short times, the vibrational transitions are inhomogeneously broadened. As time proceeds, the fluctua-
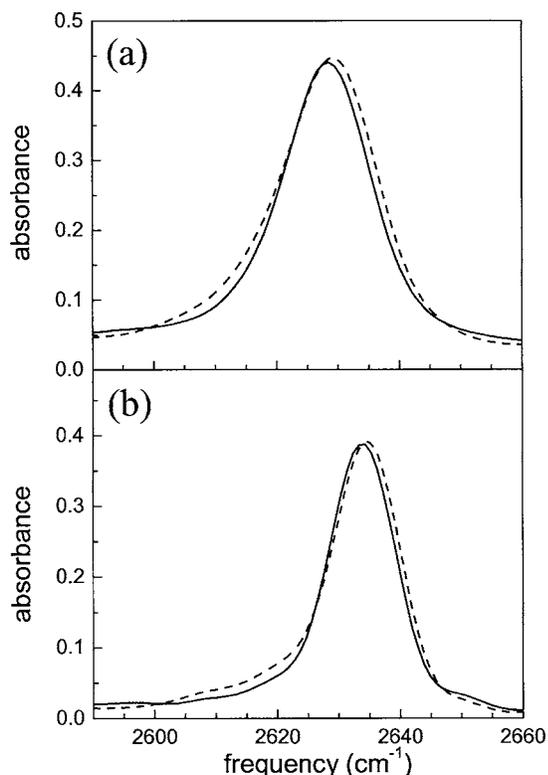
FIG. 2. FTIR spectra of OD Stretch of 2MP and 2MPD4 in (a) CCl_4 and (b) hexane.

FIG. 3. 2D IR vibrational echo correlation spectra for 2MP and 2MPD4 in CCl_4 at different T_ws. (a) 2MP at $T_w=200$ fs. (b) 2MP at $T_w=5$ ps. (c) 2MPD4 at $T_w=5$ ps. Each contour is a 10% change in amplitude. The positive peaks (+) on the diagonal reflect the 0-1 transition, while the negative (−) peaks off-diagonal reflect the 1-2 transition. In (a) and (b) the 1-2 transition display a doublet, showing that it is not a time-dependent effect. In (c) the 1-2 transition displays a single peak, demonstrating that deuterating the benzene ring eliminates that doublet.

tions in the solvent environment cause the transition frequency to sample all possible values, and the line becomes dynamically broadened. The change in shape provides a great deal of information on the dynamic solute-solvent interactions, but here our attention is directed toward the fact that the off-diagonal portion of the spectra in Figs. 3(a) and 3(b) displays a doublet. This doublet is independent of T_w. It occurs at the shortest T_ws and only decays with the entire spectrum at very long T_w. Therefore, the doublet is not a time-dependent phenomenon.

Figure 3(c) is a spectrum for 2MPD4 at $T_w=5$ ps. Compared to panels (a) and (b), there is a pronounced difference, the off-diagonal peak in (c) is a singlet. To have a singlet on the diagonal (0-1 transition) and a doublet off-diagonal (1-2 transition), it is necessary not only for the 0-1 transition to occur from a single ground-state level (0) to a single first-excited-state level (1), but also to have the 1-2 transition occur from the single $v=1$ level to a pair of $v=2$ levels. The splitting of the two levels occurs in 2MP, but not in 2MPD4. As will be shown in considerable detail below, we attribute the difference between the 2MP and 2MPD4 2D IR spectra to an accidental degeneracy. Deuteration makes a negligible change in the chemical properties of 2MP, as evidenced by the almost identical linear spectra of 2MP and 2MPD4 shown in Fig. 2, which rules out the possibility that the doublet is caused by some type of chemical process, e.g., isomerization. Figures 3(a) and 3(b) show that the doublet is not a time-dependent effect. Figure 4 shows that specific solute-solvent interactions are not responsible for the production of the doublet in the 1-2 transition. Figure 4(a) is 2MP in hexane and Fig. 4(b) is 2MP4D in hexane. Changing the

solvent does not influence the form of the spectra, but deuterating the benzene ring causes the production of a 1-2 transition singlet rather than a doublet.

The explanation for the doublet is an accidental degeneracy; that is, there is an unknown mode, which may be a combination band or overtone, having virtually the same energy as the energy of the $v=2$ level of the OD stretch (~ 5180 cm^{-1}). This mode is allowed by symmetry to couple to the OD $v=2$ level, but by itself has essentially zero oscillator strength. The coupling between the two states shifts them, and through the mixing produces two levels both with similar oscillator strength ("intensity borrowing" by the dark state). This scenario will be described quantitatively below. In this picture, 2MPD4 displays only a singlet for the 1-2 transition because the deuteration of the benzene ring changes the frequencies of the aromatic CH vibrational modes and other ring modes, breaking the accidental degeneracy. If the energy of the dark state is shifted by substantially more than coupling to the OD $v=2$ level, there will be no intensity borrowing and the 1-2 transition in the 2D spec-
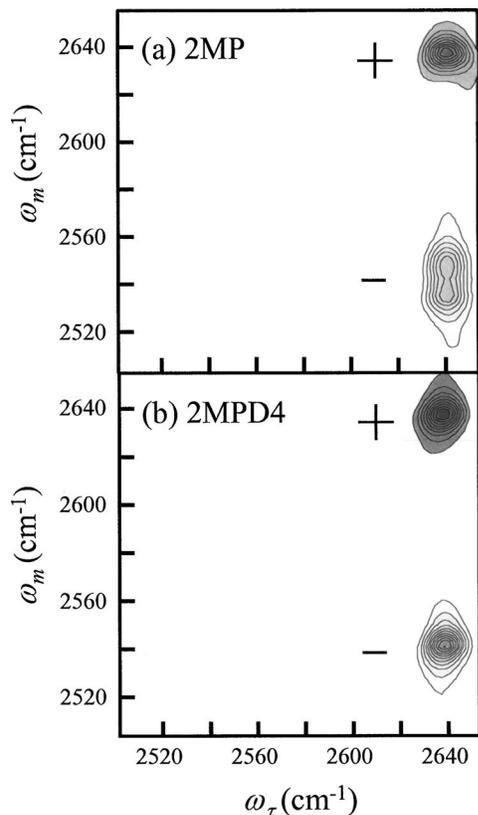
FIG. 4. 2D IR correlation spectra of 2MP (a) and 2MPD4 (b) in hexane, which demonstrate that the appearance of a doublet or a singlet does not depend on the specific solvent as the spectra are basically the same as those in Fig. 3 for which the data were taken in CCl_4.

FIG. 5. 2D IR correlation spectra of 4M2MP (a), $F_3$2MP (b), and 2EP (c) in CCl_4. The presence of the doublet in the 1-2 transition is influenced by chemical substitution.

trum will be a singlet. Below, electronic structure calculations are used to give some feel for the shifts of various modes that can be expected for a number of chemical changes in 2MP.

Figure 5 shows the 2D IR spectra for three molecules closely related to 2MP in structure (see Fig. 1). Figure 5(a) is for 4M2MP, which has a methyl group on the ring para to the hydroxyl position of 2MP. The methyl group only slightly affects the chemical properties of 2MP. The frequency of the OD 0-1 transition of 4M2MP is ~2.5 cm^{-1} higher than 2MP, but the methyl substitution will have a significant influence on modes involving the benzene ring. As can been seen in Fig. 5(a), the 1-2 transition is a singlet. The accidental degeneracy is broken. Figure 5(b) shows a 2D IR spectrum for $F_3$2MP, a molecule in which the methyl group of 2MP is replaced by CF_3. The CF_3 group is strongly electron withdrawing, which weakens the intramolecular hydrogen bond. The frequency of OD stretch is increased by ~22 cm^{-1} compared to 2MP. This is consistent with the fact that as the strength of a hydrogen bond to a hydroxyl increases, the stretch frequency decreases.[10] The CF_3 substitution also substantially changes other mode frequencies (see below, Table I). These changes are sufficient to break the accidental degeneracy, and the 1-2 transition is a singlet in Fig. 5(b). Figure 5(c) is a 2D IR spectrum for 2EP, which has the methoxy group of 2MP replaced with an ethoxy group. The ethoxy substitution changes the OD stretch frequency negligibly (~1 cm^{-1}), and it has virtually no effect on the ring

motions and aromatic CH motions. As seen in Fig. 5(c), the 1-2 transition is a doublet, demonstrating that the ethoxy substitution for methoxy does not break the accidental degeneracy. This result indicates that the modes involved in the dark mode do not involve the methoxy (ethoxy) group. Details of the frequency shifts of various modes for the species shown in Fig. 1 will be discussed below in connection with Table I.

B. Coupling strength and uncoupled level energies

To obtain the coupling strength between the OD stretch $v=2$ level and the dark level, the energies of these levels in the absence of coupling, and transition probabilities, it is sufficient to use a quantum-mechanical model consisting of two levels.[14] The kets representing the states in the absence of coupling are $|D\rangle$ for the dark state and $|2\rangle$ for the $v=2$ level of the OD stretch in the absence of coupling (see Fig. 6). The corresponding energies are E_D and E_2. The coupling constant is γ. The 2×2 Hamiltonian matrix is
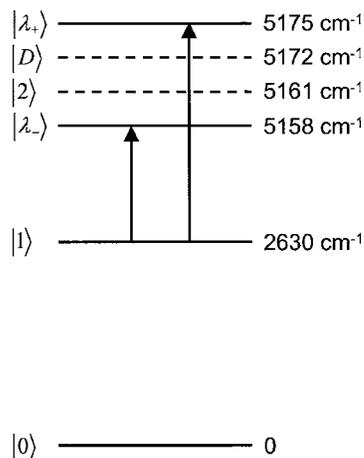
FIG. 6. Energy-level diagram for 2MP in CCl_4. The arrows indicate the transition eigenstates (solid lines) that give rise to the doublets in the 1-2 transition regions of the 2D correlation spectra in Figs. 3(a) and 3(b). The dashed lines represent the basis states.

$$H = \begin{bmatrix} E_D & \gamma \\ \gamma & E_2 \end{bmatrix}, \qquad (1)$$

with eigenvalues λ_+ and λ_- and corresponding eigenkets $|+\rangle$ and $|-\rangle$ (see Fig. 6):

$$\lambda_+ = \frac{E_D + E_2}{2} + \left[\left(\frac{E_D - E_2}{2} \right)^2 + \gamma^2 \right]^{1/2}, \qquad (2)$$

$$\lambda_- = \frac{E_D + E_2}{2} - \left[\left(\frac{E_D - E_2}{2} \right)^2 + \gamma^2 \right]^{1/2}. \qquad (3)$$

The eigenvalues are obtained from the 2D IR spectrum of Fig. 3(b). To determine the energies accurately, the 1-2 portion of the spectrum was fit with two overlapping two-dimensional Gaussians. This fitting procedure produced a virtually perfect reproduction of the spectrum. The frequency of each 1-2 peak is added to the frequency of the 0-1 peak to give $\lambda_+ = 5175$ cm^{-1} and $\lambda_- = 5158$ cm^{-1} for 2MP in CCl_4. The state with energy λ_+ is associated with the peak in Fig. 3(b) at 2545 cm^{-1} and the state with energy λ_- is associated with the peak at 2528 cm^{-1} on the ω_m axis. The uncoupled energy E_2 was obtained using the 2D spectrum of 2MPD4 in CCl_4 (see Fig. 4). Because of the change caused by deuteration in the frequencies of the modes that give rise to the $|D\rangle$ (see Sec. III C), the state $|2\rangle$ in 2MPD4 is unshifted by coupling to $|D\rangle$. The 0-1 transition frequency of 2MPD4 is 1.5 cm^{-1} higher than MP. It is reasonable to assume the 1-2 transition is also 1.5 cm^{-1} higher because this very small shift in the transition frequency indicates that there is a negligible change in the anharmonicity. Then the 0-2 transition frequency of 2MP, which corresponds to E_2, is 3 cm^{-1} lower than the 0-2 transition frequency of 2MPD4. From the 2D correlation spectrum [Fig. 3(c)], both the 0-1 and 1-2 transition frequencies of 2MPD4 are known. Therefore, $E_2 = 5161$ cm^{-1}.

With the values of λ_+, λ_-, and E_2, Eqs. (2) and (3) become two equations in two unknowns, γ and E_D. Solving, we obtain $\gamma = 6.5 \pm 1$ cm^{-1} and $E_D = 5172$ cm^{-1} for the coupling constant and the frequency of the dark mode in the absence
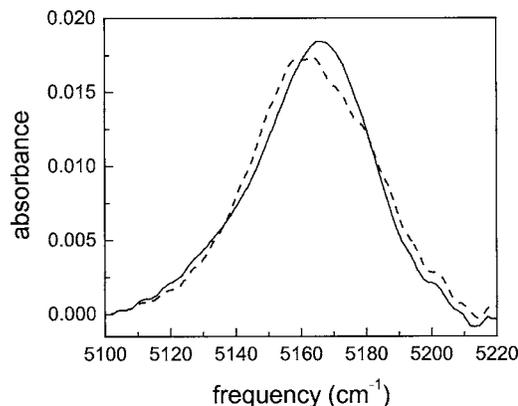
FIG. 7. Near-IR spectra of 2MPD4 (solid curve) and 2MP (dashed curve) in CCl_4. The 2MP curve is somewhat broader, but a doublet cannot be resolved.

of coupling. Figure 6 shows the energy-level diagram. The arrows indicate the transitions observed in the 1-2 transition portion of the correlation spectrum [Figs. 3(a) and 3(b)]. These are the transitions to the eigenstates $|+\rangle$ and $|-\rangle$. The dashed lines in Fig. 6 represent the energies of the basis states, $|2\rangle$ and $|D\rangle$, in the absence of coupling. We have taken γ to be positive because its sign does not change any of the observables. In terms of the basis kets, $|D\rangle$ and $|2\rangle$, the normalized eigenkets corresponding to the eigenvalues λ_+ and λ_-, $|+\rangle$ and $|-\rangle$ are

$$|+\rangle = 0.91|D\rangle + 0.42|2\rangle, \qquad (4)$$

$$|-\rangle = 0.42|D\rangle - 0.91|2\rangle. \qquad (5)$$

The transition probabilities P_i that give rise to the peaks in the doublet in Fig. 3(a) and elsewhere are proportional to the square of the absolute value of the transition dipole bracket between the first excited vibrational state of the OD stretch, $|1\rangle$, and the states $|+\rangle$ and $|-\rangle$:

$$P_+ \propto |\langle 1|\underline{\mu}|+\rangle|^2 = |\langle 1|\underline{\mu}[0.91|D\rangle + 0.42|2\rangle]|^2, \qquad (6)$$

$$P_- \propto |\langle 1|\underline{\mu}|-\rangle|^2 = |\langle 1|\underline{\mu}[0.42|D\rangle - 0.91|2\rangle]|^2, \qquad (7)$$

where $\underline{\mu}$ is the transition dipole operator. The P_i's are proportional to the volumes of the peaks in the doublet. These volumes are similar, but not identical. In Fig. 3(a) it can be seen that the lower-energy member of the doublet is slightly larger than the higher-energy member. The ratio of the peak volumes is 1.02. To reproduce this ratio, using Eqs. (6) and (7), it is found that the transition probability from $|1\rangle$ to $|D\rangle$ is $\sim 10\%$ of the transition probability from $|1\rangle$ to $|2\rangle$. Analysis using the ~ 1 cm^{-1} error bars on the various measured frequencies, it is found that the transition probability from $|1\rangle$ to $|D\rangle$ can be as small as $\sim 2\%$, but not larger than $\sim 10\%$. This is the transition probability from the first excited state of the OD stretch to the dark state in the absence of coupling between $|2\rangle$ and $|D\rangle$, not the transition probability from the ground state of the dark state to $|D\rangle$.

In principle, it is possible to detect the eigenstates $|+\rangle$ and $|-\rangle$ by direct absorption from the ground state using near-IR measurements. Figure 7 shows the peaks at
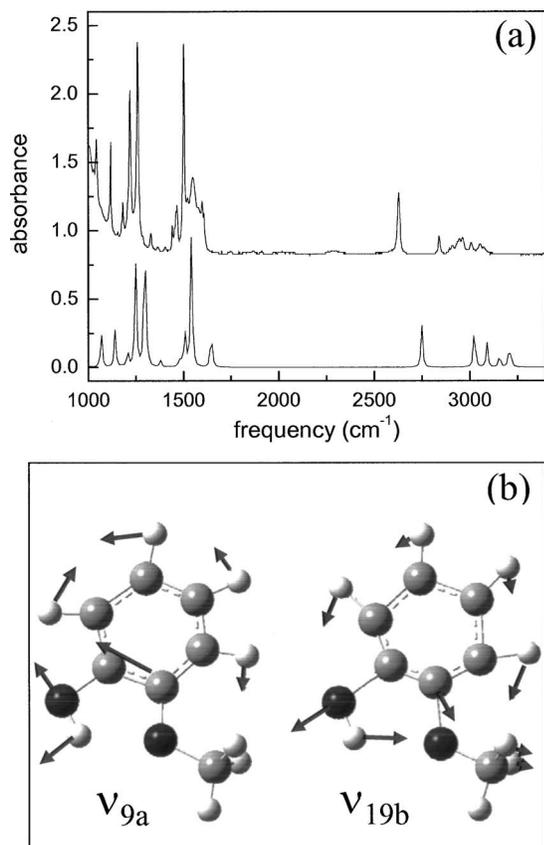
FIG. 8. (a) FTIR spectrum and DFT-calculated spectrum of 2MP. The calculated spectrum is shifted below the experimental spectrum for clarity of presentation. The calculated spectrum is reasonable, but not quantitatively accurate. (b) The nature of the two modes (ν_{9a} and ν_{19b}) that combine with the first vibrationally excited state of the OD stretch to produce the state $|D\rangle$ that is coupled to $|2\rangle$ the second vibrationally excited state of the OD stretch.

TABLE I. Mode Frequencies (cm^{-1}).

	2MP	2EP	4M2MP	2MPD4	F$_3$2MP
ν_{19a}	1502	1501.5	1514.5	1423	1500
ν_{9b}	1118	1121	1128	⋯	1112.5
$\nu_{OD}(|1\rangle)$	2630	2629	2632.5	2631.5	2650
$|2\rangle$	5161	5159[a]	5167.5	5164	5210
$|D\rangle$	5172	5171	⋯	⋯	⋯
$|D\rangle - |2\rangle$	11	12	⋯	⋯	⋯

[a]The 2EP OD stretch anharmonicity is assumed to be the same as that of 2MP.

sumption was made that the OD stretch anharmonicity is the same as it is for 2MP. The analysis of the 2EP in CCl$_4$ data gives the following results: $\lambda_+=5174$ cm^{-1}, $\lambda_-=5156$ cm^{-1}, $E_2=5159$ cm^{-1}, $E_D=5171$ cm^{-1}, and $\gamma=6.7$ cm^{-1}. For both 2MP in hexane and 2EP, the transition probabilities from $|1\rangle$ to $|D\rangle$ are small, but not zero.

C. Possible assignment for $|D\rangle$

We combined FTIR measurements and density-functional theory (DFT) electronic structure calculations (B3LYP/6-31+G(d,p) level) to make a tentative assignment of the modes that comprise $|D\rangle$. From the experimental results, we know that the frequency of $|D\rangle$ is 5172 cm^{-1} for 2MP in CCl$_4$. None of the second excited vibrational states of the modes of 2MP is in the appropriate frequency range except for the OD stretch. Therefore, $|D\rangle$ must be either a combination band or a high-order overtone of some mode. $|D\rangle$ cannot be a combination of only two modes because no two fundamentals of 2MP have energies that sum to ~5172 cm^{-1}. In 2MP, only the frequencies of CH stretching modes are higher than the OD stretch. They are ~3000 cm^{-1}. A mode at ~2200 cm^{-1} would be needed for the sum to be ~5172 cm^{-1}. From FTIR measurements and DFT calculations shown in Fig. 8(a), there are no modes between 1700 and 2600 cm^{-1}. The experimental spectrum has been displaced upward slightly for clarity. Figure 8(a) shows that the DFT calculations are not quantitative, but give reasonable values for the modes, making the calculation useful in terming the nature of the modes. The FTIR measurements would not pick up modes that are very weak, but the DFT calculations show that there are no modes in the required range. Thus $|D\rangle$ is composed of at least three modes.

We will only consider three modes, because it is possible to find a combination of three modes that has the required energy. Since $|D\rangle$ is coupled to the OD stretch, we assume one of the components of $|D\rangle$ is the OD stretch first excited state, $|1\rangle$. From the experimentally measured spectrum of 2MP, it is found that only two modes can combine with $|1\rangle$ to produce the desired results. They are ν_{19a} at 1502 cm^{-1} and ν_{9b} at 1118 cm^{-1}. The names and nature of these two bands come from comparing the calculated results for 2MP and literature values for phenol.[15] Summing the three mode frequencies; that is, the frequencies of $|1\rangle$, ν_{19a}, and ν_{9b} gives 5250 cm^{-1}. Then a combination band shift of -78 cm^{-1} gives the desired values 5172 cm^{-1}. Doing the same analysis for 2EP gives a combination band shift of -80.5 cm^{-1}. These are

~5160 cm^{-1} corresponding to the OD stretch 0-2 transitions of 2MPD4 (solid curve) and 2MP (dashed curve) in CCl$_4$. The 2MP peak in Fig. 7 seems to display some structure and is slightly broader than the 2MPD4 peak. Given the ~39 cm^{-1} width of the 2MPD4 peak, and the $|+\rangle$ and $|-\rangle$ splitting of only 17 cm^{-1}, a splitting would not be observable if each component of the doublet has the same width as 2MPD4 with a 17 cm^{-1} separation. As a heuristic exercise, it is interesting to model the 2MP band as the sum of two 2MPD4 bands separated by 17 cm^{-1}. The 2MPD4 band was taken to be Gaussian in shape. The sum of the two Gaussians produced a band 44 cm^{-1} in width, which is comparable to the observed ~45 cm^{-1} width of the 2MP band. The broadening and width of the 2MP peak is suggestive, but inconclusive. As can be seen in the 2D IR spectrum (Fig. 3), 2MPD4 does not display a doublet, while 2MP clearly does. The ability to observe the splitting and determine the interactions is a clear advantage of the 2D IR spectroscopy.

Following the identical procedure as used above, the doublet spectrum for 2MP in hexane [Fig. 4(a)] and 2EP in CCl$_4$ [Fig. 5(c)] were analyzed. The analysis of the 2MP in hexane data gives the following results: $\lambda_+=5182$ cm^{-1}, $\lambda_- =5167.5$ cm^{-1}, $E_2=5163$ cm^{-1}, $E_D=5176.5$ cm^{-1}, and $\gamma =7$ cm^{-1}, which is within experimental error of the value found in CCl$_4$. In analyzing the 2EP data, a reasonable as-

consistent and reasonable values. Table I lists the various mode frequencies measured with FTIR and near-IR spectroscopy for 2MP and 2EP in CCl_4 as well as values for the other three molecules shown in Fig. 1. Figure 8(b) shows the nature of the modes ν_{19a} and ν_{9b} obtained from the DFT calculations. While the assignment of the state $|D\rangle$ to a combination of $|1\rangle$, ν_{19a} and ν_{9b} is consistent with all of the data, this assignment should be viewed as a plausible rather than definitive.

IV. CONCLUDING REMARKS

A new feature in 2D IR ultrafast vibrational echo spectroscopy has been observed and explained. In the 2D spectra of the OD stretch of 2-methoxyphenol-OD and 2-ethoxyphenol-OD, the 0-1 transition is a single peak, while the 1-2 transition displays a doublet. By performing 2D IR and linear absorption IR experiments on a variety of molecules, it has been demonstrated that the doublet in the 1-2 spectrum arises from an accidental degeneracy between the $\upsilon=2$ state of the OD stretch and another mode at approximately the same energy. The peaks in the doublet give the frequencies of the eigenstates that arise from the coupling. Analysis of the data provides the frequencies of the states prior to coupling and the strength of the coupling, which is ~ 7 cm^{-1}.

IR and near-IR absorption experiments combined with DFT electronic structure calculations led to a tentative assignment of the state that interacts with the $\upsilon=2$ level of the OD stretch. The state is a combination of three modes. Near-IR experiments are unable to resolve the doublet directly because the bands are broad compared to the splitting.

Therefore, 2D IR vibrational echo spectroscopy is able to observe and measure small intermode interactions that are masked in linear absorption spectroscopy.

[1] W. A. Guillory, *Introduction to Molecular Structure and Spectroscopy* (Allyn and Bacon, Boston, 1977).
[2] J. B. Asbury, T. Steinel, C. Stromberg, K. J. Gaffney, I. R. Piletic, A. Goun, and M. D. Fayer, Chem. Phys. Lett. **374**, 362 (2003).
[3] O. Golonzka, M. Khalil, N. Demirdoven, and A. Tokmakoff, Phys. Rev. Lett. **86**, 2154 (2001).
[4] R. R. Ernst, G. Bodenhausen, and A. Wokaun, *Nuclear Magnetic Resonance in One and Two Dimensions* (Oxford University Press, Oxford, 1987).
[5] J. Zheng, K. Kwak, J. B. Asbury, T. Steinel, X. Chen, I. R. Piletic, and M. D. Fayer, Science **309**, 1338 (2005).
[6] J. B. Asbury, T. Steinel, K. Kwak, S. Corcelli, C. P. Lawrence, J. L. Skinner, and M. D. Fayer, J. Chem. Phys. **121**, 12431 (2004).
[7] M. Khalil and A. Tokmakoff, Chem. Phys. **266**, 213 (2001).
[8] Y. Kim and R. M. Hochstrasser, J. Phys. Chem. B **109**, 6884 (2005).
[9] J. B. Asbury, T. Steinel, and M. D. Fayer, J. Lumin. **107**, 271 (2004).
[10] D. Hadzi and H. W. Thompson, *Hydrogen Bonding* (Pergamon, London, 1959).
[11] A. Tokmakoff, A. S. Kwok, R. S. Urdahl, R. S. Francis, and M. D. Fayer, Chem. Phys. Lett. **234**, 289 (1995).
[12] S. Mukamel, Annu. Rev. Phys. Chem. **51**, 691 (2000).
[13] S. Mukamel, *Principles of Nonlinear Optical Spectroscopy* (Oxford University Press, New York, 1995).
[14] M. D. Fayer, *Elements of Quantum Mechanics* (Oxford University Press, New York, 2001).
[15] M. Rospenk, B. Czarnik-Matusewicz, and T. Zeegers-Huyskens, Spectrochim. Acta, Part A **57**, 185 (2001).