Tensor Components in Three Pulse Vibrational Echoes of a Rigid Dipeptide

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The effects of different polarization conditions on vibrational echo signals are systematically explored for the rigid cyclic dipeptide 2,5-diazabicyclo[2,2,2]octane-3,6-dione. An anharmonic vibrational Hamiltonian is constructed by computing energy derivatives to fourth order using density functional theory. Molecular frame transition dipole orientations are then used to calculate polarization dependent orientational factors corresponding to various Liouville space pathways. Enhancement and elimination of specific peaks in two-dimensional correlation plots is accomplished by identifying appropriate pulse configurations.

Key Words: Vibrational echo, Dipeptide

Introduction

Two-dimensional IR spectroscopy provides new insight into structural dynamics of molecular systems with femtosecond time resolution. Cross peaks in 2D correlation plots directly reveal the anharmonic coupling between different vibrational modes in the molecule. Frequencies of these peaks represent the coherent evolution of the system between interactions with the laser pulses. The intensities depend on the mutual orientations of the transition dipole moments of the respective vibrational transitions in the molecular frame as well as on the orientations of the IR pulses in the laboratory frame. Structural characteristics of the molecule are therefore represented by peak positions and intensities.

For pairs of modes with frequency differences that are comparable to the linewidth, the extraction of structural information may be restricted by the overlap of intense diagonal peaks with the desired cross peaks. For this reason, techniques to eliminate the diagonal peaks by taking advantage of the polarization dependence of the nonlinear IR signal have been developed. The ensemble averaged formula for the third order orientational factor given in Reference 3 assumes that the transition dipoles are fixed in the molecular frame during the course of an experiment (~1-2 ps). Although molecular rotation is likely to be negligible on this time scale, contributions resulting from changes in internal degrees of freedom can be significant for flexible systems. This formula is therefore most appropriate for relatively rigid structures.

Structural parameters of peptides have been determined by measuring the polarization dependence of 2D IR spectra using double-resonance as well as heterodyned techniques. Resolution enhancement of the structurally sensitive cross peaks can be achieved by subtracting different tensor components to yield spectra without diagonal peaks. However, this approach is complicated by the need to normalize spectra obtained in two different measurements with respect to each other, and may result in imperfectly subtracted diagonal peaks due to inequivalent contributions from reorientational dynamics. These difficulties are avoided by applying specific polarization conditions in single measurements that are equivalent to linear combinations of certain tensor components.

In order to analyze 2D IR spectra and to design new experiments independent simulations of the spectra are necessary. To this end, we have developed a new approach to predict coherent third order spectroscopic signals from first principles. We generate an anharmonic force-field up to fourth-order as well as dipole derivatives to second order for a number of selected local oscillators represented by internal coordinates. Higher-order force constants are calculated by numerical differentiation of second-order (harmonic) force constants obtained from standard quantum chemical methods such as Hartree-Fock or density functional theory. An anharmonic vibrational Hamiltonian is then generated and diagonalized. The representation of the dipole is then transformed into the eigenstate basis, resulting in transition dipole moments between all the eigenstates. Those together with the eigenstate energies are used to calculate nonlinear coherent signals applying the sum over states approach.

Scheme 1
Different coherent nonlinear techniques are classified by their phase matching conditions, four of them being independent. In this contribution we analyze the effect of different polarization conditions on nonlinear 2D IR spectra generated in the $k_i = -k_1 + k_2 + k_3$ wavevector direction calculated for a model dipeptide, 2,5-diazabicyclo[2.2.2]octane-3,6-dione (DABCODO, Scheme 1). DABCODO exists in a single and rather rigid bicyclic conformation, making it consistent with the approximations inherent in our calculations of the orientational part of the response function.

Theory

The third order nonlinear polarization is a convolution of the response functions $R^{(3)}_{ijk \ell}$ and the three incoming pulsed laser fields $E_a$

$$ R^{(3)}_{ijk \ell}(t, t) = \sum_{a \in \{x, y, z\}} \int_0^\infty dt_1 \int_0^\infty dt_2 \int_0^\infty dt_3 R^{(3)}_{ijk \ell}(t_1, t_2, t_3) \times E_r(t, \tau_3 = t - t_3) E_k(t, \tau_2 = t - t_3) \times E_l(t, \tau_1 = t - t_3 - t_2 - t_1) , \tag{1} $$

where $t_1$ and $t_2$ are the delay times between the three pulses and $t_3$ is the time between the third pulse and the time $t$ when the signal is detected. The third-order response functions $R^{(3)}_{ijkl}$ describe the microscopic behavior of the system under the influence of the laser pulses. In the sum over states approach they are given by

$$ (R_1)_{ijk \ell}(t_3, t_2, t_1) = \sum_{a,b,c,d} P(a) (i_{cd}^a b_k^a l_{da}^a) \times \mu_{ab}^a h_{bc}^a \mu_{cd}^a I_{da}^a (t_1) I_{db}^a (t_2) I_{da}^a (t_3) \tag{2} $$

$$ (R_2)_{ijk \ell}(t_3, t_2, t_1) = \sum_{a,b,c,d} P(a) (i_{cd}^a b_k^a l_{da}^a) \times \mu_{ab}^a h_{bc}^a \mu_{cd}^a I_{da}^a (t_1) I_{db}^a (t_2) I_{ab}^a (t_3) \tag{3} $$

$$ (R_3)_{ijk \ell}(t_3, t_2, t_1) = \sum_{a,b,c,d} P(a) (i_{cd}^a b_k^a l_{da}^a) \times \mu_{ab}^a h_{bc}^a \mu_{cd}^a I_{da}^a (t_1) I_{ab}^a (t_2) I_{ab}^a (t_3) \tag{4} $$

$$ (R_4)_{ijk \ell}(t_3, t_2, t_1) = \sum_{a,b,c,d} P(a) (i_{cd}^a b_k^a l_{da}^a) \times \mu_{ab}^a h_{bc}^a \mu_{cd}^a I_{da}^a (t_1) I_{db}^a (t_2) I_{da}^a (t_3) \tag{5} $$

with the lineshape function in the homogeneous limit

$$ I_{vv'}(t) = \theta(t) \exp(-i \Omega_{vv'}t - \Gamma_{vv'}t) . \tag{6} $$

$\Omega_{vv'}$ are the transition frequencies between two vibrational eigenstates $v$ and $v'$, $\Gamma_{vv'}$ is a homogeneous dephasing linewidth, and $\mu_{vv'}$ are the corresponding transition dipole moments describing the coupling between the states. $\theta(t)$ is the Heavyside function and $P(a)$ is the thermal population of the initial state $a$ determined by a Boltzmann distribution.

The orientational factors $(i_{cd}^a b_k^a l_{da}^a)$ describe the polarization dependence of the response functions and are assumed to be decoupled from the vibronic dynamics. The indices $i, j, k, l \in \{x, y, z\}$ refer to the lab-frame components of the linearly polarized laser fields. The orientational factors correspond to fourth-rank tensors composed of 81 tensor elements. For isotropic materials such as liquids, there are 21 nonvanishing elements in the orientational part of the third order response function, 3 of which are independent: $(z_{x\alpha \beta}^a x_{\gamma \delta}^a)$, $(z_{x\alpha \beta}^a x_{\gamma \delta}^a)$, and $(z_{x\alpha \beta}^a x_{\gamma \delta}^a)$. All other tensor components can be expressed in terms of these 3 independent elements. For example,

$$ (z_{x\alpha \beta}^a x_{\gamma \delta}^a) = (z_{x\alpha \beta}^a x_{\gamma \delta}^a) + (z_{x\alpha \beta}^a x_{\gamma \delta}^a) . \tag{7} $$

Polarization conditions for four-wave mixing photon echo experiments have been examined by Hochstrasser. The orientational factor for isotropic systems is given by

$$ \langle i_{a\ell}^a b_{j}^a l_{j}^a \rangle = \frac{1}{30} \left[ (\cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell}) \times (4 \cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell} - \cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell}) + (\cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell}) \times (4 \cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell} - \cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell}) \right] . \tag{8} $$

Thus, the tensor components given in Eq. (7) can be expressed as

$$ (z_{x\alpha \beta}^a x_{\gamma \delta}^a) = \frac{1}{15} (\cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell}) + (\cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell}) \tag{9a} $$

$$ (z_{x\alpha \beta}^a x_{\gamma \delta}^a) = \frac{1}{30} (4 \cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell}) - (\cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell}) \tag{9b} $$

$$ (z_{x\alpha \beta}^a x_{\gamma \delta}^a) = \frac{1}{30} (-\cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell}) + 4 \cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell} \tag{9c} $$

$$ (z_{x\alpha \beta}^a x_{\gamma \delta}^a) = \frac{1}{30} (-\cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell}) - 4 \cos \theta_{a\ell} \cos \theta_{b}\phi_{\ell} \tag{9d} $$

In this work, calculations are performed in the time-domain and the pulse envelopes are introduced approximately by assuming the quasi impulsive limit; all the applied fields are taken to be delta functions so that the integrations over time intervals (Eq. 1) can be eliminated and the signal is directly proportional to the nonlinear response function. Frequency-selective excitation is accounted for by defining a finite rectangular pulse bandwidth ($\pm 100$ cm$^{-1}$). Transitions within the frequency range of the carrier frequencies and the bandwidth are resonant, whereas all other Liouville space pathways are neglected, a manual application of the rotating
wave approximation.

We report logarithmic two-dimensional absolute value plots of the complex signals after Fourier transformation with respect to either $t_1$ and $t_3$

$$S_{ijkl}(\omega_3,t_2,\omega_4) = \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{\infty} dt_1 R_{ijkl}^S(t_3,t_2,t_1) \times \exp(-i\omega_3 t_3 - i\omega_1 t_1)$$

or similarly $t_2$ and $t_1$

$$S_{ijkl}(\omega_2,\omega_1,t_3) = \int_{-\infty}^{\infty} dt_3 \int_{-\infty}^{\infty} dt_1 R_{ijkl}^S(t_3,t_2,t_1) \times \exp(-i\omega_1 t_3 - i\omega_2 t_1).$$

### Results and Discussion

We investigate the dipeptide model system DABCODO because of its relatively rigid structure and its small size which allows the use of high-level quantum chemistry calculations. We applied density functional theory at the B3LYP/6-31G(d,p) level,15–18 as implemented in Gaussian 98,19 to optimize the structure and calculate harmonic force constants with respect to internal coordinates. Anharmonic force constants were calculated for the subspace of 6 local vibrational modes, the C=O, N-H and C-N stretches of the two peptide bonds. An effective exciton Hamiltonian constructed in a basis state manifold of up to 10 excitation quanta was diagonalized and resulted in a total of 2153 eigenstates.12

Spectra are simulated in the frequency range of the symmetric ($\alpha$) and antisymmetric ($\alpha$) C=O stretching vibrations, $v_{\alpha}(\text{C=O}) = \omega_{\alpha} = 1780.8 \text{ cm}^{-1}$ and $v_{\alpha}(\text{C=O}) = \Omega_{\alpha} = 1773.8 \text{ cm}^{-1}$. Anharmonic shifts of the overtones and combination bands are $\Delta_u = 4.6 \text{ cm}^{-1}$, $\Delta_{uu} = 12.3 \text{ cm}^{-1}$ and $\Delta_{uu} = 16.9 \text{ cm}^{-1}$. We calculate signals for one-color experiments with carrier frequencies $\omega_1 = \omega_2 = \omega_3 = 1700 \text{ cm}^{-1}$. In the phase matching direction $k_f = -k_1 + k_2 + k_3$ the 3 Feynman diagrams $R_2$, $R_3$ and $R_1$ contribute (Fig. 1).

All polarization conditions investigated here are summarized in Table 1. They are designed to eliminate certain groups of peaks, for instance diagonal or cross peaks, to improve resolution of specific peaks by removing overlaps with others.3,8 Orientational factors are calculated using linear combinations of the 4 basic tensor elements (Eq. 7). Diagonal peaks (DP) result from the Feynman diagrams $R_2$ and $R_3$ when the 4 interactions are with the same mode, either $v_{\alpha}(\text{C=O})$ or $v_{\alpha}(\text{C=O})$; the corresponding Liouville space pathways are denoted ssss or aaaa, respectively (cf. Table 1). Cross peaks arise from interactions with different modes, either asas/sasa ($R_2$) or aass/ssaa ($R_1$). In $t_1$ and $t_3$ the coherences for the $R_2$ and $R_3$ pathways are identical, so their intensities contribute to the same diagonal and cross peaks. This is not the case for the $(\omega_2, \omega_3)$ dimensions; diagonal peaks at $(\omega_2 = 0)$ arise from one $R_2$ pathway but two $R_3$ pathways, while cross peaks at $(\omega_2 = \Omega_3 - \Omega_4, \Omega_4)$ and

![Figure 1. $k_f = -k_1 + k_2 + k_3$: Feynman diagrams ($R_2 = R_3 + R_1 - R_1'$) and energy level schemes (dashed arrows: interaction from the right; solid arrows: interaction from the left; wavy arrows: signal pulse) for $\omega_1 = \omega_2 = \omega_3 = 1770 \text{ cm}^{-1}$ ($\nu_1(\text{C=O})$).](image)

### Table 1. Polarization factors $\langle i_{ij}k^l\rangle$

| Tensor element | Polarization Configuration | Feynman pathways
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$^{a}$DP = diagonal peak, CP = cross peak, $a = v_{\alpha}(\text{C=O})$, $s = v_{\gamma}(\text{C=O})$. 

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C=O stretching modes (eigenstate picture) are orthogonal to dipole moments between the symmetric and antisymmetric degenerate and split symmetrically. Thus, the two transition complete set of diagonal, cross, overtone and combination components are shown in Figure 2. The spectra contain the sign of the sum of contributions to the cross peaks is negative for the zyyz polarization configuration in contrast to zzzz, zyyz and zzyyz configurations.

The effect of taking linear combinations of different tensor elements is now easily evaluated from the linear combinations of the coefficients (see Table 1). It follows that diagonal peaks are eliminated by the linear combinations zyzy–zyyz, zyzy–zyyz and zzyy–zyzy as well as by zzzz–3zyyz, zzzz–3zyyz and zzzz–3zyyz. In addition, cross peaks vanish for the zzyy–zyyz combination.

The effects of forming the combinations zyzy–zyyz and zzyy–zyyz (Fig. 3) are similar in the (−ω1, ω3) dimensions; the diagonal peaks are eliminated and the cross peaks intensities are enhanced.

The relative intensities of the overtone peaks for the antisymmetric stretch at (Ω1, Ω2, −Δωi) are significantly reduced, whereas those of the combination bands at (Ω1, Ω2, −Δωi) are increased, which improves the resolution of the combination bands by reducing their overlap with the stronger overtone peaks. The intensities of the peaks at (Ω1, 2Ω2−Δωi) are slightly reduced but remain comparable in strength to the cross peak at (Ω1, Ω2) with which they overlap. Conversely, the overtone and combination band peak intensities for (−ω1, ω3) are all enhanced.

In contrast to the (−ω1, ω3) plots, the two combinations zyzy–zyyz and zzyy–zyyz differ considerably in the (ω2, ω3) dimensions. All diagonal peaks in which (ω2 = 0) vanish for the zyzy–zyyz combination, whereas the intensities of the cross peaks with (ω2 = Ω2 − Ωa) and (ω3 = Ω3 − Ωa) are identical to those in the (−ω1, ω3) plots. In contrast, the cross peaks at (Ω1, −Ω2, Ωa) and (Ω1, −Ω2, Ωa) cancel but the diagonal peaks survive for the zzyy–zyyz tensor combination.

Both diagonal and cross peaks which access only singly excited levels are entirely eliminated in the zzyy–zyyz combination. These peaks vanish due to destructive interferences between the Liouville space pathways (Table 1). The most intense peaks in these spectra appear at (Ω1, Ω2 − Δωi) and (Ω1, Ω2 − Δωi). Thus, the resolution of the peaks at (Ω1, 2Ω2 − Δωi, −Ωa) and (Ω1, Ω2, −Δωi) is improved. However, no clear improvement in resolution is gained in the (ω2, ω3) dimensions where all peaks persist.

In addition, the linear combinations zzzz–3zyyz, zzzz–3zyyz and zzzz–3zyyz (Figure 4) can also be employed to eliminate diagonal peaks from the (−ω1, ω3) spectra. The advantage of these combinations compared to zyzy–zyyz and zzyy–zyyz spectra is the greater overall intensity of the remaining peaks. As in the zzyy–zyyz combinations, no peaks are eliminated in the (ω2, ω3) plots.

In summary, we have simulated the effect of different polarization conditions on 2D IR spectra generated in the k∥ = −k1 + k2 + k3 wavevector direction. We demonstrated how diagonal and/or cross peaks can be eliminated from the spectra, facilitating the observation of peaks which are unresolved due to overlap with these stronger bands.
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