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TIME RESOLVED VIBRATIONAL Spectroscopy

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R. VENKATRAMANI,^{1,2} T. LA COUR JANSEN,¹ J. DREYER³ and S. MUKAMEL¹

INTRAMOLECULAR AND SOLVENT CONTRIBUTIONS TO AMIDE-I VIBRATIONAL ECHO LINESHAPES OF A CYCLIC DIPEPTIDE

Abstract – We simulate the linear and 2D photon echo spectra for the cyclic dipeptide DABCODO in DMSO. A time dependent, fluctuating, quartic hamiltonian is constructed by combining Density functional Theory (DFT) calculations of the isolated molecule with classical MD simulations. Unlike the linear absorption lineshapes which are not affected by other solute modes, the 2D photon echo spectra are sensitive to these anharmoni-cally coupled modes.

Multidimensional, coherent, vibrational spectroscopy provides more information than one dimensional linear absorption by spreading the information in multiple time, frequency or mixed time-frequency domains^{1,2}. Different structures which appear identical under linear absorption can show different nonlinear signatures³. In this work we examine the effects of intramolecular modes on the lineshapes in linear and nonlinear spectra of the Amide-I stretches of a cyclic diglycine: diazabicyclo[2.2.2]octane-3,6-dione (DABCODO)⁴ in dimethyl sulfoxide (DMSO). The peak pattern of various third order signals of the molecule was studied recently⁵.

In the first step an optimized DABCODO geometry (Fig. 1a) was obtained using DFT (B3LYP/6-31g**). This geometry was used as a

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¹ Department of Chemistry, University of California, Irvine, CA 92697.

² Department of Physics and Astronomy, University of Rochester, Rochester, NY-14627.

³ Max-Born-Institut Für Nichtlineare Optik und Kurzzeitspektroskopie, D-12489 Berlin, Germany.

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starting point for an MD simulation in the polar solvent DMSO using a classical (CHARMM) force field.

We chose the two C = O and N = H stretches in DABCODO as primary coordinates (PC). All bond lengths for the solvent molecules and PC of the solute were held fixed during the simulation. The PC are treated quantum mechanically as described below.

The average structure from the simulation was found to deviate very slightly from the vacuum geometry (0.04 Å RMSD). We thus used the vacuum structure as a reference to perform *ab initio* calculations, which yielded parameters for the solute potential energy surface (PES) expanded to quartic order in the PC⁵.

A new PES in the solvent was constructed for the solute using an analytical form (Coulomb plus Lennard-Jones with parameters from CHARMM) of the solute-solvent interaction and expanding it around the PC. Along the MD trajectory, the force constants of the solute PES were expressed in terms of the reference force constants and the instantaneous coordinates of solute and solvent atoms. This time dependence of the force constants leads to a fluctuating Hamiltonian⁶, which was expanded in a harmonic basis of the PC. The ma-

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trix elements of the Hamiltonian in this basis gave the fluctuating frequencies, couplings and anharmonicities. The average Hamiltonian was then calculated and diagonalized to give the eigenstates of the system. The fluctuating matrix elements and the transition dipole operator (assumed to be linear in PC) from the local basis, were transformed to the eigenstate basis.

This semiclassical procedure^{7,8,9} treats the solute vibrations of interest (PC) quantum mechanically while the remaining degrees of freedom of the solute, termed SC (secondary coordinates) as well as the solvent degrees of freedom are assumed to be classical. Table 1 shows the lowest six energies for this system used in our simulations.

Eigenenergy (cm ⁻¹)	Transition
0.0	(gs)
1750.7	CO (as)
1759.1	CO (s)
3487.0	2CO (as)
3488.0	2CO (comb)
3515.2	2CO (s)

Table 1. Lowest six eigenstates and their energies. Abbreviations: (gs)-ground; (as)-antisymmetric; (s)-symmetric; (comb)-combination band.

From the correlation functions of fluctuating energies, we computed the lineshape functions^{10,11}, which were then used to calculate the linear absorption and 2D photon echo spectra generated in the direction $\mathbf{k}_{\rm I} = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3^{12}$. Here $\mathbf{k}_1, \mathbf{k}_2$ and \mathbf{k}_3 are the wavevectors of three time ordered incident fields, separated by time intervals t_1 and t_2 while t_3 is the time interval between the third incident field \mathbf{k}_3 and the signal field. The impulsive, time gated, homodyne signal is $|S(\omega_3, t_2, \omega_1)|^2$ with $S(\omega_3, t_2, \omega_1) = \iint \exp(-i(\omega_1 t_1 + \omega_3 t_3)) R(t_3, t_2, t_1)$. R is the third order non-linear response function¹⁰ represented by the feynman diagrams shown in Fig 1b.

We have calculated the linewidth for two models: with (A) and without (B) interactions between the primary and secondary coordinates. Fig. 2 shows normalized linear absorption spectra for the amide-I region (1600-1900 cm⁻¹). The calculated peak position (1750 cm⁻¹) and linewidth (FWHM 44 cm⁻¹ for model A) for

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Fig 2. Normalized linear absorption spectra in the amide-I region.

the amide-I band, are in good agreement with experiment⁴ (peak position $\sim 1700 \text{ cm}^{-1}$ and FWHM $\sim 50 \text{ cm}^{-1}$). The linear absorption spectra for the two models are very similar (the linewidths are 44 cm⁻¹ and 41 cm⁻¹ for models A and B respectively).

Figs. 3a and 3b show the simulated 2D photon echo, $(|S(\omega_3, t_2, \omega_1)|^2)$ in the amide-I region for models A and B respectively. Unlike the linear absorption these plots show clear differences. The linewidths along the ω_3 axis are narrower for model A. The $(\epsilon_2, \epsilon_7 - \epsilon_2)$ peak, arising from the pathway involving GS \rightarrow CO (as) transition during the first time interval t₁ and CO (as) \rightarrow 2CO (as) during the third time interval t₃, can be resolved from the dominant peak at $(\epsilon_2, \epsilon_6 - \epsilon_2)$ which arises from the pathway involving GS \rightarrow CO (as) transition during t₁ and CO (as) \rightarrow 2CO (s) during t3. The effect of intramolecular modes is stronger on the CO overtones, which are more clearly resolved in nonlinear spectra. There are 16 peaks in the 2D plot and even small changes in lineshapes will lead to large changes in the signal due to interference effects. In contrast, there are only three CO overtone peaks in the linear spectra and this together with the weak strengths of the ground-2CO transitions makes it difficult to observe the effect of anharmonicities in the linear absorption. The linear absorption for the CO overtone (Fig. 4) is dominated by the combination band and a single unresolved peak (FWHM 78 cm⁻¹ for model A) appears at 3490 cm⁻¹. The 2D signal, on the other hand, is dominated by transitions to the antisymmetric overtone (CO (as) \rightarrow 2CO (as)) and smaller

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contributions from transitions to the symmetric overtone (CO (as) \rightarrow 2CO (s)). Thus, by highlighting different overtone transitions than shown in the linear absorption, the 2D signal provides a more sensitive probe of changes in lineshapes.

Figs. 3 and 4 show that the effect of intramolecular interactions is greater for the overtones than the fundamentals (the linewidth increases from 78 cm⁻¹ for model A to 87 cm⁻¹ for model B in Fig. 4) suggesting that fluctuations in anharmonicities are more sensitive to intramolecular interactions.



Fig. 3. 2D photon echo $(-k_1 + k_2 + k_3)$ spectra for $t_2 = 0$ for (a) Model A and (b) Model B.





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In conclusion, our simulated photon echo signals from the cyclic dipeptide DABCODO in DMSO carry signatures of intramolecular interactions which are absent in the linear absorption. We found that the fluctuations of the anharmonicities are more sensitive to intramolecular interactions than those of the fundamentals.

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