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Lineshapes and Correlations in Two Dimensional Vibrational Signals of NMA

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Abstract. The coherent nonlinear response of the entire amide lineshapes of N-methyl acetamide (NMA) to three infrared pulses is simulated using an Electrostatic DFT map. Positive and negative cross-peaks contain signatures of correlation between the fundamentals and the combination state. The coupled amide I – III cross-peak lineshapes indicate an anti-correlation of frequency fluctuations, which is ascribed to the correlated hydrogen bond dynamics at C=O and N=H sites.

1. Introduction

Coherent multidimensional infrared spectroscopy provides a valuable tool for protein structure determination¹. The amide infrared absorption provides a useful probe for secondary-structure changes because of its sensitivity to hydrogen bonding, dipole-dipole interactions and geometry of the peptide backbone. Most effort has been focused on the Amide I band^{2,3}. However, the cross peak pattern of other amide bands can provide additional structural information.

In our earlier study on N-methyl acetamide (NMA)⁴, which is the simplest model for the amide system, the fluctuating Hamiltonian was developed and the linear infrared spectrum was calculated based on a complete electrostatic DFT map (EDM)⁴ of the amide I, II, III, A fundamental, overtone and combination frequency fluctuations and their transition moments. Frequencies of the different amide states are determined by different collective coordinates which are linear combinations of the electric field and its derivatives. In order to study protein dynamics, it is important to establish the connection between the cross-peaks lineshapes and the correlated frequency fluctuations due to the correlated protein and solvent dynamics. We present a study of the lineshape dependence of amide I and III photon echo cross peak of NMA on the degrees of correlation between these modes. These are connected to the correlated hydrogen bonding forming and breaking dynamics at C=O and N-H sites⁵.

2. Computation

We calculated the entire amide (I, II, III, A) modes of NMA in water employing the EDM with a MD simulation⁴. The third-order response functions were calculated using the cumulant expansion of Gaussian fluctuations model (CGF)⁴. The three pulse photon echo infrared spectra was calculated for the amide I, II, III region (Fig. 1(A)) and the amide A cross peaks region (Fig.2(D)). A good agreement of the amide I and II anharmonicities was found with recent experiment⁶.

The absorptive part of the amide I-III cross peak is plotted in Fig. 1(B) together with the Feynman diagram for the Liouville paths contributing to the signal (Fig. 1(C)). The stimulated emission/ground state bleach (a), and the excited state absorption (b) contribute to the negative and positive peaks, respectively, which carry information on the correlation between the two fundamental fluctuations, and between the fundamental and the combination frequency fluctuations. Frequency-frequency correlation function of the state i , C_{ii} can be written as $C_{ij}(t) = \eta_{ij} \Delta_{ii} \Delta_{jj} \bar{C}_{ij}(t)$, where Δ_{ii} is a fluctuation amplitude, \bar{C}_{ii} is a normalized correlation function, $\eta_{ij} = \langle \delta\omega_i \delta\omega_j \rangle / (\langle \delta\omega_i^2 \rangle \langle \delta\omega_j^2 \rangle)^{1/2}$ which represents the correlation coefficient of the two frequency fluctuations varies between 1 (full correlation), 0 (no correlation), and -1 (anti-correlation). In order to investigate the signatures of correlations between different modes, the line broadening functions were calculated by scaling $C_{ij}(t)$ obtained from the real MD trajectory using three different values of $\eta_{ij}=1, 0, -1$ for the relevant modes, $i, j = 1$ (amide III fundamental), 3 (amide I fundamental), or 9 (amide I + III combination).

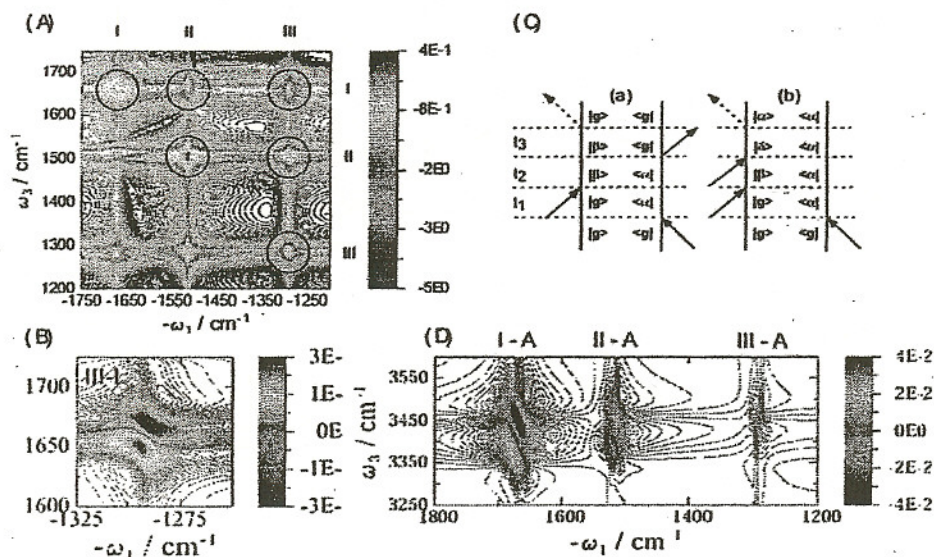


Fig. 1 (A) Three pulse photon echo signal in the amide I, II and III region (log scale). (B) Absorptive part of the amide I-III cross peak (C) Liouville Paths contributing to the signals. (D) Photon echo signals of the amide A cross peaks.

3. Results and Discussion

The degree of correlation between different amide modes is found to strongly affect the signal. The absorptive part of the amide I-III cross peaks of the k_1 signal ($\text{Im}[-\omega_1, t_2=0, \omega_3]$) is plotted in Fig. 3 for various combinations of the correlation coefficients. The correlation between the amide I and III fundamentals ($\eta_{1,3}$) contributes to the negative bandshape, and the correlation between the amide III fundamental and the combination state I+III ($\eta_{1,9}$) contributes to the positive bandshape. The negative peak decreases as $\eta_{1,3}$ changes from the +1 to -1, but does not depend significantly on $\eta_{1,9}$. The bandwidth also becomes broader with smaller $\eta_{1,9}$. On the other hand, the positive peak becomes weaker and broader as $\eta_{1,9}$ is

varied from +1 to -1. The positive bandshape becomes more elongated along ω_3 as $\eta_{1,9}$ is varied from +1 to -1.

The actual lineshape derived from the correlations obtained by the MD simulation has a distinct signature of anti-correlation (-0.71) between the amide I and III fundamentals.

The kinetics of the hydrogen bonding forming and breaking based on the same MD trajectory was investigated by employing the geometric criteria. We found positive correlation (0.673) of the hydrogen bond formation at C=O and N-H sites. Free energy analysis shows the extra stabilization energy (0.03 kcal/mol) when both hydrogen bonds at C=O and N-H sites are formed which can be rationalized since the hydrogen bond at one site creates the electric field parallel to the C=O and N-H bond stabilizing the other hydrogen bond.

The amide I frequency is anti-correlated to hydrogen bonding at C=O site (-0.473) and amide III frequency is correlated to N-H site (0.364). This explains the anti-correlation of the amide I and III fundamental frequencies.

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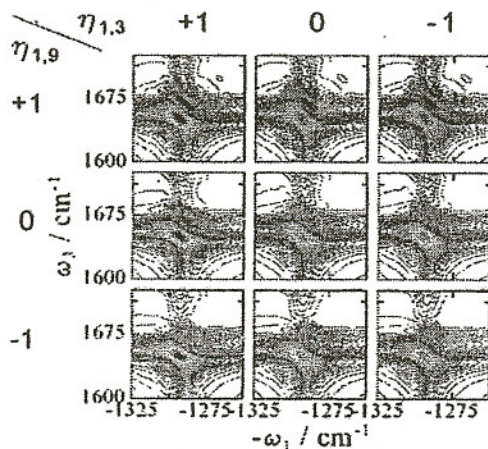


Fig. 2 The amide III and I cross-peak for various correlation coefficients.