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Following the Excited State Dynamics of β -apo-8'-carotenal with Two-Dimensional Electronic-Vibrational Spectroscopy

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Abstract: Two-dimensional electronic-vibrational spectroscopy is used to study the excited state evolution of the carotenoid β -apo-8'-carotenal in solution. This new multidimensional spectroscopy is unique in its ability to directly follow the electronic and nuclear degrees of freedom simultaneously.

1. Introduction

The non-radiative decay pathways of the first optically bright state (S_2) of carotenoids in solution are complex. How the S_2 state relaxes is still poorly understood despite a vast number of studies. The main points of contention are the number, nature and role of lower lying electronic states. It is generally accepted that the optically dark S_1 state plays a role, however, whether its involvement is immediate in the reaction co-ordinate, or whether intermediate states such as S^* , S^+ etc. are involved remains unclear.[1] The rapid depopulation of the S_2 state is thought to be mediated by a conical intersection[2,3]- a region of the potential energy surface where it is unreasonable to assume that the electronic and vibrational degrees of freedom are decoupled. Using a new experimental technique, two-dimensional electronic-vibrational (2D-EV) spectroscopy, we investigate the excited state dynamics of a model carbonyl containing carotenoid, β -apo-8'-carotenal, monitoring the electronic relaxation simultaneous to the evolution of the excited state nuclear motions.

2. Experimental

2D-EV measurements were performed using a new experimental apparatus.[4] A commercial 1 kHz regenerative amplifier pumped a homebuilt non-collinear optical parametric amplifier (NOPA) and mid-IR optical parametric amplifier. The output of the NOPA was compressed (22.5 fs, centered at 513 nm, 20 nm FWHM) with acousto-optic programmable dispersive filter (AOPDF, Dazzler, Fastlite). The AOPDF was also utilized to create a collinear pair of pump pulses, k_1 and k_2 , and generate a coherence time delay, t_1 , with control over the relative phase of the pulse pair, ϕ_{12} . The total power of these pulses was attenuated to 250 nJ, and focused into the sample. At waiting time, t_2 , the probe mid-IR pulse, k_3 (~90 fs, ~80 nJ) interrogates evolution on the ground or excited states and k_{sig} is subsequently emitted at echo time, t_3 . In a pump-probe geometry, the k_{sig} field is phase locked with the k_3 pulse and emitted in the same phase-matched direction, obviating any need to phase the resulting 2D spectra. The 2D spectrum can be retrieved by phase-cycling the pump-pulse pair, as has been demonstrated with visible and infrared multidimensional spectroscopies.[5,6] For a given waiting time, t_2 , a 2D-EV spectra was collected by frequency dispersing k_{sig} (and k_3) onto a 64-element HgCdTe detector (Infrared systems development) as t_1 and ϕ_{12} were incremented. The instability of the mid-IR laser pulses was corrected by normalizing data with respect to a reference mid-IR beam. The appropriate phase cycling scheme was applied to generate a t_1 - ω_3 matrix, which was subsequently Fourier-transformed along the t_1 axis to generate a ω_1 - ω_3 2D-EV spectrum. The pump pulses were resonant with the $S_2 \leftarrow S_0$ absorption of β -apo-8'-carotenal. 2D-EV spectra were recorded at room temperature in chloroform for various t_2 waiting times. The β -apo-8'-carotenal sample had an optical density of 0.25 at the peak of the laser spectrum in a 200 micron path length cell.

3. Results and Discussion

Fig. 1(a) displays the frequency dispersed one-dimensional visible pump, mid-IR probe spectrum of β -apo-8'-carotenal in chloroform solution. This probe region was chosen as to monitor the evolution of the C=C back-bone vibrations. The pump-probe spectra is dominated by positive features which arise from vibrations on an excited state potential energy surface. The vibrational assignments are labeled in Fig. 1(a).[7] We assign the negative feature at 1660 cm^{-1} to evolution on the ground state of the C=C symmetric stretch vibration. The vibrations on the excited potential energy surface are pertinent because the $S_2 \rightarrow S_1$ relaxation mechanism is proposed to involve a change in

bond-order along the C=C/C–C backbone. [2] Therefore these vibrations should be sensitive to the populated electronically excited state.

Preliminary 2D-EV spectra are shown in Fig. 1(b-d). Note that excited state vibrations are now displayed in blue (negative). These data are real total spectra recorded at the displayed t_2 waiting times. For every feature present in the pump probe, there is a less intense (by a factor of ~ 2) feature of the opposite sign at lower excitation energies. In the first few hundred femtoseconds the line shape along the visible axis evolves: the main double features shift to higher excitation energies; the spacing between the two peaks on the visible axis are also reduced by $\sim 500\text{ cm}^{-1}$ over the course of 1 ps. Furthermore, the peaks lose correlation with respect to the initial excitation in the first picosecond, as represented by the dashed line. The 2D-EV measurement is sensitive to the correlation between the electronic-vibrational manifold initially excited and the vibration in the mid-IR that is subsequently probed.

Figure 1. (a) 1-D vis-IR pump probe spectrum, (b-d) 2D-EV spectra for given values of t_2 . The dashed lines in (b-d) display the evolving nodal plane between the two features on the visible axis. All data were collected with vis and IR pulses at magic angle.

4. Conclusion

The first 2D-EV measurements of a carotenoid in solution were demonstrated, revealing an evolution of the visible line shape within the first few hundreds of femtoseconds after photoexcitation to the S_2 state of β -apo-8'-carotenal. The line shapes along the vibrational axis evolve on a picosecond timescale. The evolution of the whole line shape is under further investigation and how it relates to the non-radiative decay from the S_2 state.

5. Acknowledgements

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