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# Following the Excited State Dynamics of $\beta$ -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  $\beta$ -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  $S^*$ ,  $S^{\ddagger}$  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,  $\beta$ -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,  $\phi_{12}$ . 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  $\phi_{12}$  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  $t_1$ - $\omega_3$  matrix, which was subsequently Fourier-transformed along the  $t_1$  axis to generate a  $\omega_1$ - $\omega_3$  2D-EV spectrum. The pump pulses were resonant with the  $S_2 \leftarrow S_0$  absorption of  $\beta$ -apo-8'-carotenal. 2D-EV spectra were recorded at room temperature in chloroform for various  $t_2$  waiting times. The  $\beta$ -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  $\beta$ -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  $1660 \text{ cm}^{-1}$  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  $\sim 2$ ) 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.

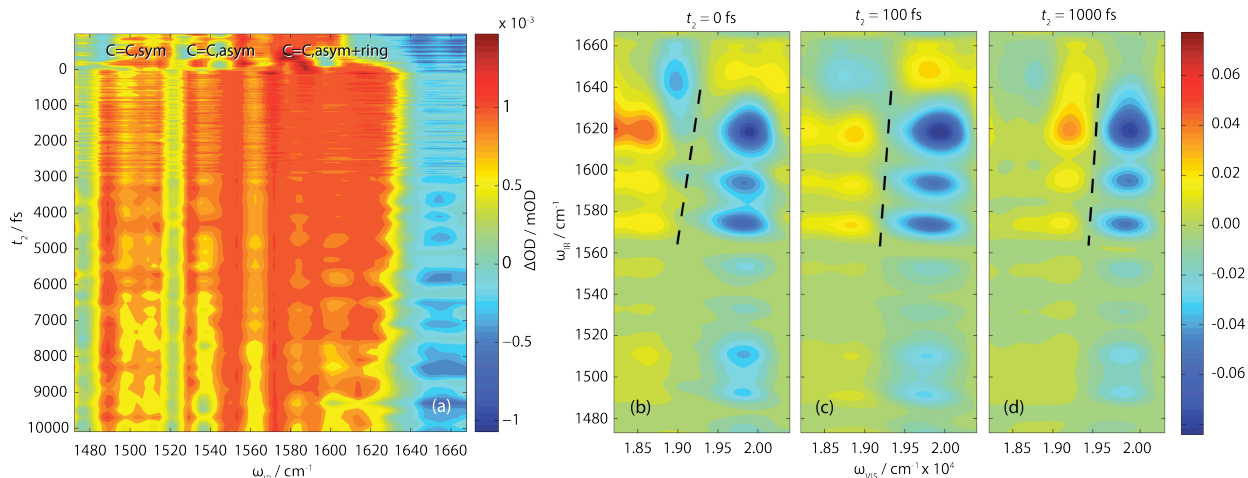


Figure 1. (a) 1-D vis-IR pump probe spectrum, (b-d) 2D-EV spectra for given values of  $t_2$ . The dashed lines in (b-d) display the evolving nodal plane between the two features on the visible axis. All data were collected with vis and IR pulses at magic angle.

#### 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  $\beta$ -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.

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