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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 relaxation of β -apo-8'-carotenal in acetonitrile solution. This new multidimensional spectroscopy technique is unique in its ability to directly follow the electronic and nuclear degrees of freedom simultaneously.

Introduction

The precise molecular mechanisms underlying the non-radiative decay pathways of the first optically bright S_2 state of carotenoids are complex and poorly understood, despite a vast number of studies. The main points of contention are the number, nature and role of lower lying electronic states couple to the S_1 state, and role that nuclear motion plays driving the non-radiative transfer. It remains unclear if the reaction co-ordinate involves direct S_2 - S_1 relaxation, or whether intermediate states such as S^* , S^\ddagger *etc.* are involved.[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 (2DEV) spectroscopy, we investigate the excited state dynamics of a model carbonyl containing carotenoid, β -apo-8'-carotenal (displayed in Fig. 1a), correlating the evolution of the electronic and nuclear degrees of freedom simultaneously.

Experimental

2DEV 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 (20 fs, centered at 515 nm, 26 nm FWHM) with an acousto-optic programmable dispersive filter (AOPDF, Dazzler, Fastlite). The AOPDF was also utilized to create a collinear pair of pump pulses, \mathbf{k}_1 and \mathbf{k}_2 , generating the coherence time delay, t_1 , with control over the relative carrier envelope phase, ϕ_{12} . The total power of these pulses at the sample position was attenuated to 250 J. At waiting time, t_2 , the probe mid-IR pulse, \mathbf{k}_3 (~90 fs, ~80 nJ) interrogate evolution on the ground or excited states and \mathbf{k}_{sig} is subsequently emitted at echo time, t_3 . In the pump-probe geometry, \mathbf{k}_{sig} is phase-locked with respect to the \mathbf{k}_3 pulse, obviating any need to phase the resulting 2D spectra. The 2D spectrum can be retrieved by phase-cycling the pump-pulse pair, as previously demonstrated with visible and infrared multidimensional spectroscopies.[5,6] For a given waiting time, t_2 , a 2DEV spectrum was collected by frequency dispersing \mathbf{k}_{sig} (and \mathbf{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 second mid-IR reference pulse that passed through the sample, but not spatially overlapped with the pump pulse pair. A 1×3 phase cycling scheme was used to acquire data, from which a t_1 - ω_3 matrix was generated for the respective re-phasing and non-rephasing pathways. These were subsequently apodized, zero-padded and Fourier-transformed along the t_1 axis to generate a ω_1 - ω_3 2DEV spectrum. The pump pulse pair were resonant with the $S_2 \leftarrow S_0$ absorption of β -apo-8'-carotenal. 2DEV spectra were recorded at room temperature in deuterated acetonitrile for many t_2 times. The β -apo-8'-carotenal sample had an optical density of 0.3 at the peak of the laser spectrum in a 250 μm path length flow cell.

Results and Discussion

Fig. 1(b) displays the frequency resolved one-dimensional visible pump, mid-IR probe spectrum of β -apo-8'-carotenal in acetonitrile solution. This probe region was chosen as to monitor the evolution of the C=C and mixed C=C/C-C backbone vibrations. The spectrum is dominated by negative features: indicative of vibrational evolution on excited potential energy surface(s). The vibrational assignments are labeled in Fig. 1(b).[7] 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 of the C=C/C-C backbone. [2] The kinetics of the three main vibrational features in Fig. 1b all decay with the same time constants and in good agreement with the S_2 and S_1 lifetimes (<200 fs and 9 ps, respectively). The frequency-dispersed pump-probe spectrum the central frequency for these bands does not shift, indicative of no change in bond order upon $S_2 \rightarrow S_1$ relaxation.

Real total 2DEV spectra are shown in Fig. 1(c-e) for $t_2 = 0, 125$ and 450 fs. Within the first few hundred femtoseconds, the center of the electronic lineshape shifts to lower frequencies (~ 100 cm^{-1}) within the convolution of our laser bandwidth and the absorption spectrum, indicative of a ballistic exit from the S_2 state. We interpret the subtle change in lineshape from square like ($t_2 = 0$ fs) to more elliptical in the first few hundreds of femtoseconds (see Fig 1c-e) as a loss of correlation between the initially excited low frequency modes that comprise the electronic lineshape and the high frequency IR active mode probed.

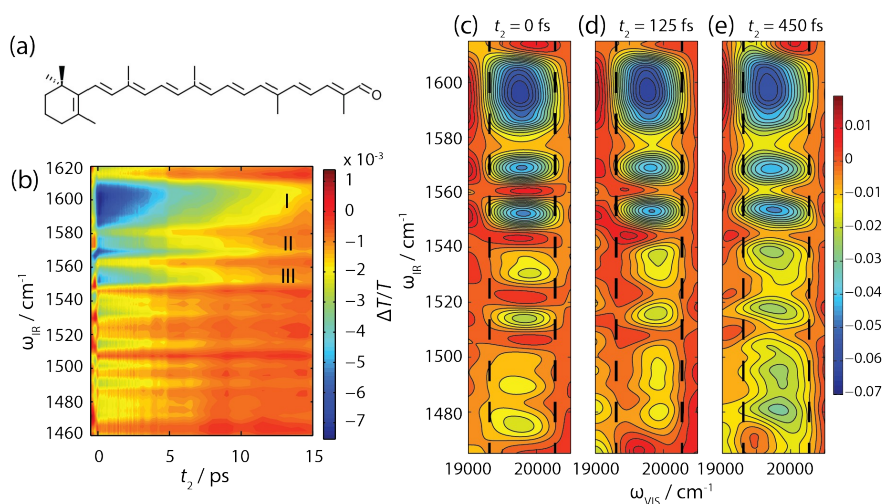


Fig. 1 (a) Skeletal structure of β -apo-8'-carotenal (b) 1D pump-probe spectrum, transient species I-III are assigned to the C=C symmetric, C=C anti-symmetric and C=C with ring breathing mo-

tions, respectively (c-e) 2DEV spectra for given values of t_2 . Dashed lines indicate the initial bounds of peaks at $t_2 = 0$ fs. Data were collected under the magic angle polarization condition.

Conclusions

We performed the first 2DEV measurements of a carotenoid (β -apo-8'-carotenal) in solution. We observe an evolution along the electronic axis within the first few hundreds of femtoseconds. The absence of any change in fundamental frequencies of the C=C/C-C back-bone vibrations is contrary to prior expectations,[2] and requires high level theoretical studies in order to understand this observation. Further analysis of the lineshapes in 2DEV spectra [4] is required to ascertain how to interpret the correlation function between the low-frequency modes and the probed mid-IR active vibration. Future 2DEV studies will seek to probe the dynamics of the carbonyl mode and its role in the S_2 relaxation.

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