Population Dynamics in Vibrational Modes during Non-Born−Oppenheimer Processes: CARS Spectroscopy Used as a Mode-Selective Filter

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The mechanism of nonradiative transitions such as internal conversion (IC) between electronic states of a molecular system has been the object of intensive theoretical and experimental studies.[1] For processes of this type, the adiabatic picture which has its roots in the Born−Oppenheimer approximation breaks down, and a coupling between electronic and nuclear degrees of freedom of the molecular system facilitates a transition in the region where the potential energy surfaces (PES) of the participating states approach one another energetically. This nonadiabatic coupling via the normal modes of the system is decisive for the mechanism of photochemical reactions and constitutes the primary step in photobiological processes such as vision and photosynthesis.[2]

To experimentally explore the role of different normal modes of a molecular system during a nonadiabatic process such as IC, a real-time, mode-selective monitor of the population flow must be employed. For this purpose, coherent anti-Stokes Raman-scattering (CARS) is used as a probe mechanism in a time-resolved pump−probe scheme as shown in Figure 1. A short overview of the experimental methodology is given here,[3] while a detailed description of femtosecond time-resolved CARS can be found in the literature.[4]

The mechanism, with which the CARS process can act as a selective probe of the population within the vibrational states of a specific normal mode has its foundation in the strong enhancement of the CARS intensity when the energy difference, $\Delta\tilde{v}$ between the *pump* and *Stokes* laser (**1** and **2** in Figure 1) is resonant to a Raman transition. The resonance enhancement by means of a Raman transition is the result of an effective projection of an initial population in a vibrational state (with the quantum number, $v = n$; $n = 1, 2, 3, ...$), into a intermediate vibrational state ($v = n + 1$) through the interaction with the *pump* and *Stokes* lasers **1** and **2**. In the case of a Raman resonance, an effectively prepared, intermediate vibration state ($v = n + 1$) of a specific normal mode will lead to a strong inelastic scattering of *pump* laser **3**, and subsequently to the generation of an intense anti-Stokes signal **4**. The lack of a Raman resonance forces the CARS process to go through a virtual intermediate state, making the generation of the CARS signal out of the initial state ($v = n$) through the interaction with lasers **1**−**3** extremely ineffective.

Furthermore, the energy level of the quantum state with $v = 0$ in the electronic ground state will not be uniform for different normal modes leading to an offset in the progression of energy levels ($v = 0, 1, 2, ..., n$) among the different normal modes. Therefore, a Raman resonance enhancement can only be fulfilled, if the CARS process takes place out of an initial vibrational state of the normal mode to which the energy difference, $\Delta\tilde{v}$ is tuned to. If the CARS process initiates from a vibrational state of a normal mode that does not correspond to $\Delta\tilde{v}$, then the energetic offset among the vibrational states of different normal modes will not
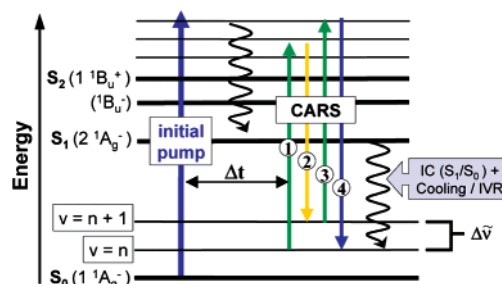
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Figure 1. Schematic energy diagram of *all-trans-β*-carotene in *n*-hexane illustrating the excitation by means of an *initial pump* laser and a mode-selective interrogation via a time-variable CARS process.

allow for a resonant Raman enhancement. The effect of an anharmonic potential on the energy gap between the vibrational states of a specific mode will be compensated by the broadband nature of the femtosecond laser pulses applied in the experiment. In summary, CARS as a probe mechanism, will act as a filter for interrogating the progression of vibrational states ($v = 0$ to n) of a specific normal mode, that shows an energy difference among its vibrational states equal to $\Delta\tilde{v}$ of lasers **1** and **2**.

This selectivity is utilized for interrogating the population flow in normal modes of β-carotene after the S_1/S_0 IC using the experimental scheme shown in Figure 1.[3] The relaxation dynamics from the S_2 into the S_1 state taking place after photoexcitation of β-carotene with the *initial pump* laser *(IP)* into the S_2 state are well characterized.[5] To resolve the dynamics of the subsequent population flow from the S_1 state into the different normal modes of the S_0 state, a variable delay time, Δt is introduced between the *IP* laser and the lasers of the CARS process. For delay times $\Delta t \geq 0$ (panel A of Figure 2), the experimental scheme corresponds to the probing of an electronic ground-state bleach induced by the population transfer into the S_2-state via the *IP* laser.

By tuning the CARS process to different Raman modes of β-carotene in the electronic ground state and observing the dynamics at a spectral position of the CARS signal that can be associated with a Raman transition (see panel B, Figure 2), a superposition of the dynamics taking place in the vibrational states ($v = 0$ to n) of a specific normal mode can be observed. This population flow taking place as the result of the S_1/S_0 IC and subsequent internal vibrational energy redistribution (IVR) and vibrational cooling can be characterized with a monoexponential recovery time-constant, τ as shown in panel A of Figure 2.[6] This was carried out for the normal modes in the electronic ground state of β-carotene that showed adequate spectral separation form other modes to be differentiated with the broadband femtosecond pulses. The results are summarized in Table 1, and the values for τ clearly show that the population flow from the S_1 state into the electronic ground state is not uniform for the normal modes that were interrogated. With this information, it is possible to gain direct insight into the exact mechanism of the S_1/S_0 IC with respect to the nuclear dynamics involved in this electronic transition.
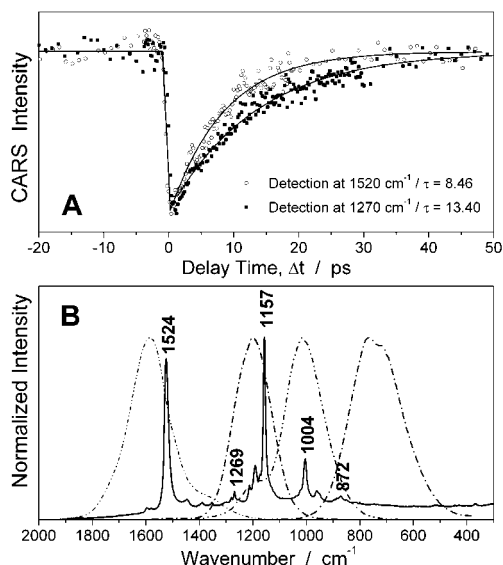
Figure 2. (A) Intensity of the CARS signal plotted as a function of the delay time Δt, between the *initial pump* laser and the CARS process, which is tuned resonant with two different normal modes. (B) Resonance Raman spectrum of β-carotene (solid line) and spectral profile of the CARS signal at $\Delta t = 1$ ps, tuned to the different normal modes of β-carotene in the S_0 state (dotted lines).

Table 1. Overview of the Recovery Time, τ, for Different Normal Modes

wavenumber (cm^{-1})	recovery time, τ (ps)	characteristic motion
1524	8.46 ± 0.23	C=C symmetric stretch
1269	13.40 ± 0.27	C–H bending
1157	8.92 ± 0.27	C–C symmetric stretch
1004	9.13 ± 0.43	methyl to chain stretch
872	10.90 ± 0.63	C=C–C bending

Particularly interesting is the fastest recovery time of $\tau = 8.46$ ps for the normal mode at 1524 cm^{-1}, dominated by the C=C symmetric stretch along the polyene backbone. The comparison to other modes shows that this normal mode acts as the primary funnel for the population flow from the S_1 to the S_0 PES, and this is supported by a variety of experimental findings in the literature placed in the theoretical framework of IC. According to the Engelman–Jortner theory[8] of IC, coupling modes that show large nuclear displacements are particularly suited as accepting modes in the transition between two PES due to the advantageous Franck–Condon factors. This criterion is met by the C=C symmetric stretch of model polyenes. Transient S_1 state IR-absorption experiments[5a] and theoretical calculations[9] confirm that the equilibrium bond length of this mode displays a large nuclear displacement to a longer bond length from the S_1 to the S_0 state, in comparison to all other modes in the S_1 state. Additionally, lifetime broadening seen in the much larger FWHM of the S_1 Raman band at 1790 cm^{-1}, assigned to the C=C symmetric stretch in the S_1 state, supports population flow out of the S_1 state through this mode.[10] Further support is given by a full ^{13}C substitution in β-carotene which leads to much longer time constants for the S_1/S_0 IC, while a full deuteration only shows small effects. This makes normal modes with nuclear motion of carbon/carbon bonds along the polyene backbone candidates for the bottleneck of population flow, while carbon/hydrogen as well as large skeletal motion are unlikely for this role.[10] Noteworthy for this is the relatively fast recovery time of $\tau = 8.92$ ps for the C–C symmetric stretch mode, which gives further evidence that the dynamics of the S_1/S_0 IC are centered around the polyene backbone.

In the two-state/two-mode model of IC,[1] the population flow during IC is funneled into a single normal mode and then spreads out over the normal modes of the energetically lower-lying PES via IVR and cooling. A comparison of $\tau = 8.46$ ps with the time constant for the S_1/S_0 IC of $\tau_{IC} = 9.92$ ps by a probe mechanism that gives a mode-averaged rate of the S_1 depopulation[10] in combination with the arguments mentioned above, shows that the C=C symmetric stretch with $\tau = 8.46$ ps is (i) the nuclear motion representing the bottleneck for the population flow between the S_1 and S_0 PES since it is clearly faster than the mode-averaged rate and (ii) primarily determined by the dynamics of S_1/S_0 IC and not cooling effects since this can only lead to time constants that are slower than the mode-averaged time constant exclusively characterizing the S_1/S_0 IC. For the other normal modes in Table 1, the slower recovery times of $\tau = 9.13-13.4$ ps indicate a strong influence of IVR and cooling effects. This would support a mechanism in which the C=C symmetric stretch mode first populates the S_0 state with subsequent population flow in other modes via IVR. Nonetheless, it cannot be ruled out that the varying τ for the modes in Table 1 are caused by different coupling matrix elements for the S_1/S_0 IC.

In summary, it has been shown in this work that the CARS process used as a probe mechanism in a time-resolved *pump–probe* scheme is a powerful tool in optical time-resolved spectroscopy for determining the population flow in specific normal modes of a molecular system. It is possible to directly determine that the nuclear motion involved in the S_1/S_0 IC in β-carotene is dominated by dynamics of the polyene backbone. With this, insight to the mechanism of non-Born–Oppenheimer dynamics with respect to the role of specific normal modes is gained. For further work, the CARS process shows the potential to act as a powerful tool for determining the reaction coordinate and with this, the precise mechanism of photochemical reactions and electron transfer in which the change in electronic distribution is substantial, leading to the dissociation and formation of chemical bonds.

References

(1) See, e.g. (a) Stock, G.; Domcke, W. *Adv. Chem Phys.* **1997**, *100*, 1–169. (b) Blanchet, V.; Zgierski, M. Z.; Seideman, T.; Stolow, A. *Nature* **1999**, *401*, 52–54 and references cited in a and b.

(2) See, e.g. (a) Schoenlein, R. W.; Peteanu, L. A.; Mathies, R. A.; Shank, C. V. *Science* **1991**, *254*, 412–415. (b) Hahn, S.; Stock, G. *J. Phys. Chem. B* **2000**, *104*, 1146–1149, and references cited in a and b.

(3) As shown in Figure 1, an *initial pump* laser ($\lambda_{IP} = 400$ nm, FWHM = 250 fs), transfers population to the first optically accessible S_2 state. The subsequent S_1/S_0 IC, vibrational cooling, and IVR is interrogated mode-selectively via a time-variable CARS process consisting of two *pump* lasers (**1** and **3** in Figure 1, $\lambda_{pump} = 510$ nm) that also utilizes the $S_2 \leftarrow S_0$ optical transition and a *Stokes* laser (**2** in Figure 1, $\lambda_{Stokes} = 530-550$ nm) which allows for the CARS process to be tuned to different normal modes ($\Delta \tilde{\nu}$) in the S_0 state. The CARS probe is characterized by a FWHM of 120 fs in the convolution of (**1**–**3**). Lasers **1**–**3** generate the CARS signal (**4**, in Figure 1) which is monitored as a function of the delay time, (Δt) between the *initial pump* laser and the CARS process.

(4) See, e.g. (a) Motzkus, M.; Pedersen, S.; Zewail, A. H. *J. Phys. Chem.* **1996**, *100*, 5620–5633. (b) Mukamel, S. *Principles of Nonlinear Optical Spectroscopy*; Oxford University Press: New York, 1995.

(5) See, e.g. (a) Polívka, T.; Zigmantas, D.; Frank, H. A.; Bautista, J. A.; Herek, J. L.; Koyama, Y.; Fujii, R.; Sundström, V. *J. Phys. Chem. B* **2001**, *105*, 1072–1080. (b) Yoshizawa, M.; Aoki, H.; Hashimoto, H. *Phys. Rev. B* **2001**, *64*, 18301-1–18301-4.

(6) The repopulation of the normal modes in the S_0 state can be attributed solely to nonradiative processes, since the $S_0 \leftarrow S_1$ optical transition is optically forbidden, ruling out fluorescence. With $\lambda_{pump} = 510$ nm, contributions of the dynamics in S_1 state Raman modes to the CARS signal via the $S_n \leftarrow S_1$ transition were ruled out by control experiments, where the CARS process was temporally resolved for a fixed $\Delta t = 1$ ps between the *IP* laser and CARS process. Fourier transformations of the transients exclusively show a spectral signature of S_0 state Raman shifts.

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