Controlling Excitations of Coupled Vibrations by Shaped Mid-Infrared Pulses

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Abstract: Mid-infrared pulse shaping was utilized for controlling excitations of coupled vibrations in metal di-carbonyls. Excitation into the combination state was maximized by simultaneous controls over vibrational ladder climbing and quantum mechanical multi-path interference.

1. Motivation and Objectives

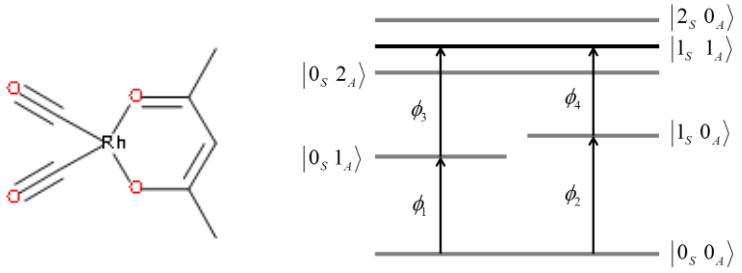
Coherent control is a quantum mechanical method that manipulates interference of wave functions by shaping their amplitudes and phases. Recent developments in the pulse shaping technique in mid-infrared (MIR) [1] may open a way toward coherent control over molecular motions/reactions along the normal coordinates. Such control may serve for novel information processing and molecular reaction controls [2-4]. So far, the MIR pulse shaping was applied to control over excitations of a single vibrational mode [5].

Here, we demonstrate that excitations of two vibrational modes in condensed-phase molecules are controlled by MIR pulse shaping. Excitation into a combination state is maximized by enhancing vibrational ladder climbing in each excitation pathway and by adjusting the quantum-mechanical interferences between different pathways to be constructive. Schemes to manipulate MULTIPLE vibrational degrees of freedom are crucial for increasing the variety of controllable reactions.

2. Shaped MIR Pump-Probe Measurements of RDC in Hexane

MIR pulses of 100-fs duration and 5-μJ energy are generated by the OPA/DFG system. Major portion of the pulse energy was delivered to the pulse shaper, consisting of diffraction gratings, concave mirrors and the germanium acousto-optic modulator [1]. The shaped pulse is characterized by the electric-field cross correlation in spectral interferometry with a reference pulse, which is characterized by an interferometric auto-correlation. The shaped pulse and the unshaped pulse with fractional energy were used as pump and probe pulses, respectively. The pump and probe pulses have parallel linear polarizations. The spectra of probe pulses transmitted through a sample are acquired by a monochromator and a HgCdTe detector array.

Acetylacetonato-dicarbonyl rhodium (RDC, Figure 1(a)) is a model compounds in 2D-IR spectroscopy [7-9]. Vibrational level structure of two coupled symmetric (S) and anti-symmetric (A) CO stretch vibrations is shown in Fig.1(b). Here $|m_S\ n_A\rangle$ denotes the eigenstate with quantum numbers m and n for S and A modes, respectively, and ϕ_i denotes the phase of the MIR frequency relevant for each transition. The pump spectrum has 200-cm^{-1} bandwidth and covers four transitions leading to the combination state $|1_S\ 1_A\rangle$.



(a) (b)

Fig. 1 (a) Molecular structure and (b) vibrational level structure for RDC.

3. Vibrational Excitation Controls in Metal Carbonyls

3.1 Enhancement of the resonant two-step excitation efficiency by introducing group delays

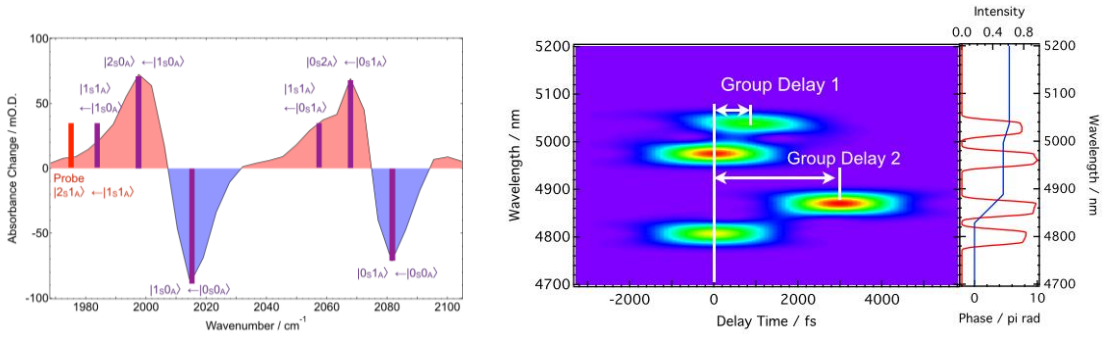
Figure 2(a) shows the time resolved IR spectra at 1 ps pump-probe delay for RDC in hexane, pumped by nearly transform-limited pulses. There observed the bleaching signal at the fundamental transition frequency for each mode and the corresponding excited-state absorptions.

In order to increase the two-step excitation efficiency into the combination state, adequate amount of group delay should be introduced between two spectral components which complete excitation into the combination state. Figure 2(b) shows the spectrogram of shaped MIR pump pulse and the corresponding spectral intensity/phase profiles (right panel). Spectral amplitude of the pump was shaped so that the pump pulse does not induce vibrational excitation other than the ones shown as arrows in Fig.1(b). In addition, the spectral phase was shaped to introduce group delays to enhance each of the two-step

resonant excitations into $|1_S\ 1_A\rangle$ state. Figure 3(a) shows the correlation map of the absorbance change of the pump-probe signal probed at 1975 cm^{-1}, which corresponds to the population of the $|1_S\ 1_A\rangle$ state. The population of the $|1_S\ 1_A\rangle$ state were maximized at the delay time 1 = 1400 fs and delay time 2 = 1600 fs, respectively, and was increased by almost twice, compared with the case of transform-limited waveform.

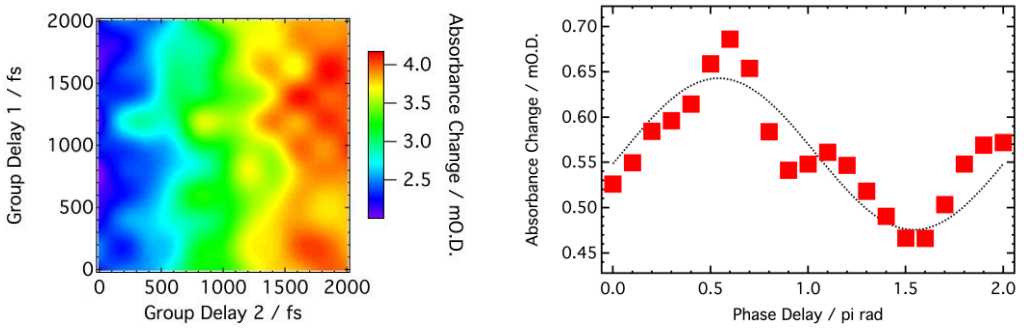
3.2 Controlling inter-pathway interference in two-step excitations by introducing the phase delay

Subsequent to introducing the group delay to enhance the population of the $|1_S\ 1_A\rangle$ state, the phase delay ϕ_4 was also introduced to control the quantum-mechanical interference among different excitation pathways toward the $|1_S\ 1_A\rangle$ state. Figure 3(b) is the phase delay ϕ_4 dependence of absorbance change for the $|1_S\ 1_A\rangle$ to $|2_S\ 1_A\rangle$ transition, reflecting population at the $|1_S\ 1_A\rangle$ state. As is clearly seen in this result, absorbance change varied sinusoidally with a period of 2 pi and 0.6 pi radians of the phase delay ϕ_4 maximizes the population of the $|1_S\ 1_A\rangle$ state. This indicates that the wavefunctions of the $|1_S\ 1_A\rangle$ state created through two excitation pathways interfere constructively at 0.6 pi radians of the phase delay on ϕ_4.



(a) (b)

Fig. 2 (a) The time-resolved IR spectra at time-delay of 1 ps pumped with nearly transform-limited pulses. (b) The spectrogram of shaped MIR pump pulse. The group delay 1 and 2 are introduced to enhance the excitation efficiency.



(a) (b)

Fig. 3 (a) Absorbance change for $|1_S\ 1_A\rangle$ to $|2_S\ 1_A\rangle$ transition plotted against group delays 1 and 2. (b) The phase ϕ_4 dependence of the absorbance change for the $|1_S\ 1_A\rangle$ to $|2_S\ 1_A\rangle$ transition.

5. Summary and Outlook

The enhancement of the two-step excitation efficiency and the quantum interference between two excitation pathways were successfully controlled in RDC in hexane by MIR phase-shaping. The results experimentally confirmed that IR coherent control over multiple vibrational degrees of freedom works properly in condensed phases.

6. References

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