

Controlling Quantum Interferences in IR Vibrational Excitations in Metal Carbonyls

S. Ashihara¹, K. Enomoto¹, J. Tayama¹

¹Department of Applied Physics, Tokyo University of Agriculture and Technology, 2-24-16, Nakacho, Koganei, Tokyo 184-8588, Japan

Abstract. Coherent controls over vibrational excitations in metal di-carbonyls were demonstrated by using phase-shaped mid-infrared pulses. The phase of the inter-state coherence between two different normal-modes was controlled by changing the phase step of the stepwise spectral phase profile. The quantum interference between multiple vibrational excitation paths in resonant two-step excitations was manipulated by the similar spectral phase control. The results experimentally confirmed that coherent control over multiple vibrational degrees of freedom works properly in condensed phases. There remains the possibility for increasing excitation efficiency by introducing group-delays and by optimizing polarization state of the excitation pulse.

1 Motivation and Objectives

Coherent control is a technique that manipulates interference of wave functions by adjusting their amplitudes and phases. Recent developments in the pulse shaping technique in MIR [1] may open a way toward coherent control over molecular motions/reactions at the electronic ground states. Such control may serve for novel information processing and molecular reaction controls, including bond breakage, structural isomerization, hydrogen bond rearrangement, proton transfer, etc. [2-4]. So far the MIR pulse shaping was applied to the ladder climbing of a single vibrational mode [5].

The broadband nature of the ultrashort MIR pulses, however, should also be able to excite multiple vibrational modes in a correlated manner to control nuclear motion in multi-dimensional coordinates and to create highly-excited vibrational states. The ability to handle multiple vibrational modes should increase the variety and efficiency of controllable reactions. For such coherent control applications, control over quantum interference as well as efficient ladder climbing is essential. In this paper, we show that the quantum interferences in IR vibrational excitations were successfully controlled for liquid-phase molecules by use of MIR phase-shaping.

2 MIR Pulse Shaping and Transient Absorption Spectroscopy

MIR pulses of 100-fs duration and 5- μ J energy were 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 AOM, developed by Zanni-group [1]. The shaped pulse was characterized by the electric-field cross correlation in the spectral interferometry with a reference

pulse, which had been characterized by an interferometric auto-correlation. With this setup, we achieved higher-order dispersion compensation and precise phase shaping [6]. The shaped pulse and the unshaped pulse with fractional energy were used as pump and probe pulses, respectively. The pump and probe pulses had linear polarizations, parallel to each other. The spectra of probe pulses transmitted through a sample were acquired by a monochromator and a HgCdTe detector array.

3 IR Coherent Control Experiments on Metal Carbonyls

3.1 Controlling the phase of the interstate coherence between two normal modes

Our samples were metal di-carbonyls $\text{Ir}(\text{CO})_2\text{C}_5\text{H}_7\text{O}_2$ (IDC) and $\text{Rh}(\text{CO})_2\text{C}_5\text{H}_7\text{O}_2$ (RDC), which have been model compounds in 2D-IR spectroscopy: vibrational couplings and population/coherence transfer in metal carbonyls have been studied [7-9]. The vibrational energy-level diagram for two anharmonically coupled symmetric (S) and anti-symmetric (A) CO stretch vibrations is shown in Fig.1(a). 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 component relevant for each transition. The center frequency of the pump with 200-cm^{-1} bandwidth was tuned so that the pump spectrum covers six transitions (shown as arrows).

Figure 1(b) shows the transient absorption spectrum at 1-ps time delay for IDC in *n*-hexane, pumped by nearly transform-limited pulses. The linear absorption for IDC (a dashed line) reveals the fundamental transition frequencies of 1999 and 2074 cm^{-1} for A and S modes, respectively. There observed the bleaching signal at the fundamental transition frequency for each mode and the corresponding excited-state absorption. The inset shows transient signals at 2065 and 2074 cm^{-1} . On top of the excited-state absorption/bleaching contributions, the oscillations with a beat frequency of the two states $|0_S 1_A\rangle$ and $|1_S 0_A\rangle$ (~ 450 fs period) were observed, indicating the coherent superposition of the two states.

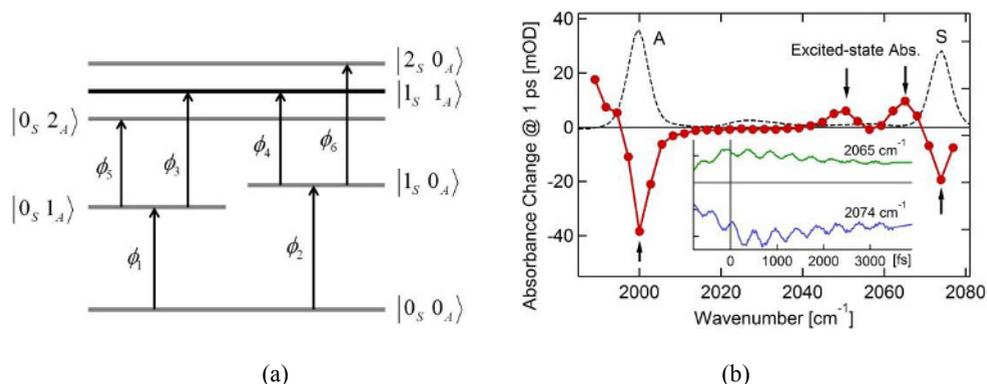


Fig. 1. (a) Vibrational energy-level diagram for IDC and RDC. (b) The transient absorption spectrum measured at time-delay of 1 ps pumped with nearly transform-limited pulses: the inset shows the transient signals at 2065 and 2074 cm^{-1} .

Now the spectral phase of the pump was shaped in a stepwise profile to control $\phi_2 - \phi_1$. Figure 2(a) shows the beat signals extracted from the transients probed at 2074 cm^{-1} . As can be seen, the phase of the beat signal changed according to the relative phase $\phi_2 - \phi_1$. Superposition of energetically close but non-degenerate two modes creates 2D vibrational trajectory, which evolves with time (as linear, circular, or elliptical). Therefore the present control corresponds to selecting the initial trajectory upon excitation. This is also interpreted as control over local-mode amplitudes at the moment of excitation.

3.2 Controlling multiple-paths interference in two-step excitations

We used similar phase-shaping scheme to control the excitation efficiency into $|1_S 1_A\rangle$ state for RDC in *n*-hexane. It is expected that there exist two of the resonant two-step excitation paths toward $|1_S 1_A\rangle$ state: the one via $|0_S 1_A\rangle$ and the other via $|1_S 0_A\rangle$. Then the efficiency of excitation into the $|1_S 1_A\rangle$ state, because of the quantum interference, should depend on the phase difference $\Delta\phi = (\phi_1 + \phi_3) - (\phi_2 + \phi_4)$. Figure 2(b) shows the absorbance change at $|1_S 1_A\rangle \rightarrow |1_S 2_A\rangle$ transition frequency (1975 cm^{-1}) measured while the phase ϕ_4 was varied. As is clearly seen, the absorbance change (proportional to the $|1_S 1_A\rangle$ population) varied sinusoidally with a period of 2π . This indicates that the quantum interference between multiple excitation paths into $|1_S 1_A\rangle$ state was controlled by the spectral phase. Additional set of experiments revealed that there are more than two excitation paths, some of which are activated by coherence transfers between S and A excitations.

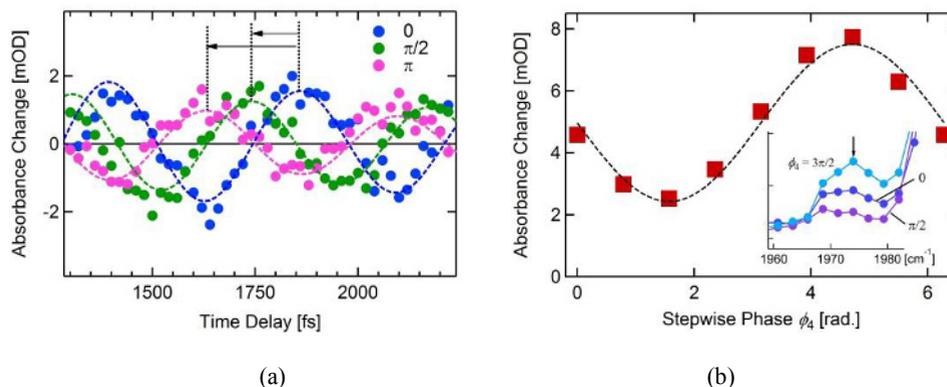


Fig. 2. (a) The beat signal at 2074 cm^{-1} probe frequency for IDC when the pump had the stepwise spectral phase of 0 , 0.5π , and 1.0π , respectively. (b) The phase ϕ_4 dependence of the absorbance change reflecting the $|1_S 1_A\rangle$ population for RDC.

4 Summary

The inter-state coherence between two vibrational modes and the quantum interference between multiple vibrational excitation paths in metal di-carbonyls were controlled by the phase-shaped MIR pulses. The results confirmed that IR coherent control over multiple vibrational degrees of freedom works properly in condensed phases. Future works include the enhancement of the two-step excitation efficiency, by introducing group-delays and by optimizing the polarization states.

References

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