

&RQWUROOLQJ 4XDQWXP ,QWHUIHUHQFHV
([FLWDWLRQV LQ 0HWDO &DUERQ\OV

6 \$VKLKD(QRPRWRD\DPD

'HSDUWPHQW RI \$SDUHQH&1KHULFW\ RI \$JULFXOWXUH DQG
1DNDFKR .RJDQHL -7RSDQ

\$EVWUD&RWHUHQW FRQWUROV RYHQHYLFDQDGLRQDORQ\0VWZ
GHPRQVWUDWHG E\ XVLQJ SKDVH VKDSHG PLG LQIUUDHG
FRKHUHQFH EHWZHHQ WZR GLIIHUHQW QRUPDO PRGHV ZDV
VWHS RI WKH VWHSZLVH VSHFWUDO SKDVH SURILOH 7KH
YLEUDWLRQDO H[FLWDWLRQ SDWKV LQ UHVRQDQW WZR V
VLPLODU VSHFWUDO SKDVH FRQWURO 7KH UUVXOWV H[S
FRQWURO RYHU PXOWLSOH YLEUDWLRQDO GHJUHHV RI IU
SKDVHV 7KHUH UHPDLQV WKH SRVVLELOLW\ IRU LQFUHDVH
JURXS GHOD\ DQG E\ RSWLPL]LQJ SRODUL]DWLRQ VWDWH

ORWLYDWLRQ DQG 2EMHFWLYHV

&RKHUHQW FRQWURO LV D WHFKQLTXH WKDW PDQLSXODW
DPSOLWXGHV DQG SKDVHV 5HFHQW GHYHORSPHQWV LQ W
ZD\ WRZDUG FRKHUHQW FRQWURO RYHU PROHFXODU PRWL
FRQWURO PD\ VHUYH IRU QRYHO LQIRUPDWLRQ SURFHVVL
EUHDNDJH VWUXFWXUDO LVRPHUL]DWLRQ K\GURJHQ ERQ
WKH 0,5 SXOVH VKDSLQJ ZDV DSSOLHG WR WKH ODGGHU FC
7KH EURDGEDQG QDWXUH RI WKH XOWUDVKRUW 0,5 SX
PXOWLSOH YLEUDWLRQDO PRGHV LQ D FRUUDHWHG PDQ
FRRUGLQDWHV DQG WR FUHDWH KLJKO\ H[FLWHG YLEUDWL
PRGHV VKRXOG LQFUHDVH WKH YDULHW\ DQG HIILFLHQF\ R
DSSOLFDWLRQV FRQWURO RYHU TXDQWXP LQWHUIHUHQFH
WKLV SDSHU ZH VKRZ WKDW WKH TXDQWXP LQWHUIHUHQFH
FRQWUROOHG IRU OLTXLG SKDVH PROHFXOHV E\ XVH RI 0,5

0,5 3XOVH 6KDSLQJ DQG 7UDQVLHQW \$EVRUSWL

0,5 SXOVHV RI IV RYHUHWLJQZHQG JHQHUDWHG E\ WKH
SRUWLRQ RI WKH SXOVH HQHUJ\ ZDV GHOLYHUHG WR WKH
FRQFDYH PLUURUV DQG WKH JHUPDQLXP \$20 GHYHORSHG
FKDUDFWHUL]HG E\ WKH HOHFWULF ILHOG FURVV FRUHO

SXOVH ZKLFK KDG EHHQ FKDUDFWHULJHG E\ DQ LQWHUIH
DFKLHYHG KLJKHU RUGHU GLVSHUVRQ FRPSHQVDWLRQ DQ
WKH XQVKDSHG SXOVH ZLWK IUDFWLRQDO HQHUJ\ ZHUH X
SXPS DQG SUREH SXOVHV KDG OLQHDU SRODULJDWLRQV
WUDQVPLWWHG WKURXJK D VDPH ZHUH DFTXLHG E\ D P

,5 &RKHUHQW &RQWURO ([SHULPHQWV RQ 0HWD

&RQWUROOLQJ WKH SKDVH RI WKH LQWHUVRQDWH FRKHU

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.

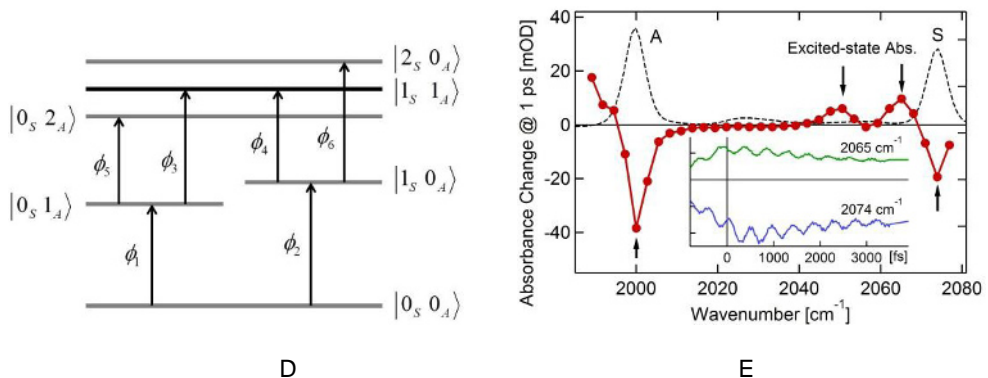
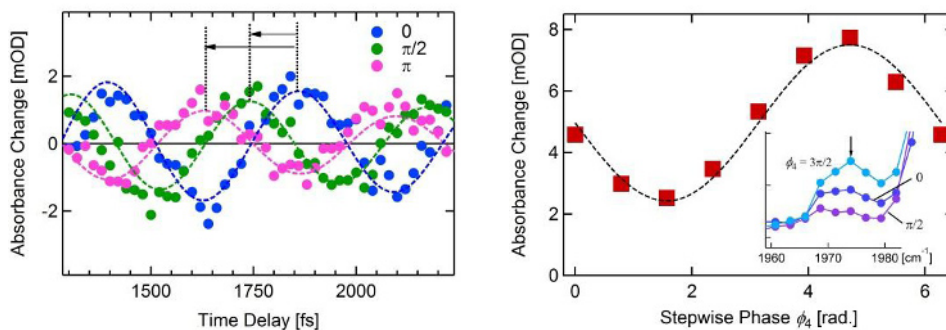


Fig. 1. D 9LEUDWLRQDO HQHUJ\ OHYHO GLDJUDP IRU , ' & DQG
VSHFWUXP PHDVXUHG DW WLPH GHOD\ RI SV SXPSHG ZLWK
VKRZV WKH WUDQVVLHQQW VLJQDOV DW DQG FP

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.

& R Q W U R O O L Q S J D P K X O W Q S O H U I H U H Q F H L Q W Z R V W H S H [F L W D

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 $\phi = (\phi_1 + \phi_3) - (\phi_2 + \phi_4)$. 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.



D

Fig. 2. D 7KH EHDW VLJCSJQR EDHWIHTXFPQF\ IRU , & ZKHQ WKH VWHSZLVH VSHFW S DDOQ SK DVHV SHFWLYHOY GEHSFIHG HQ DW HRI W H DEVRUEDQFH FKDQ J H> USR O XIG DWQR QV KRHU 5' &

6 X P P D U \

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.

5 H I H U H Q F H V

6 ±+ 6'K%P 6WUDVIHOG (&)XQ2PSHWU 14DS G 0 7 =DQQL <)XMLPX*URDQ]DOH] . +RNL - 0DQ] < 2366VVXNL &KHP 0 \$UWDPRQRY 7 6 +R + 323DELW] &KHP 3K\V & *ROOXE 0 .RZDOHZVNL 6 7KDOOPDLU DQG 5129LYLH ' % 6WU@V±HOG6KLP DQG 0 7 =DQQL 3K\V 5HY /HWW 6 \$VKLKDUD < +LUDVDZD . (QRPRWR &RQIHUHQFH R 4XDQWXP (OHFWURQLFV &RQIHUHQFH &) 0 .KDOLO 1 'HPLUGRYHQ \$ 7RN12IDNRIIHW DO - &KHP) 'LQJ&)XOPHU 0 7 =DQQ 123 - &KHP 3K\V & 5 %DL] .XEDU\FK (*HYD H5 3K\V &KHP %