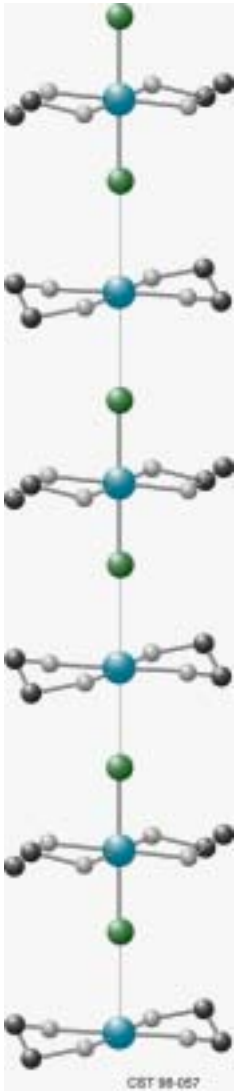
Ultrafast electronic and vibrational dynamics in quasi-one-dimensional molecular solids

Susan L. Dexheimer
Washington State University

Acknowledgments

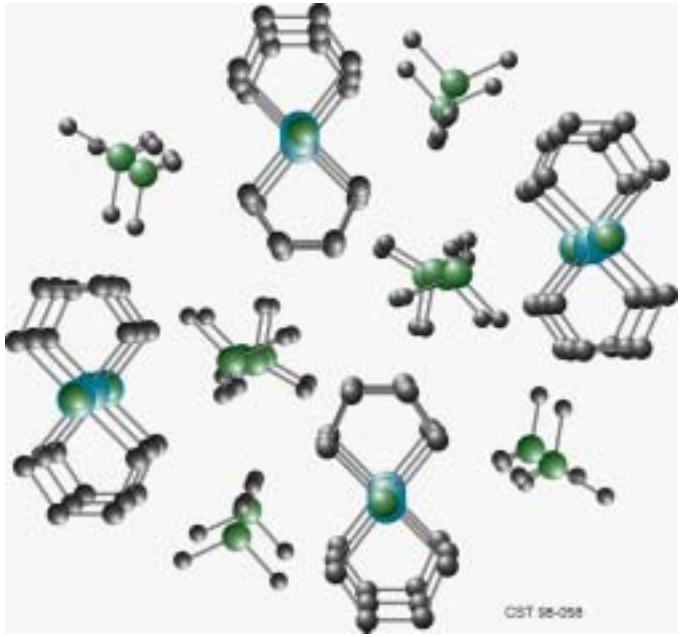
A.D. Van Pelt and F.X. Morrissey
J.A. Brozik and W.E. Buschmann
National Science Foundation CAREER Award
National Science Foundation Division of Materials Research

Quasi-one-dimensional mixed-valence chain complexes



$[\,Pt\,(en)_2\,]\,[\,Pt\,(en)_2\,X_2\,]\cdot ClO_4$ X = Cl, Br, I

X	ρ
Cl	0.743
Br	0.828
I	0.890



Schematic chain axis structures

... -------- X^---- $Pt^{+(3+\delta)}$ --- X^- -------- $Pt^{+(3-\delta)}$ -------- X^---- $Pt^{+(3+\delta)}$ --- X^--------- $Pt^{+(3-\delta)}$ -------- ...

charge density wave ground state

... -------- X^---- $Pt^{+(3+\delta)}$ --- X^- -------- $Pt^{+(3-\delta)}$ -------- X^---- $Pt^{+(3+\delta)}$ --- X^--------- $Pt^{+(3-\delta)}$ -------- ...

optical intervalence charge-transfer transition

... -------- X^---- $Pt^{+(3+\delta)}$ ----- X^- ----- Pt^{+3} ---- X^- ---- Pt^{+3} ---- X^- -------- $Pt^{+(3-\delta)}$ -------- ...

equilibrated self-trapped exciton

Chain axis vibrational modes

ν_1 ------- $Pt^{+(3-\delta)}$ ------- $\overset{\leftarrow}{X^-}$ -- $Pt^{+(3+\delta)}$ -- $\overset{\rightarrow}{X^-}$ ------- $Pt^{+(3-\delta)}$ -------

symmetric stretch (Raman active)

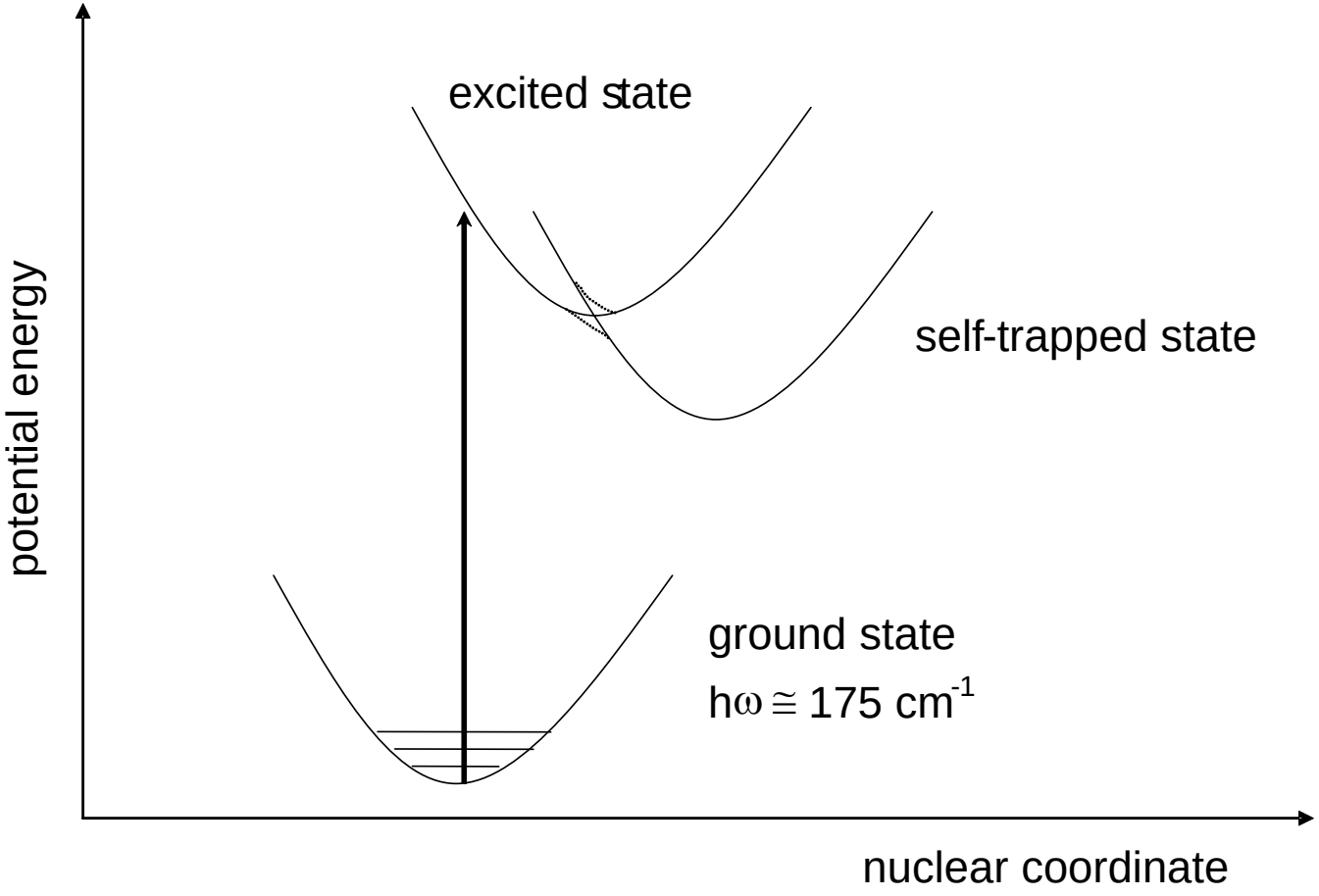
ν_2 ------- $\overset{\rightarrow}{Pt^{+(3-\delta)}}$ ------- $\overset{\leftarrow}{X^-}$ -- $Pt^{+(3+\delta)}$ -- $\overset{\leftarrow}{X^-}$ ------- $\overset{\rightarrow}{Pt^{+(3-\delta)}}$ -------

asymmetric stretch (IR active)

ν_3 ------- $\overset{\leftarrow}{Pt^{+(3-\delta)}}$ ------- $\overset{\rightarrow}{X^-}$ -- $\overset{\rightarrow}{Pt^{+(3+\delta)}}$ -- $\overset{\rightarrow}{X^-}$ ------- $\overset{\leftarrow}{Pt^{+(3-\delta)}}$ -------

low-frequency stretch (IR active)

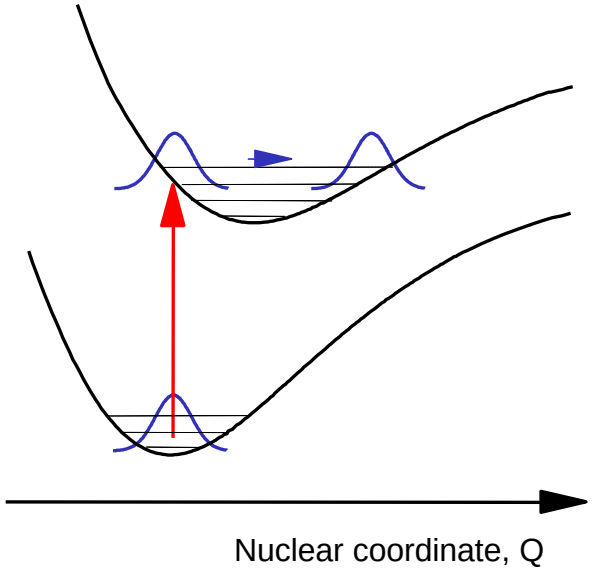
Schematic potential energy surfaces



Vibrationally impulsive excitation

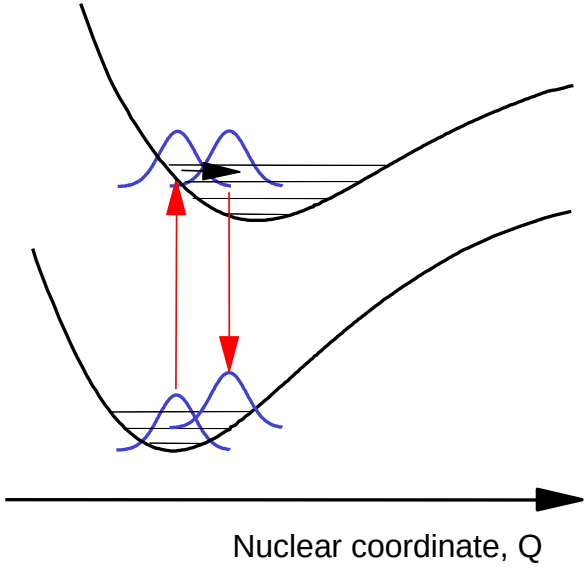
Excited state wavepacket

$$\Phi(Q,t) = \sum_n a_n \, \Phi_n(Q) \exp(-\, i\omega_n t)$$

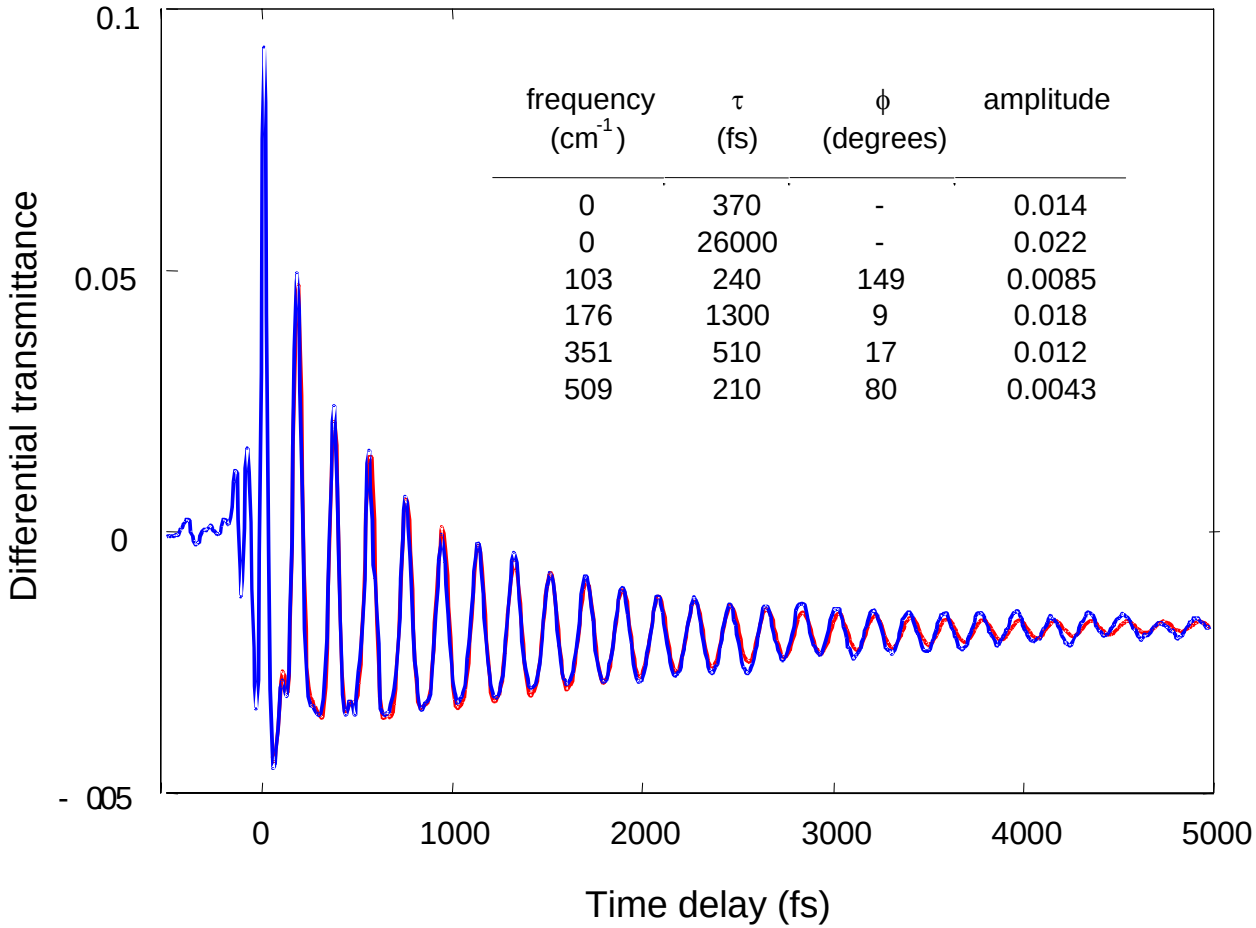


Ground state wavepacket

Resonant impulsive Raman excitation



PtBr(en) impulsive excitation response - 830 nm

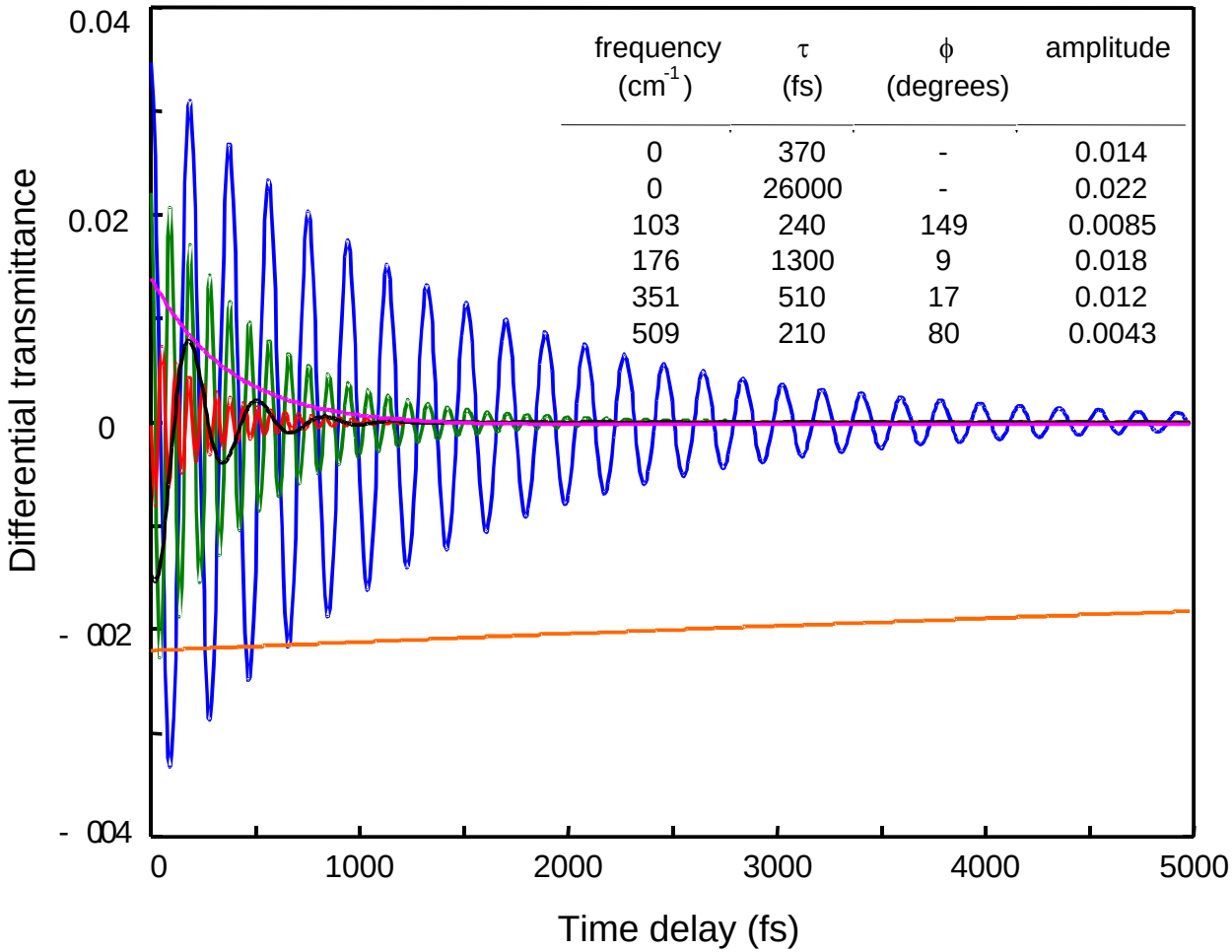


frequency (cm^{-1})	τ (fs)	ϕ (degrees)	amplitude
0	370	-	0.014
0	26000	-	0.022
103	240	149	0.0085
176	1300	9	0.018
351	510	17	0.012
509	210	80	0.0043

Phys. Rev. Lett. 84 (19) 442 (2000)

J. Phys. Chem. A 104, 4308 (2000)

PtBr(en) linear prediction components - 830 nm

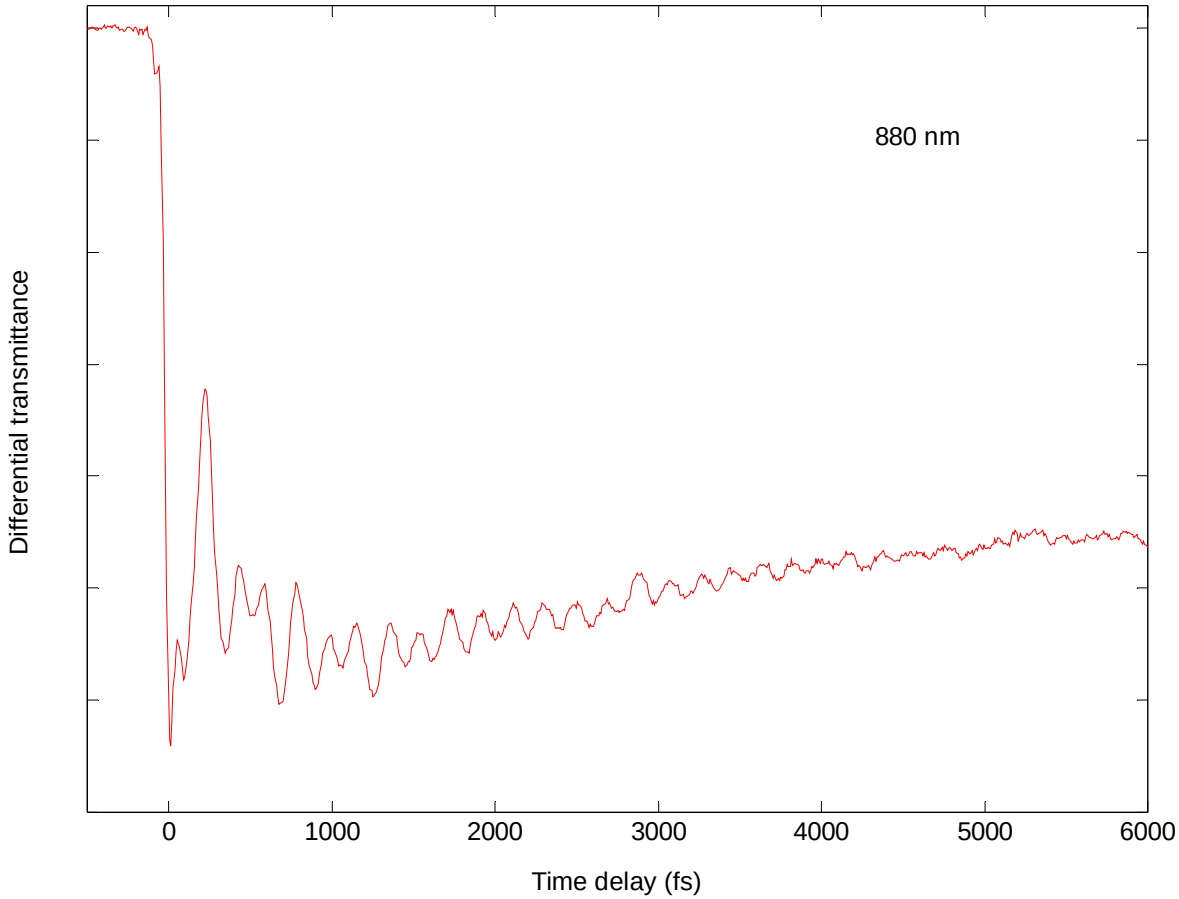


frequency (cm^{-1})	τ (fs)	ϕ (degrees)	amplitude
0	370	-	0.014
0	26000	-	0.022
103	240	149	0.0085
176	1300	9	0.018
351	510	17	0.012
509	210	80	0.0043

Phys. Rev. Lett. 84 (19) 442 (2000)

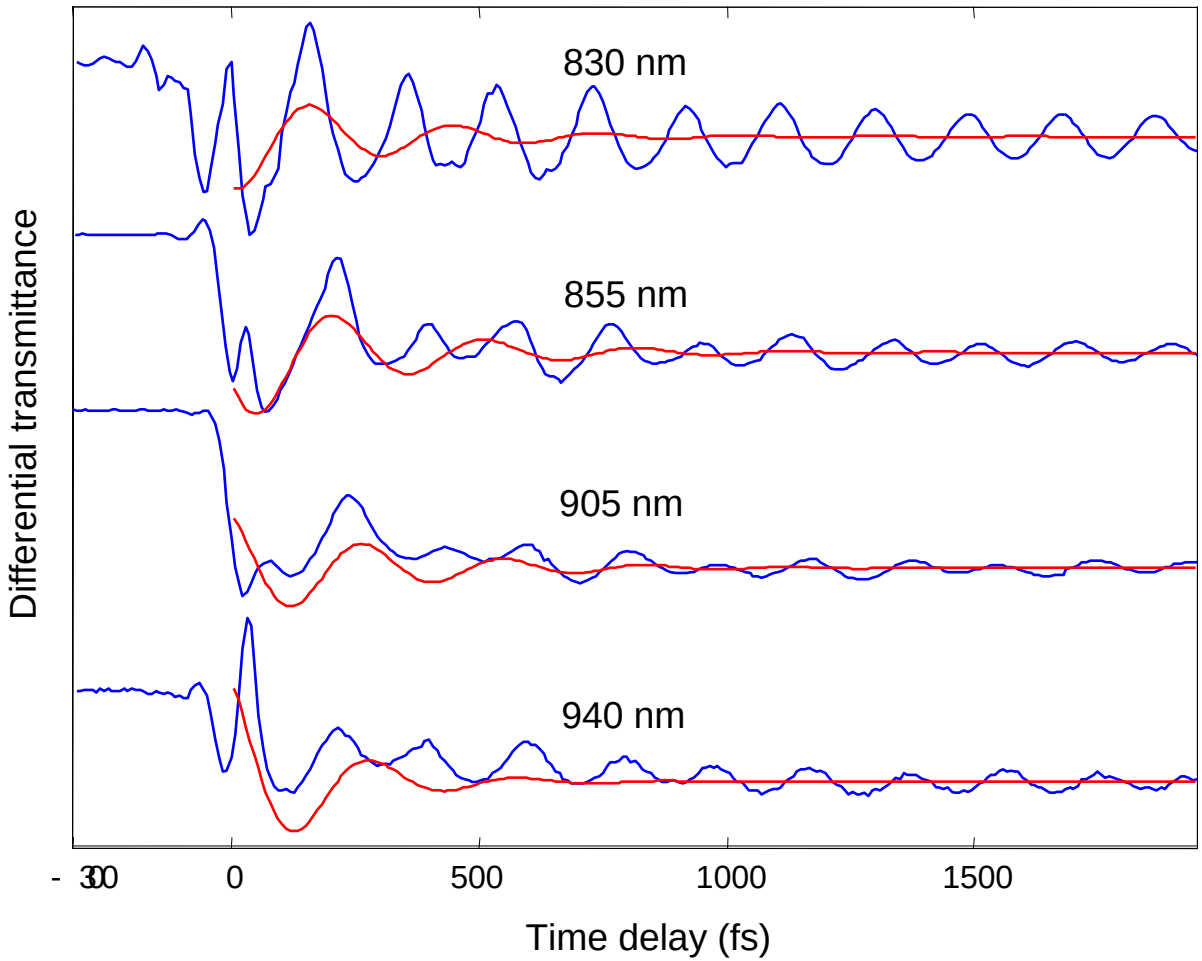
J. Phys. Chem. A 104, 4308 (2000)

PtBr(en) impulsive excitation response – 880 nm



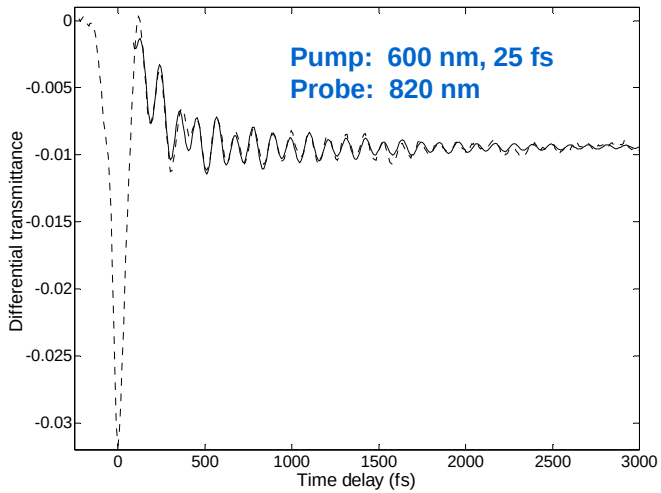
J. Phys. Chem. A 104, 4308 (2000)

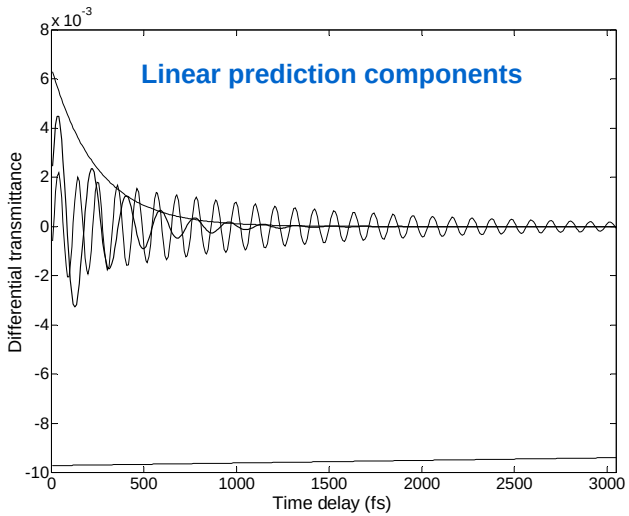
PtBr(en) continuum probe measurements

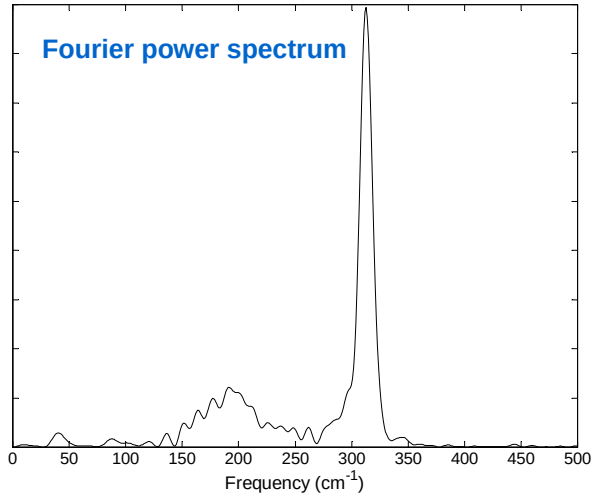


Phys. Rev. Lett. 84 (19) 442 (2000)

PtCl(en) exciton self-trapping dynamics







PtCl(en) linear prediction fit parameters

Frequency	Time constant
0	250 fs
0	90 ps
180 cm^{-1}	290 fs
314 cm^{-1}	1200 fs

Ultrafast Phenomena XII, Springer Series in Chemical Physics **66**, 393

Comparison of mode frequencies: X = Cl,Br, I

$$[\,Pt\,(en)_2\,]\,[\,Pt\,(en)_2\,X_2\,]^{\cdot}\,ClO_4$$

$$.\ \text{-------}X^{-}\text{--}\,Pt^{+(3+\delta)}\text{--}X^{-}\text{-------}\,Pt^{+(3-\delta)}\text{-------}X^{-}\text{--}\,Pt^{+(3+\delta)}\text{--}X^{-}\text{-------}\,Pt^{+(3-\delta)}\text{-------}\ \ldots$$

	Cl	Br	I
ρ	0.743	0.828	0.890
Excited state frequency	180 cm^{-1}	110 cm^{-1}	109 cm^{-1}
Ground state frequency	315 cm^{-1}	176 cm^{-1}	124 cm^{-1}
Frequency ratio	.57	.63	.88

Comparison of dynamics

- effect of geometrical distortion
- vibrational mode response

Ultrafast electronic and vibrational dynamics in quasi-one-dimensional molecular solids

Conclusions: Optical studies

- observation of lattice motions associated with self-trapping
- exciton formation time ~ vibrational period ~ wavepacket dephasing time at room temperature
- increased rate in more strongly coupled systems
- effect of geometrical distortion
- at low temperature, increased vibrational dephasing time and evidence for low-frequency lattice motions

Ultrafast electronic and vibrational dynamics in quasi-one-dimensional molecular solids

Future Directions
Time-Domain X-Ray Studies

- model system for studying localization of electronic excitations
- structural determination of metastable localized states
- ps timescale – structure and evolution of relaxed STE state
- fs timescale – lattice dynamics of self-trapping