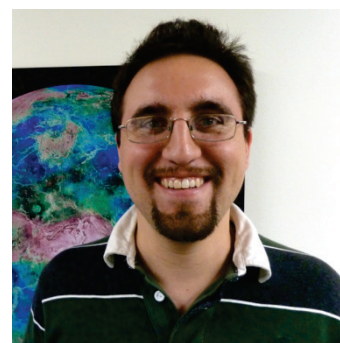
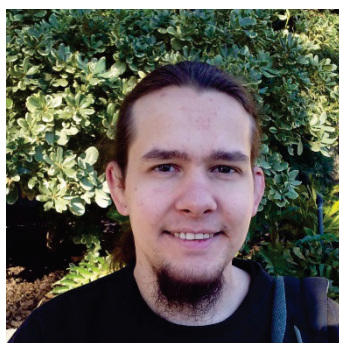
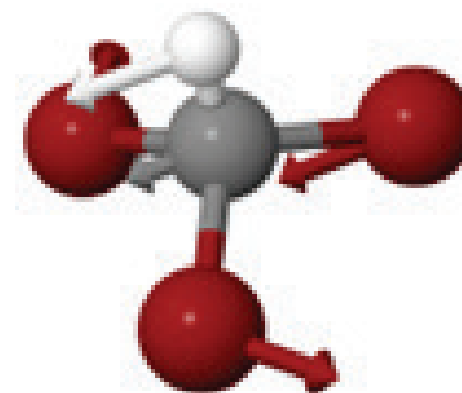
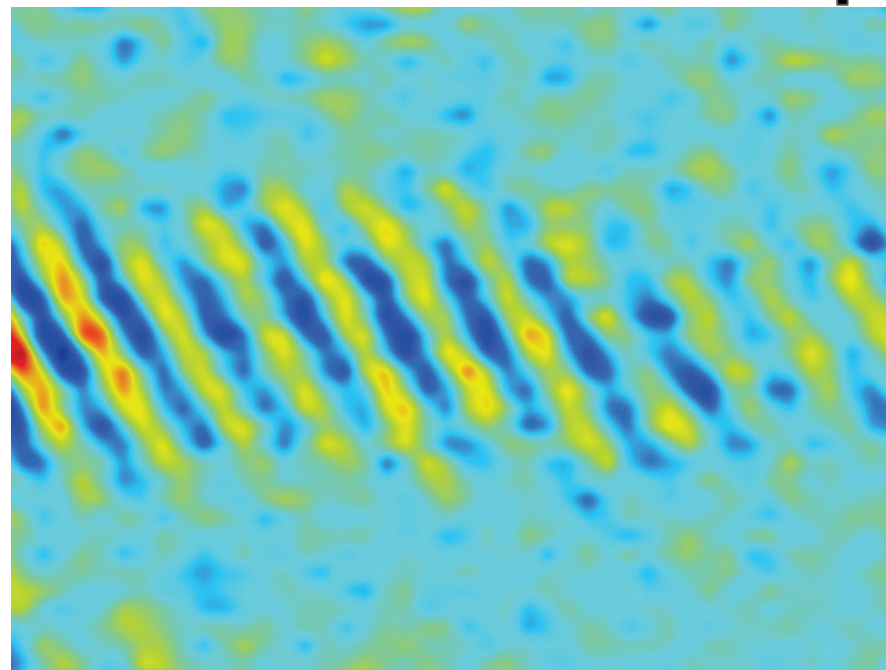
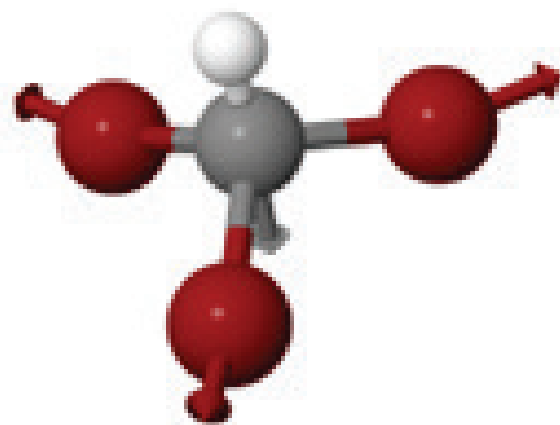




2D Terahertz-Terahertz-Raman Spectroscopy of Halomethane Liquids



Ian Finneran, Ralph Welsch, Marco Allodi,* Thomas Miller III, Geoffrey Blake

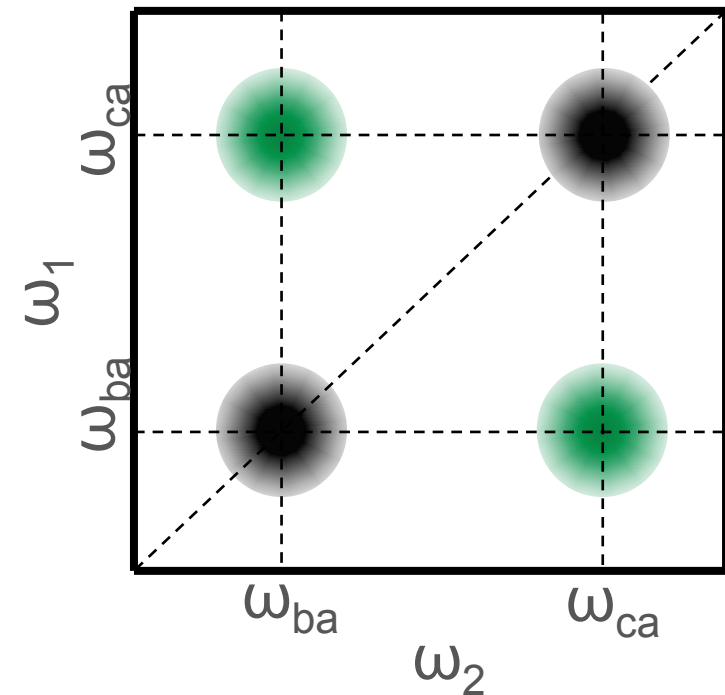
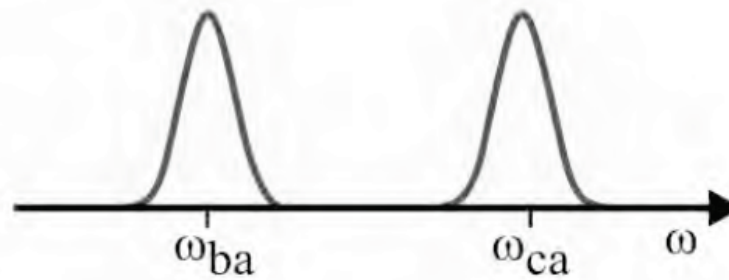
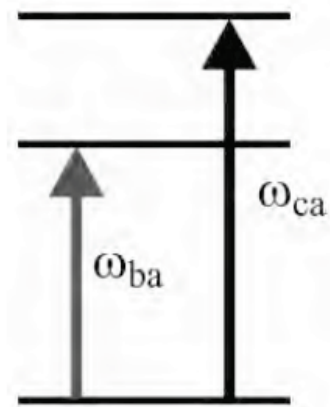
California Institute of Technology

*Current address: University of Chicago

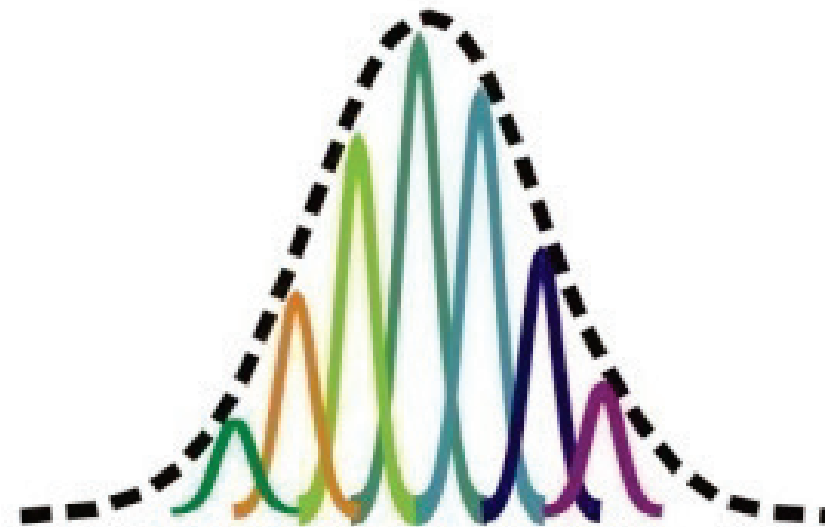


Motivation: 2D spectroscopy provides new information

Cross peaks

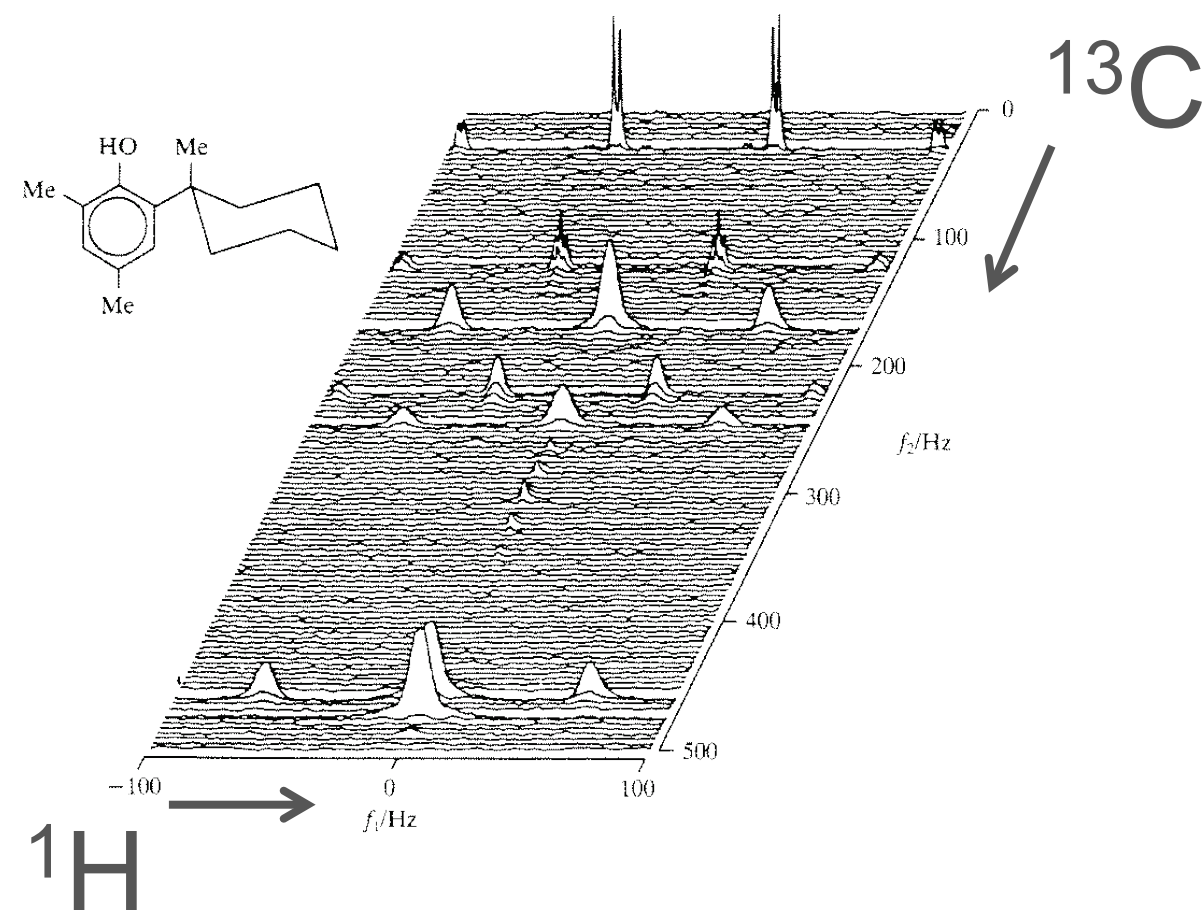
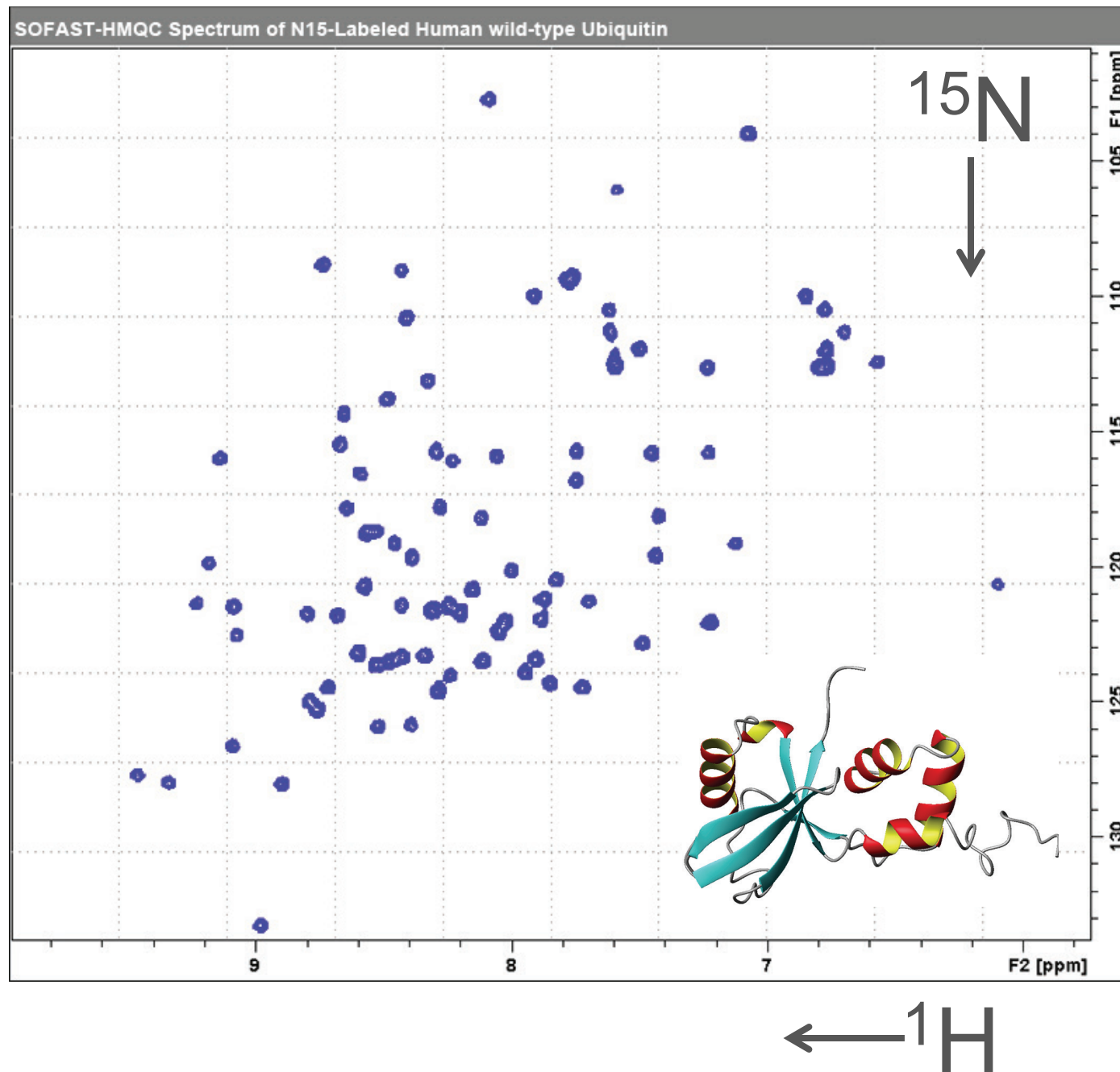


Lineshape broadening mechanisms



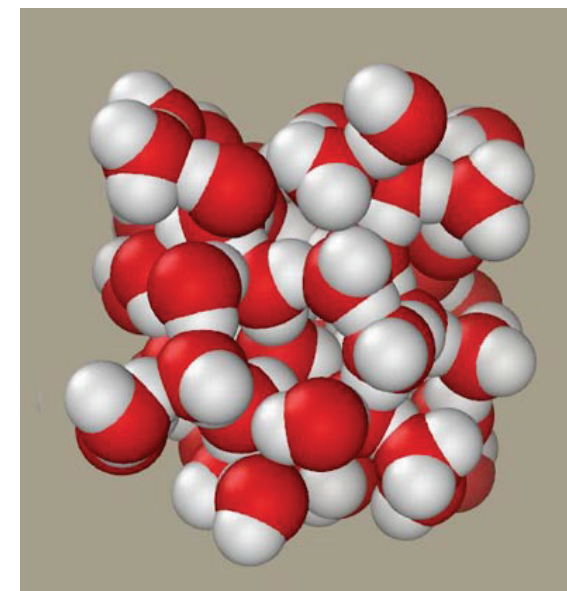
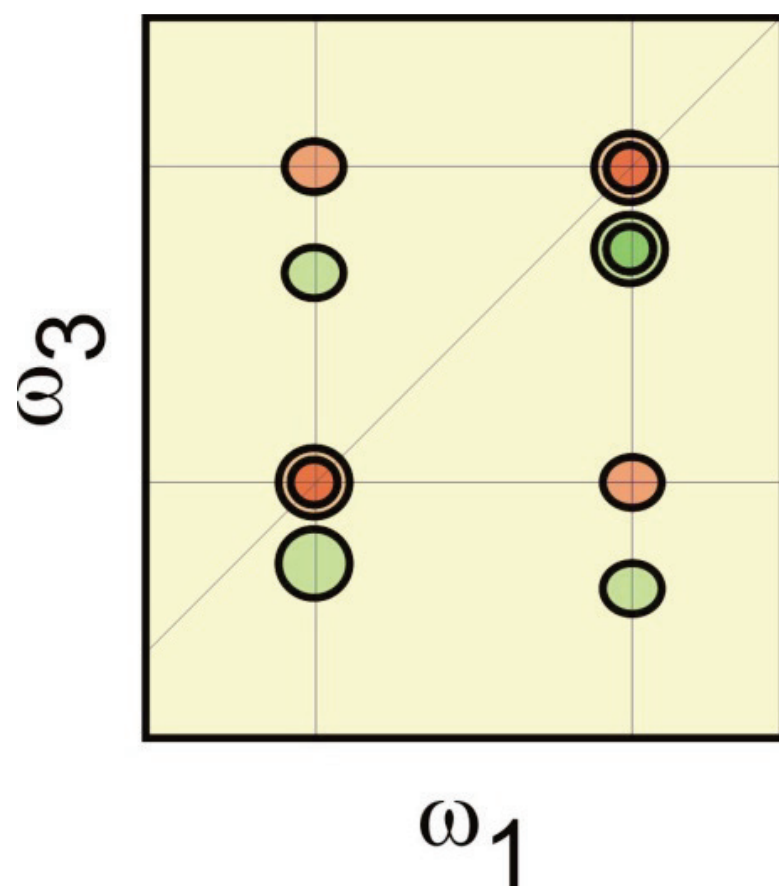
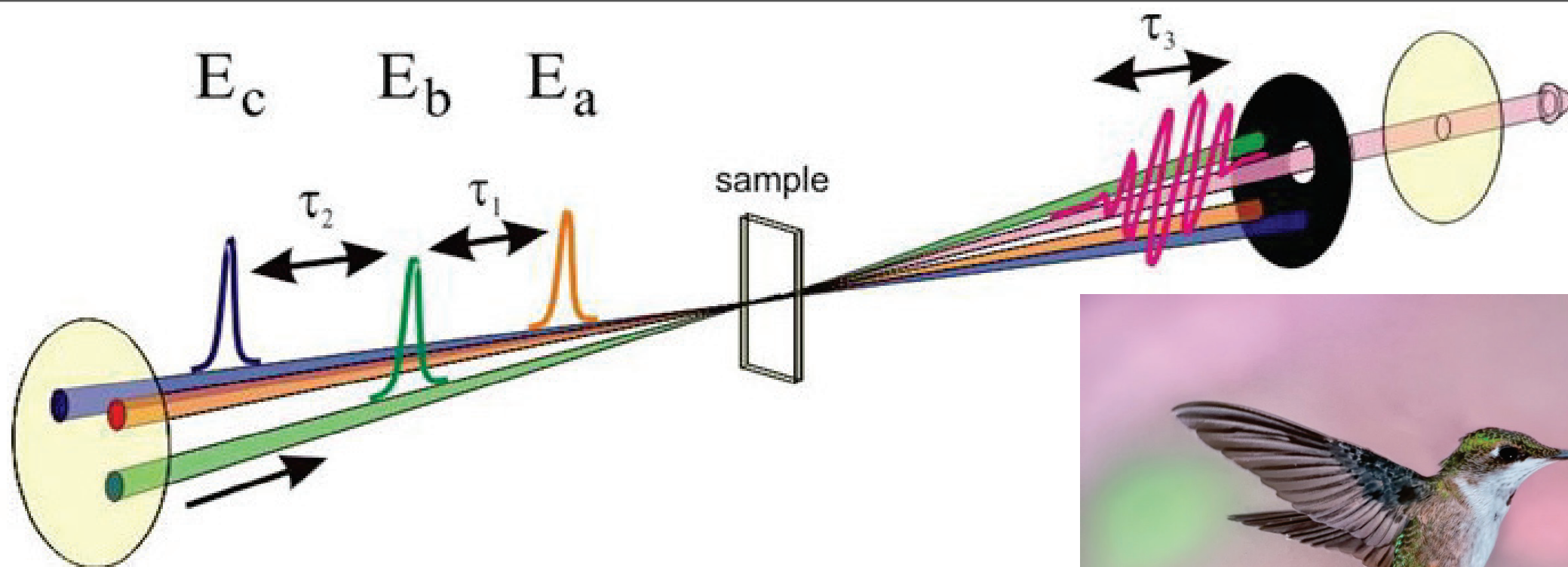


Decoding structure with 2D-NMR





Ultrafast 2D-spectroscopy in the infrared and optical





The Terahertz: $0.1\text{--}10\text{ THz} = 3\text{--}300\text{ cm}^{-1}$

kT at $300\text{ K} = 6.2\text{ THz}$

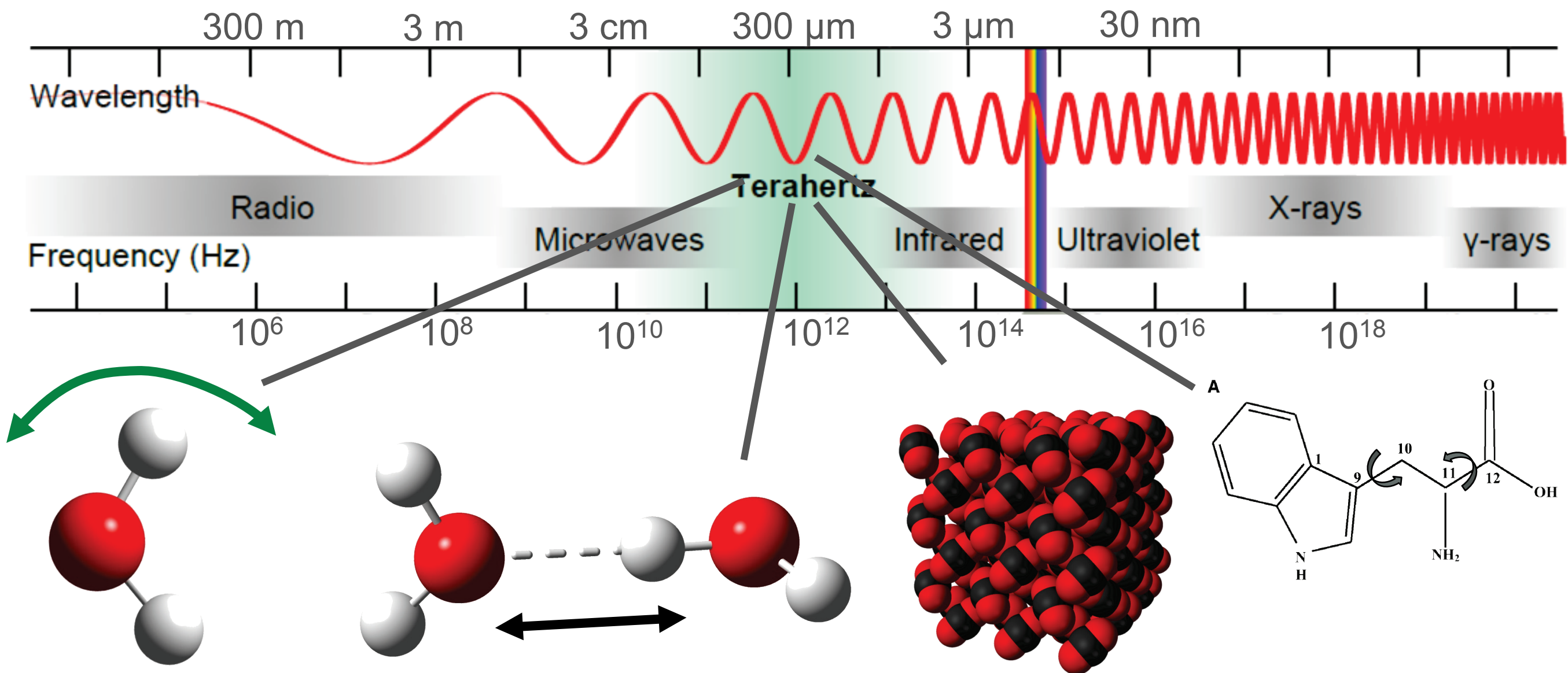
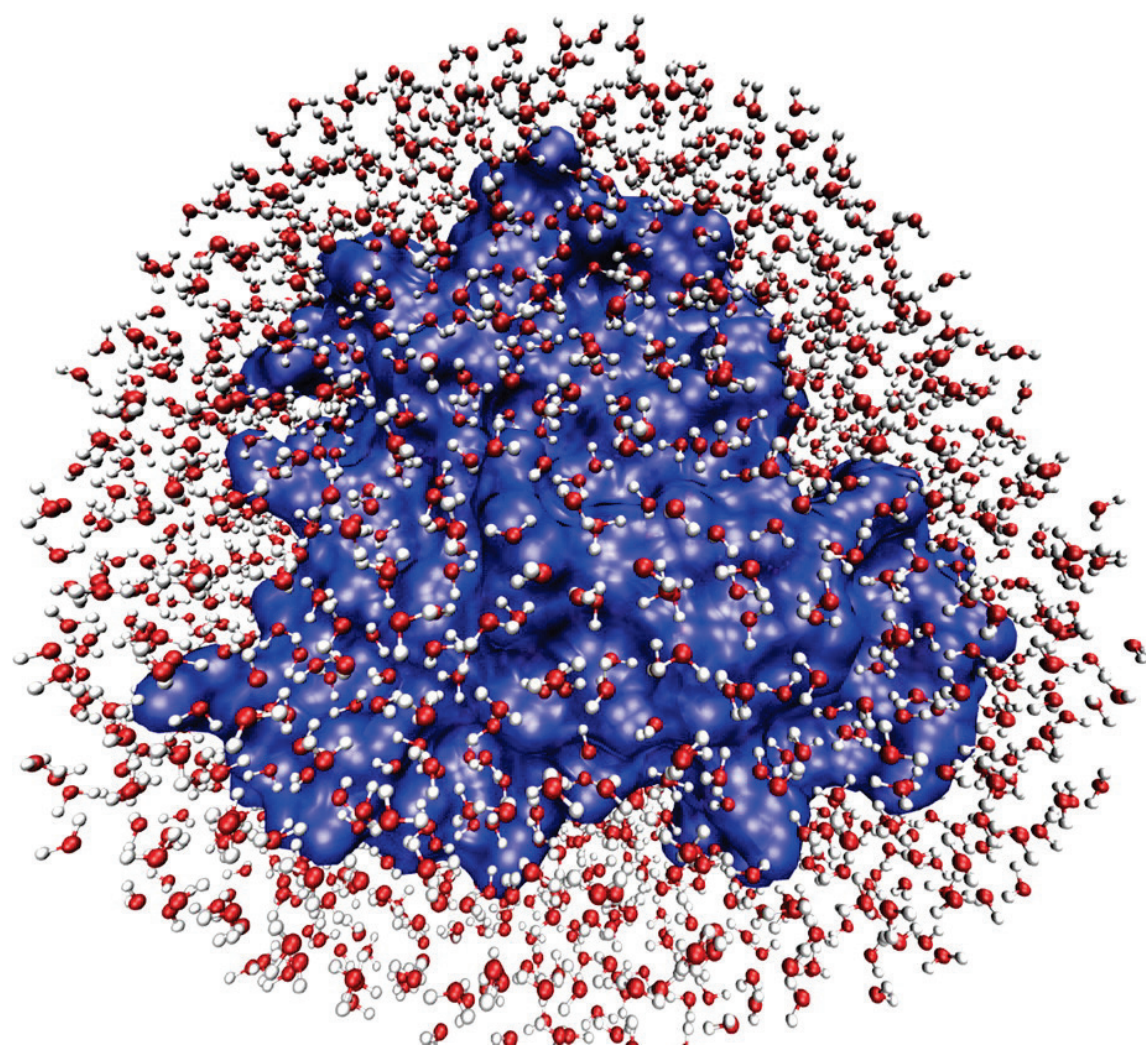


Figure credit: Dan Holland

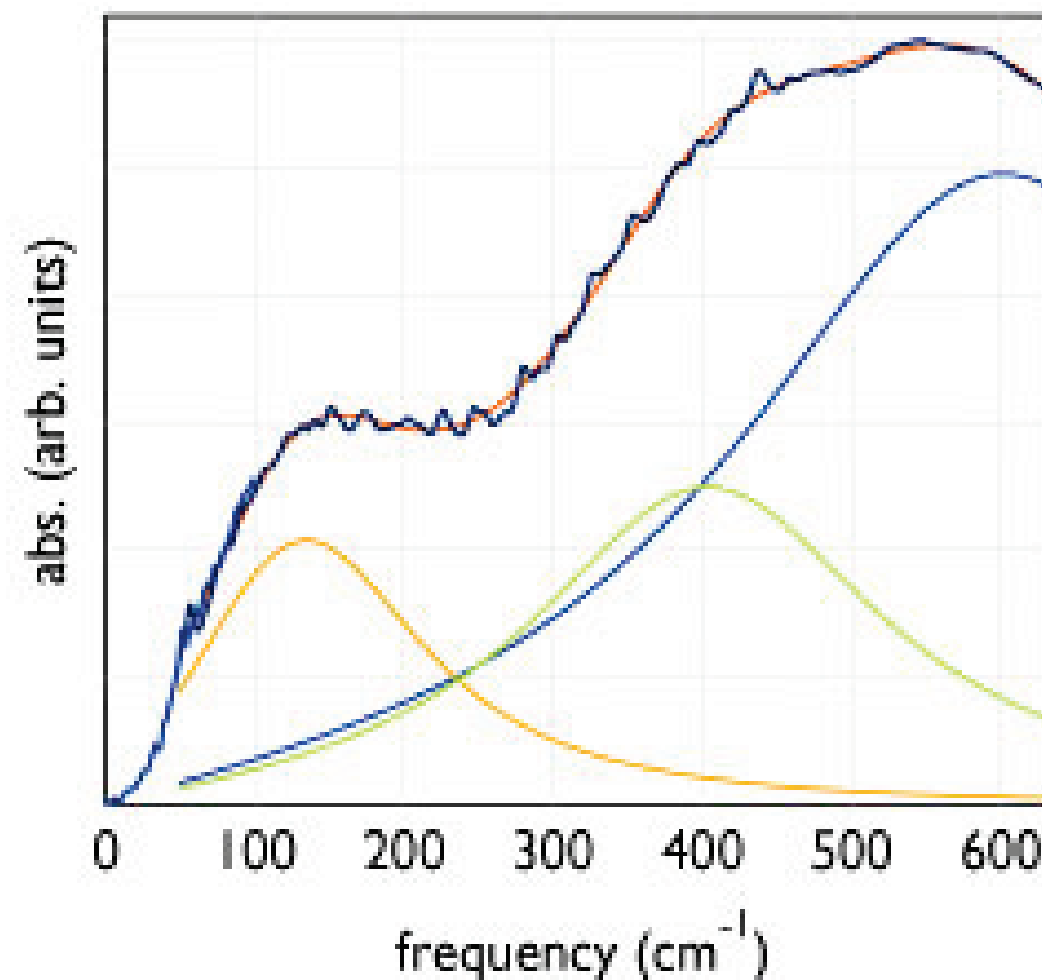


Terahertz modes are active participants in chemistry – not spectators

Solvent-solute interactions



Neat water

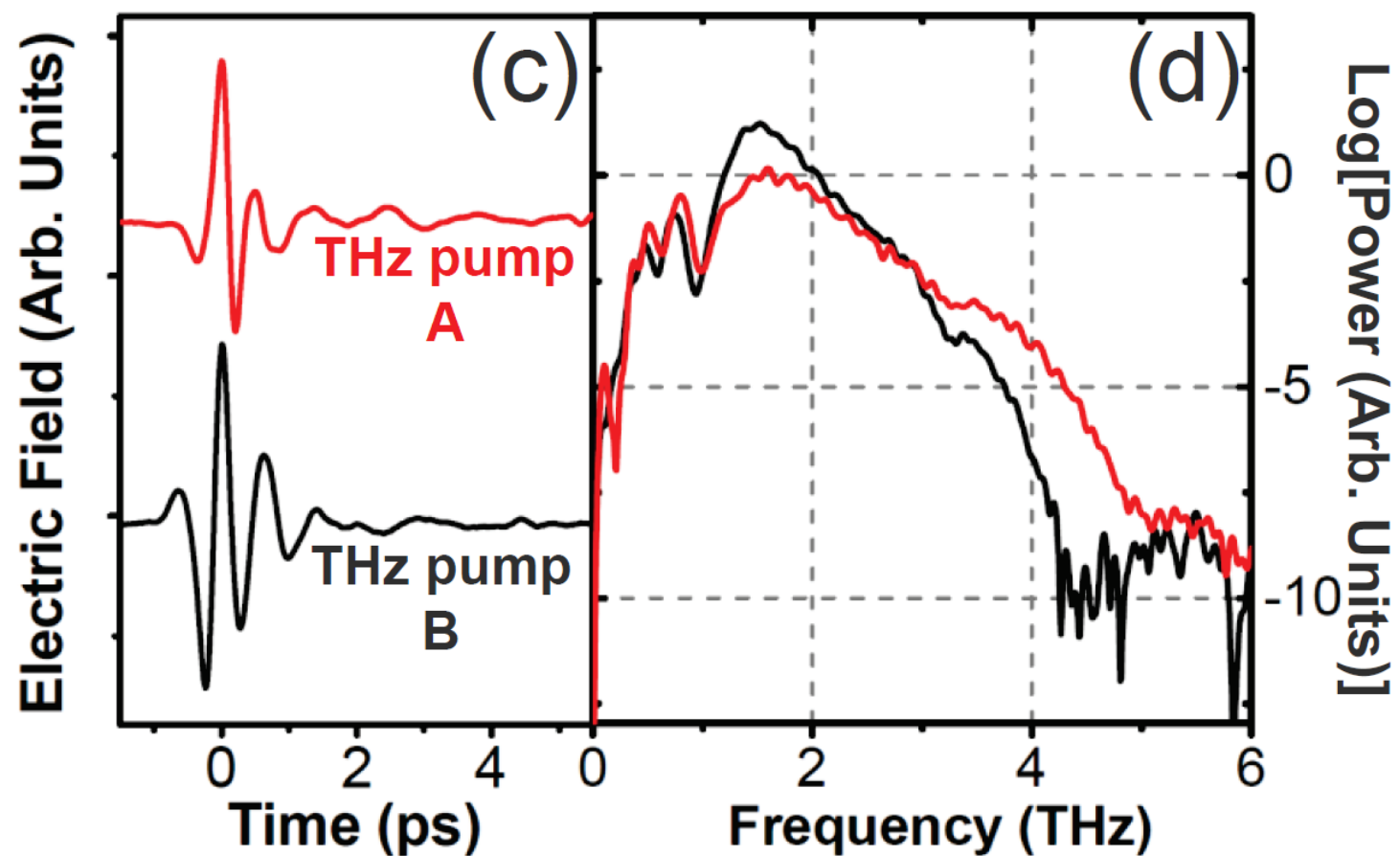
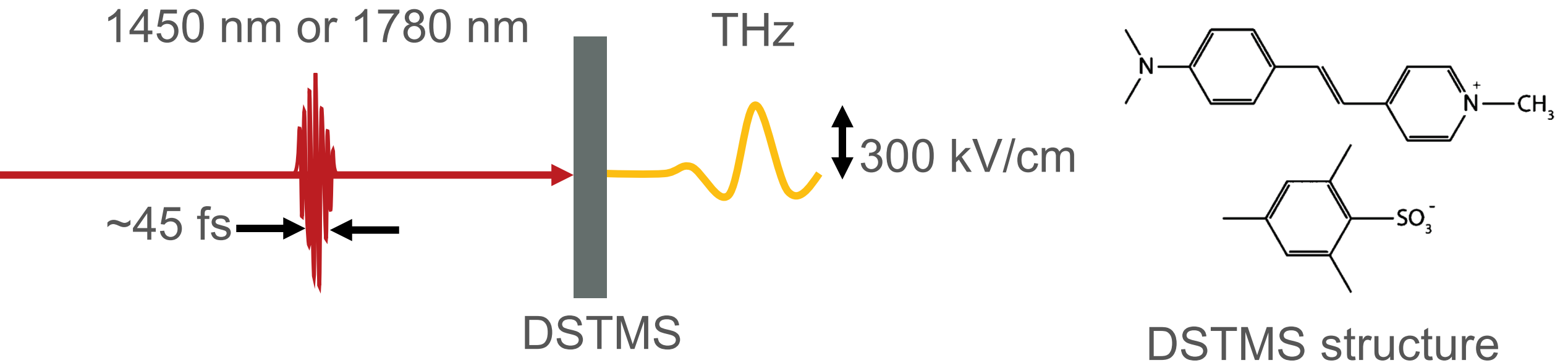


Kim, Seung Joong, et al. *Angewandte Chemie International Edition* 47.34 (2008): 6486-6489.

M Hoffmann et al. *APL*, 95.23 (2009): 231105.

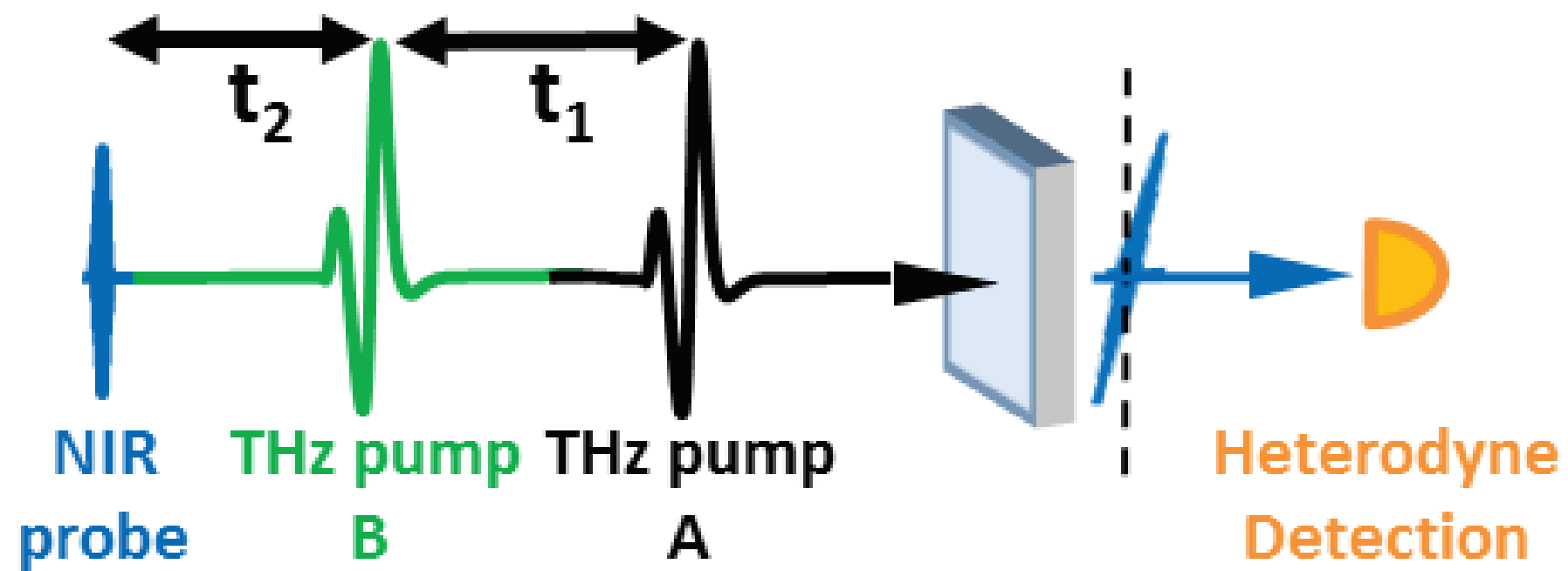
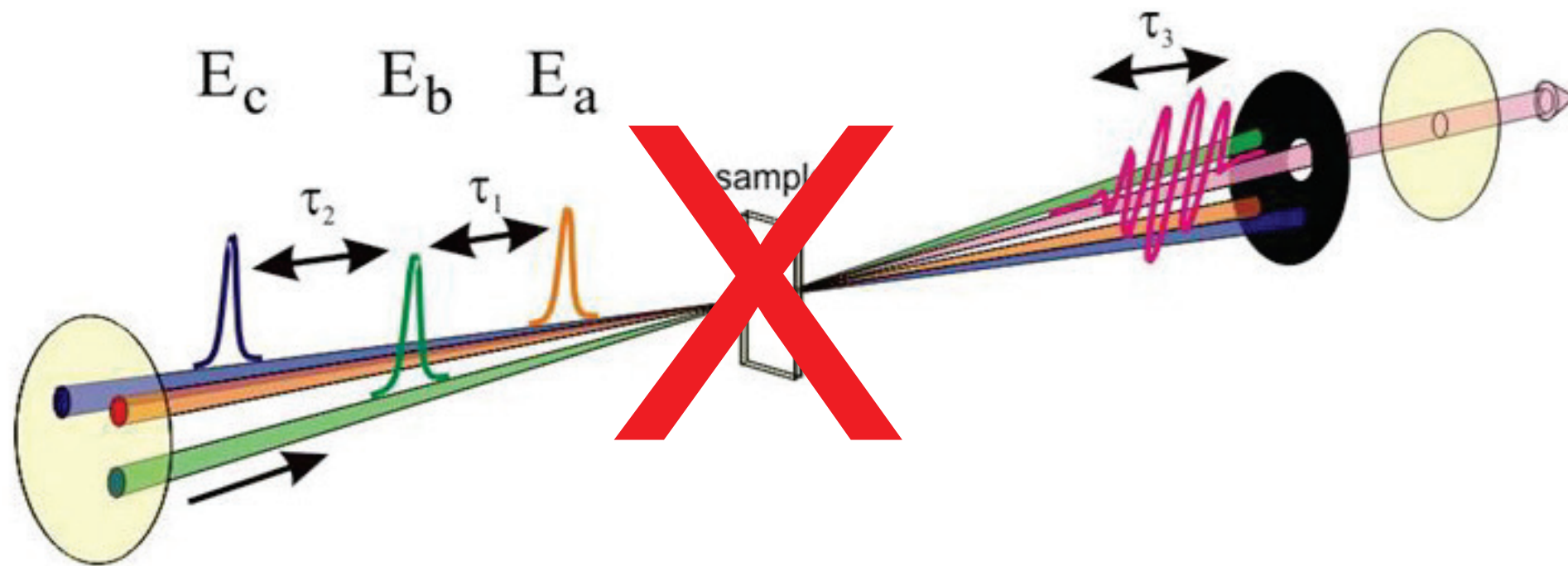


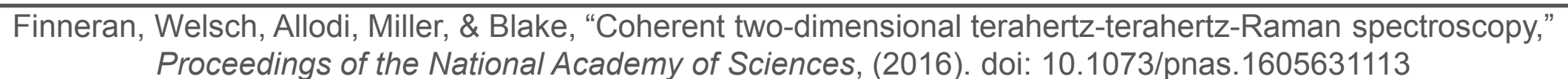
Our approach: optical rectification of an ultrafast OPA





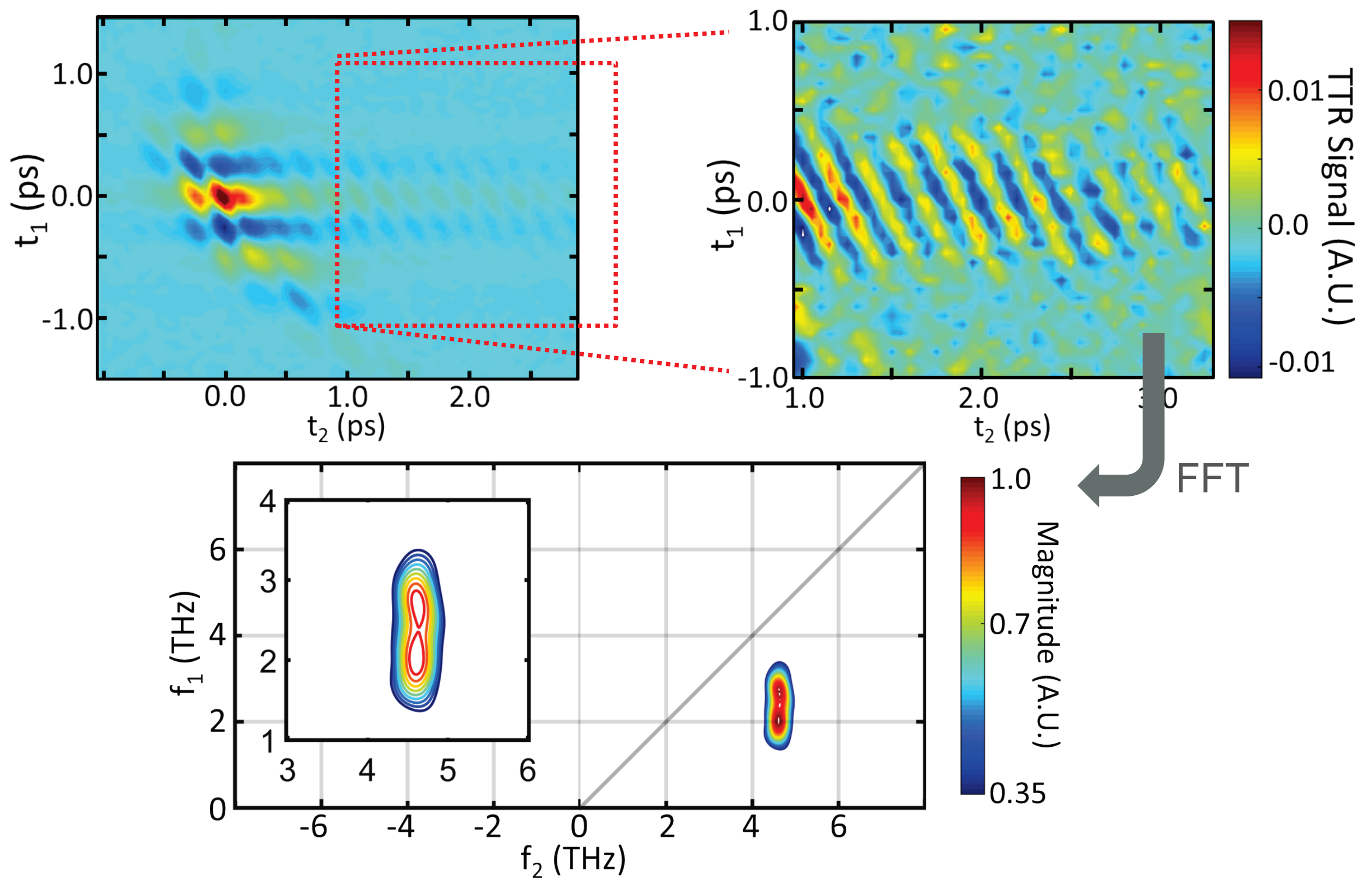
Detection: heterodyne coherent Raman





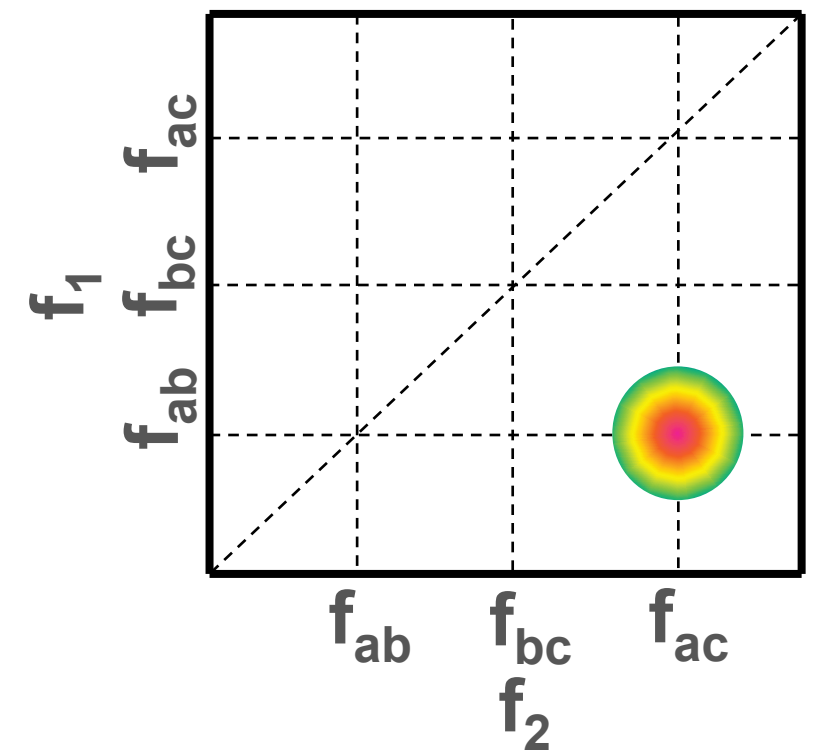
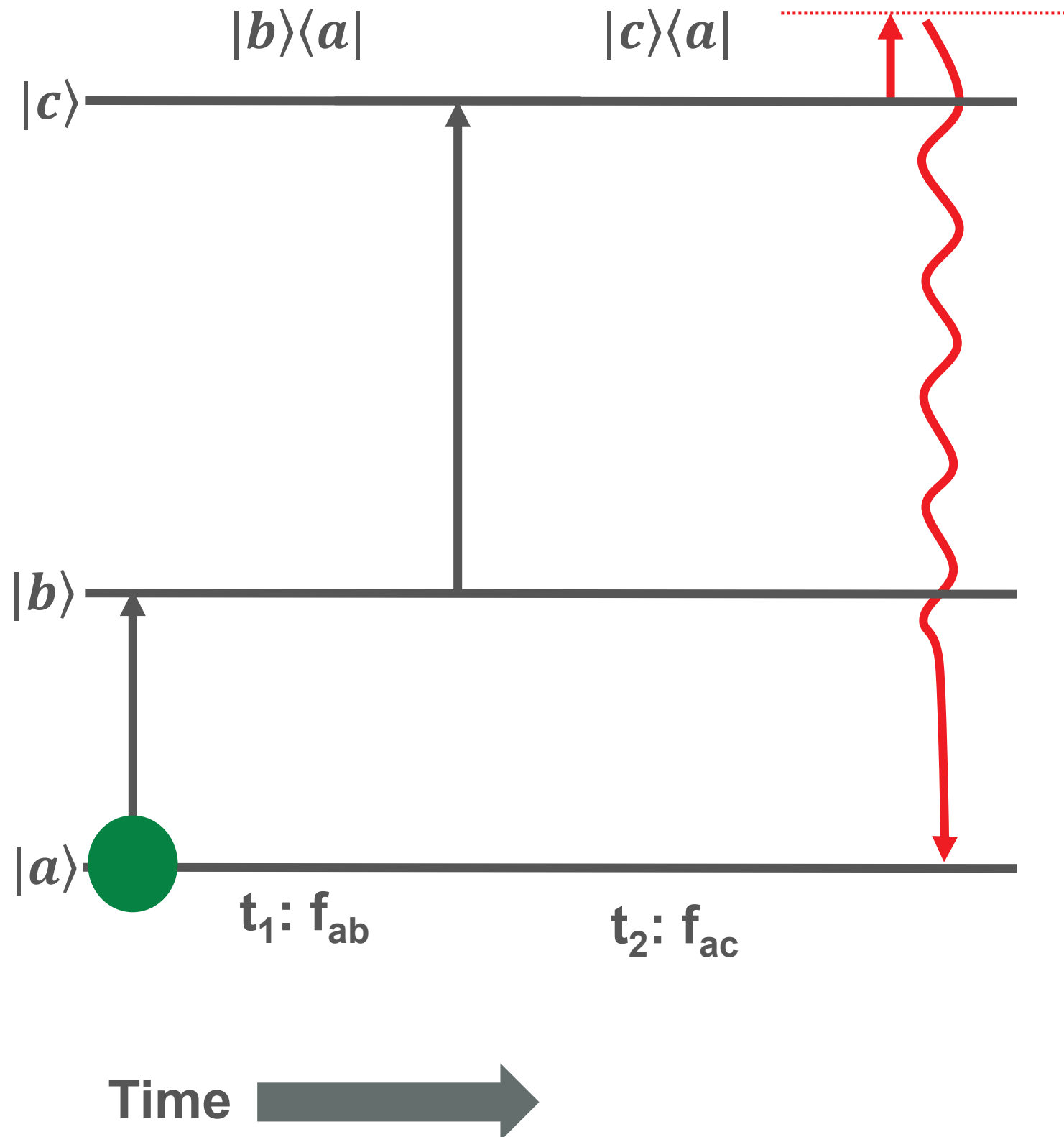


Liquid CHBr_3 : the prototype system



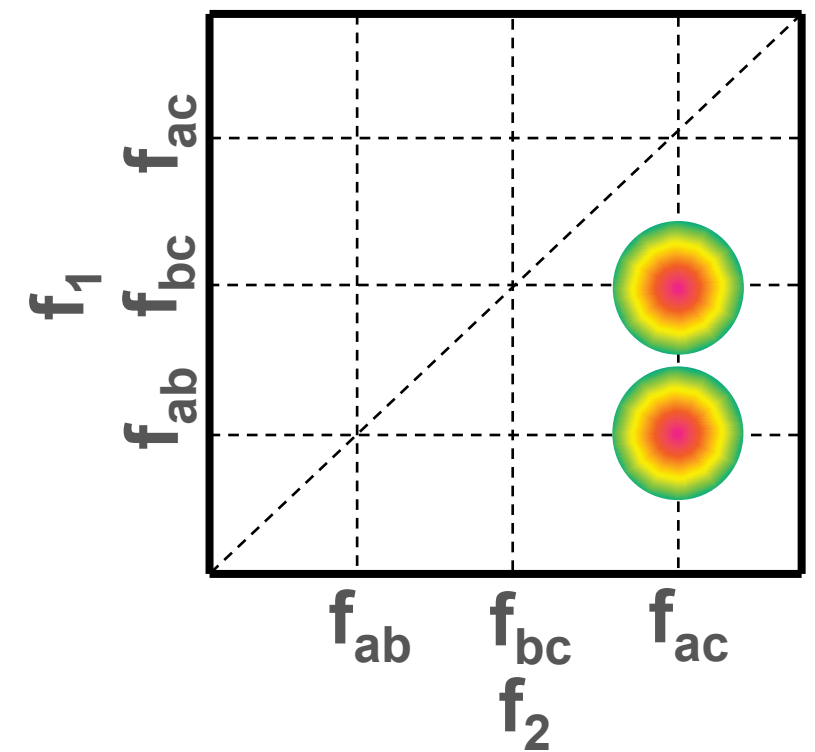
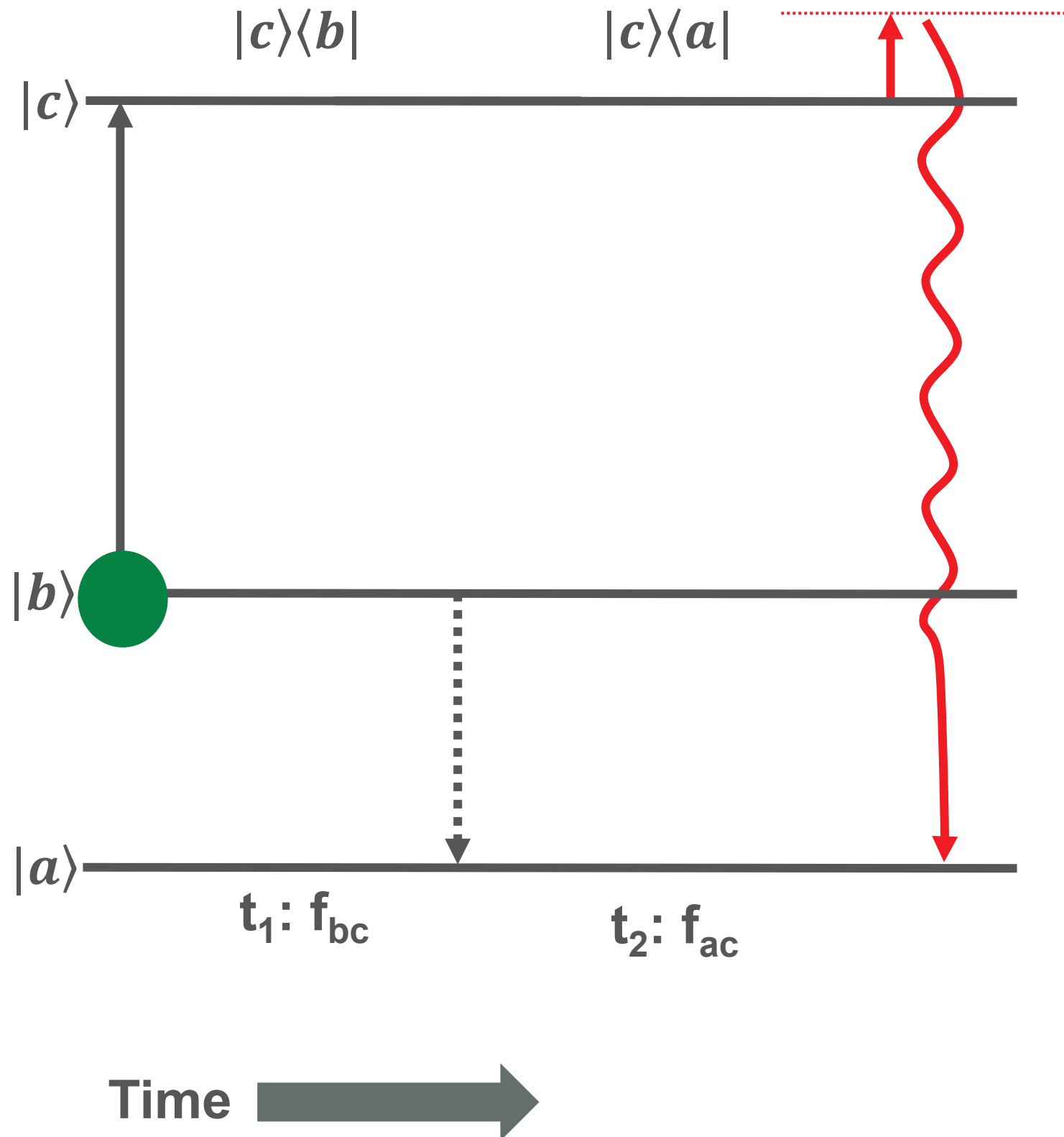


Understanding the 2D Terahertz-Terahertz-Raman spectrum with perturbation theory



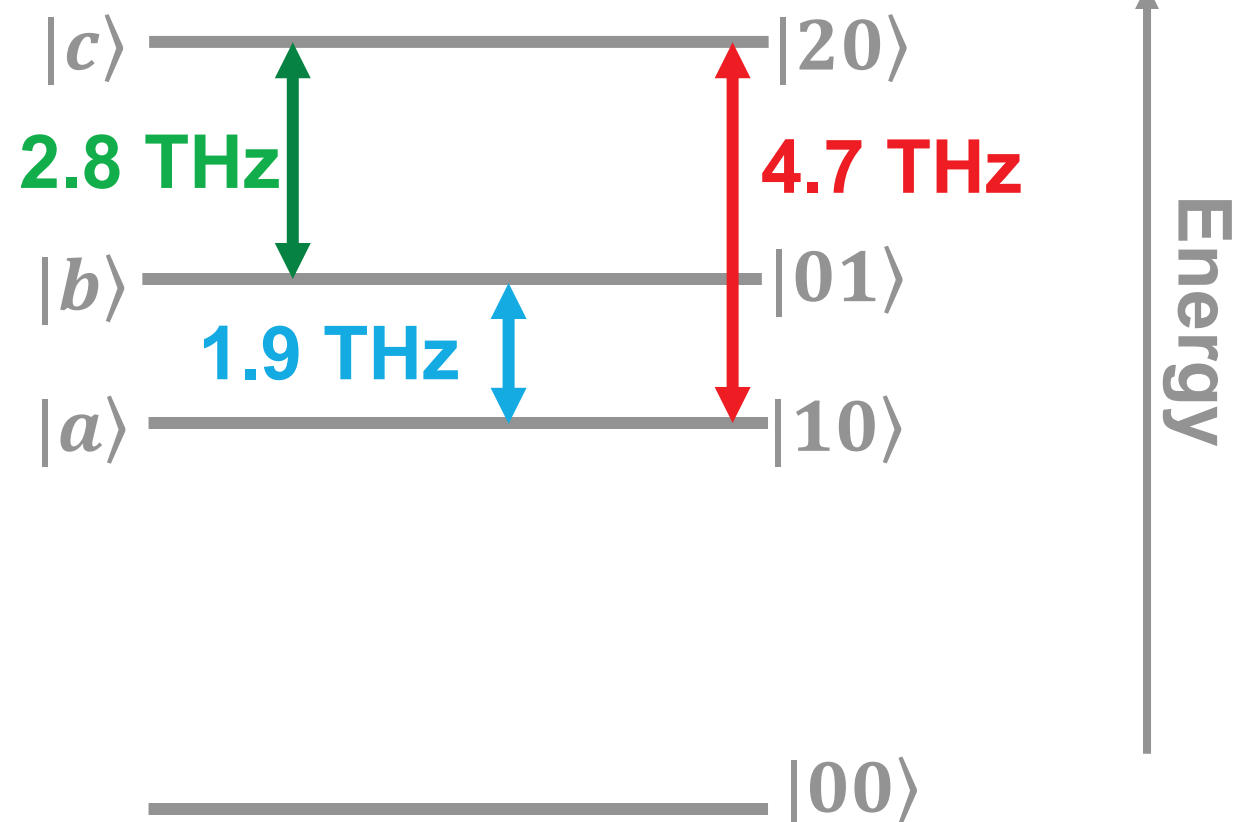
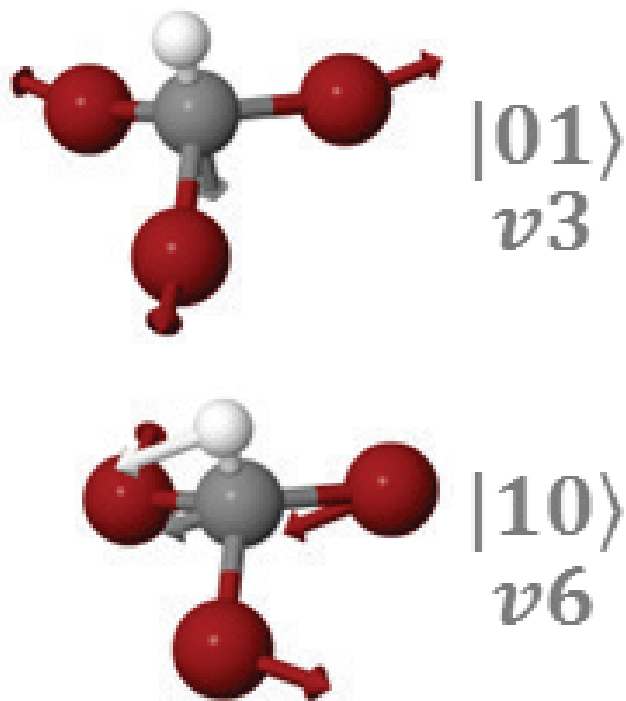
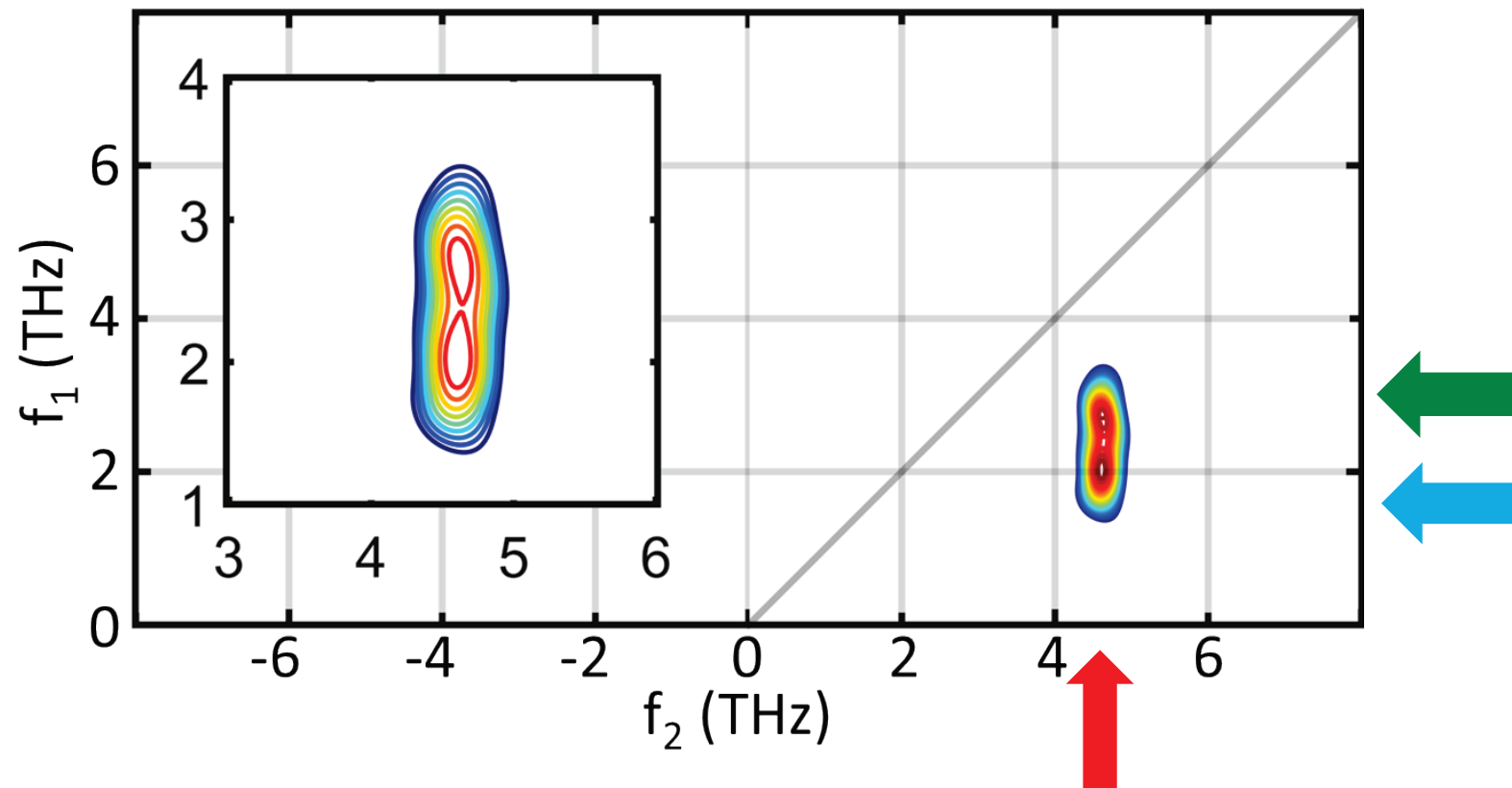


Understanding the 2D Terahertz-Terahertz-Raman spectrum with perturbation theory



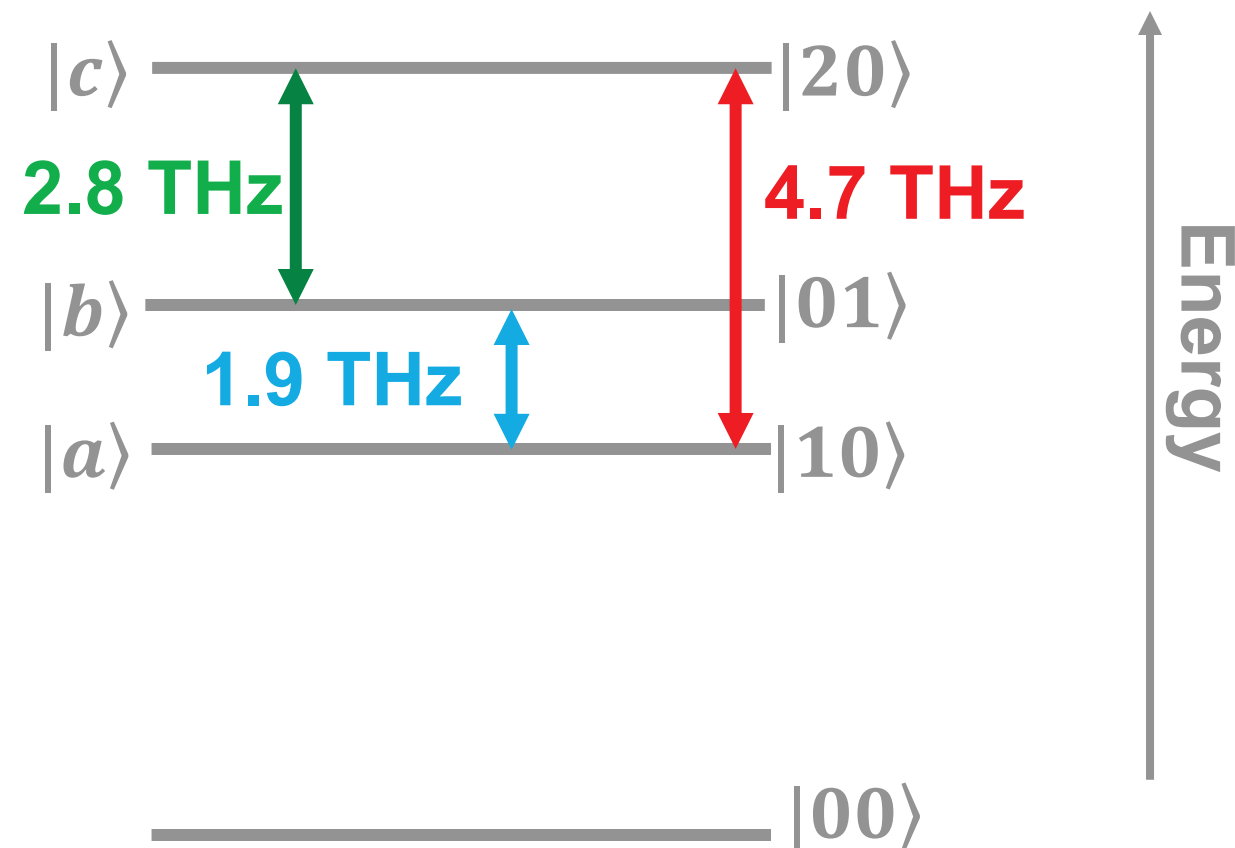
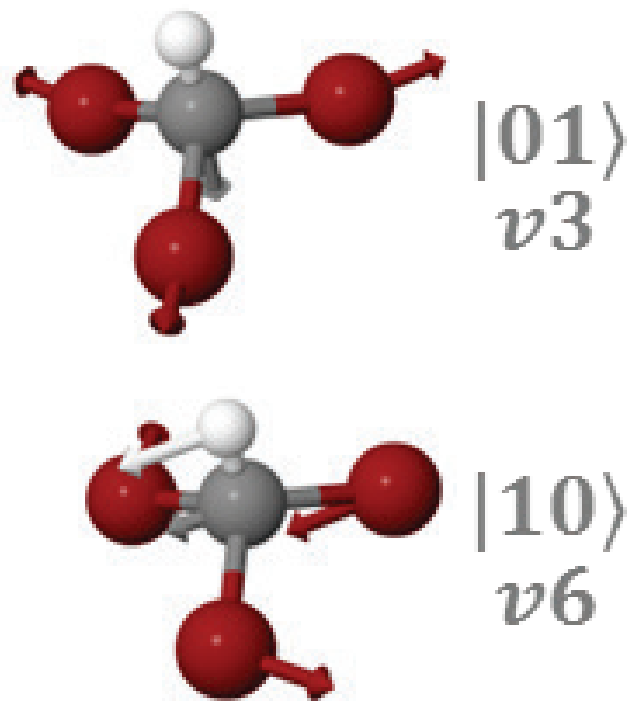
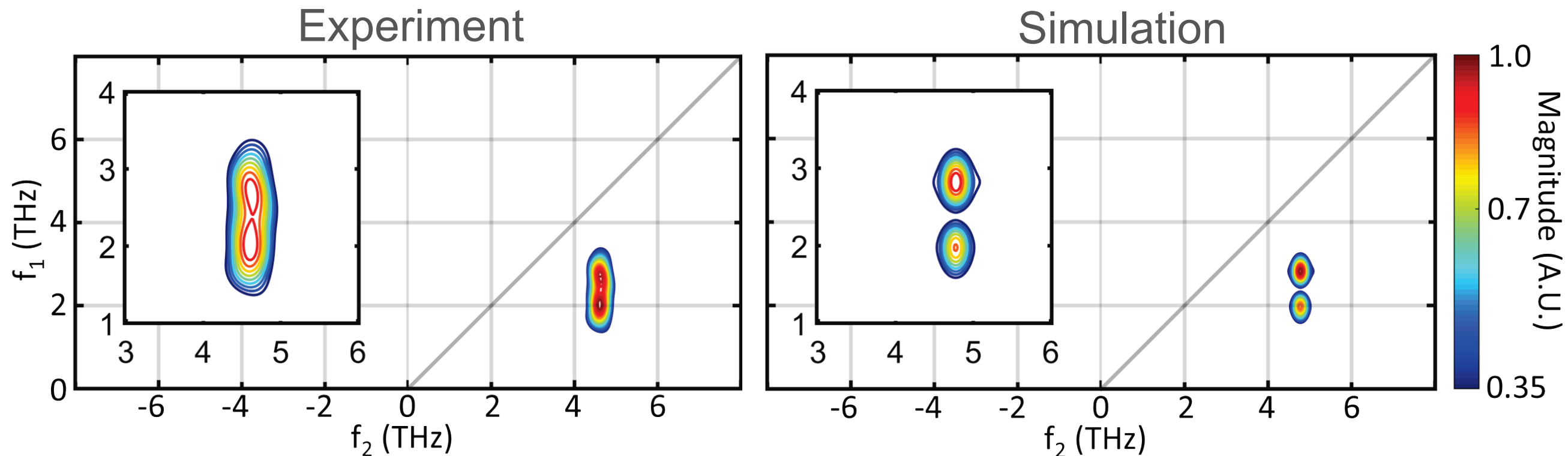


Liquid CHBr_3 : the prototype system



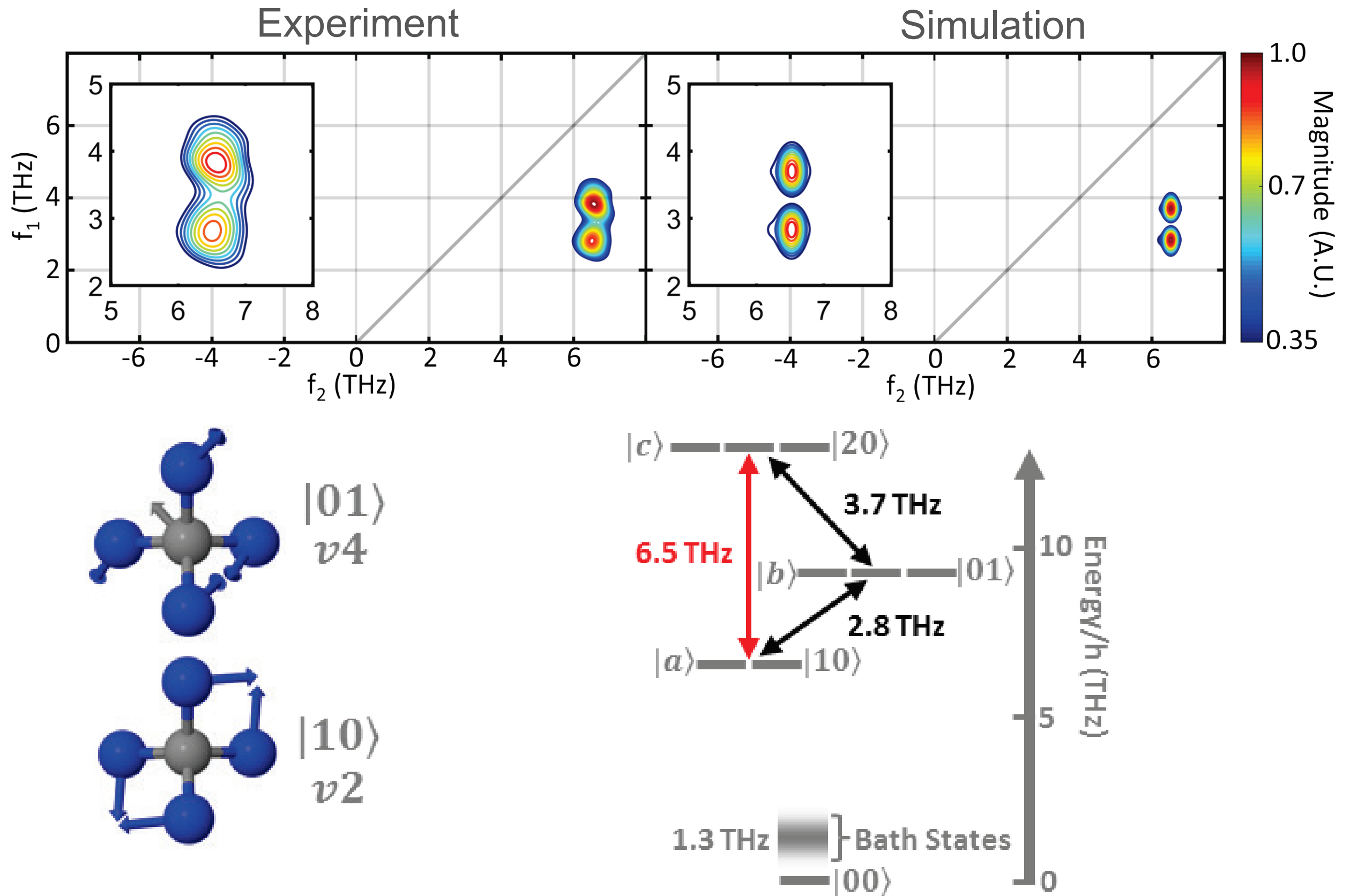


Liquid CHBr_3 : the prototype system





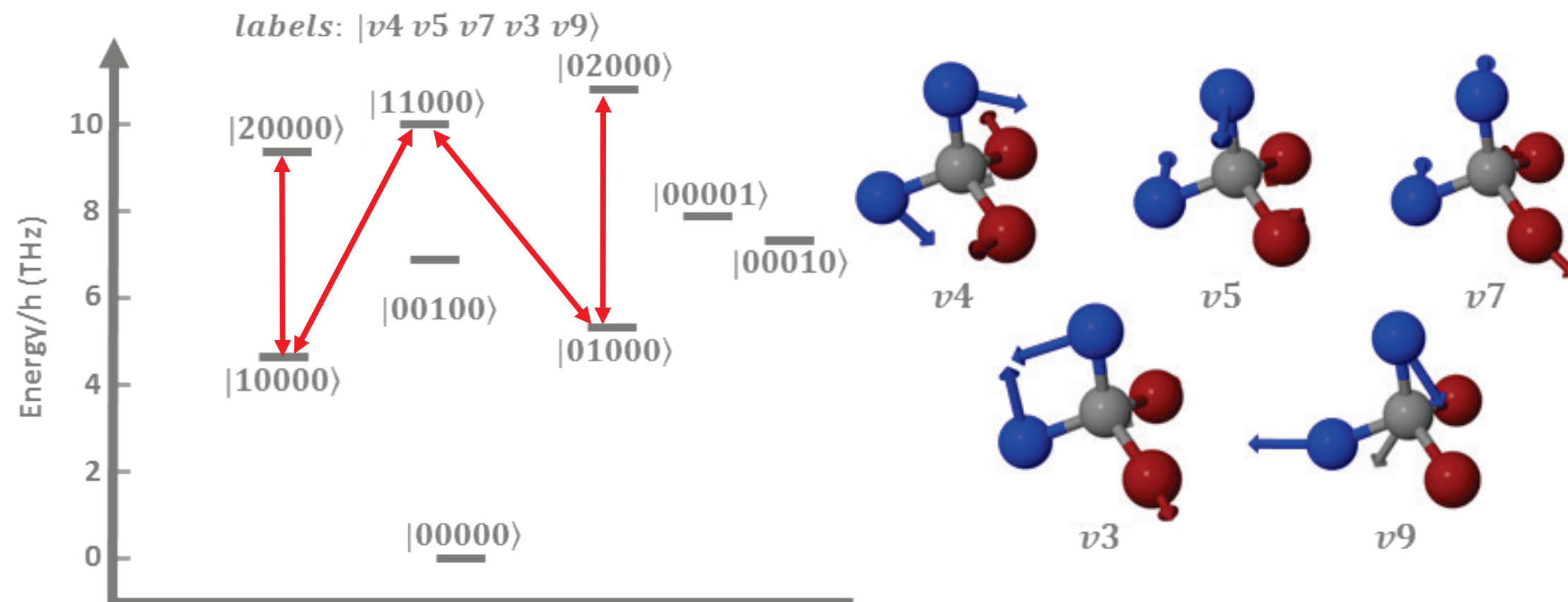
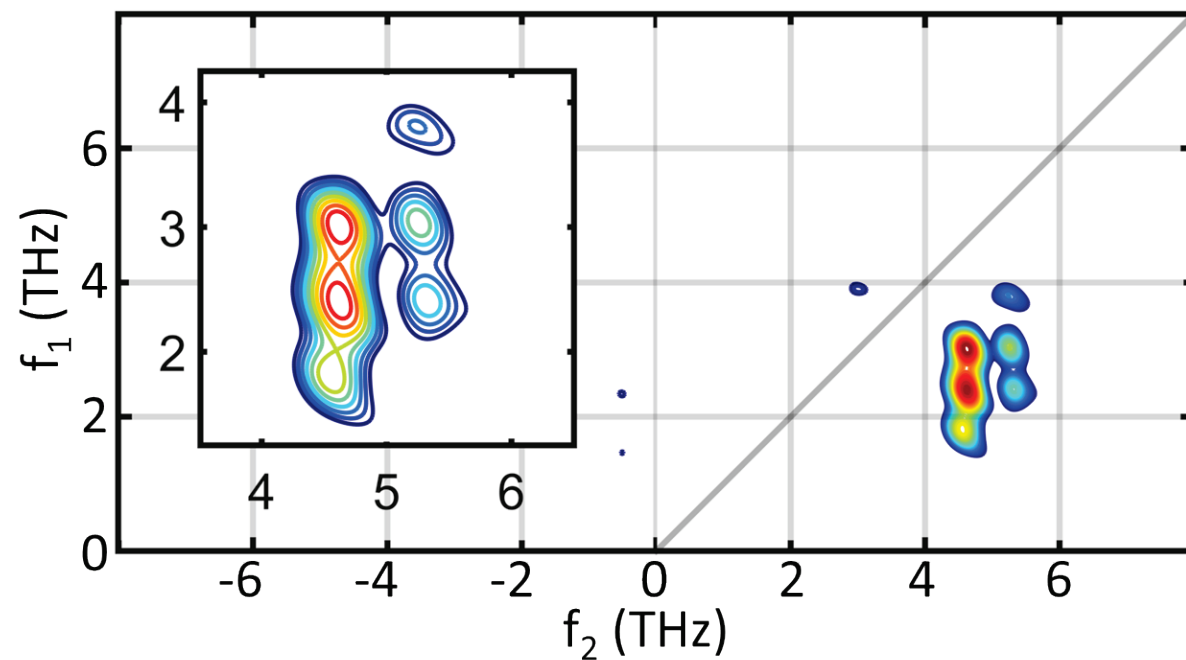
Liquid CCl_4 : a similar vibrational structure to CHBr_3





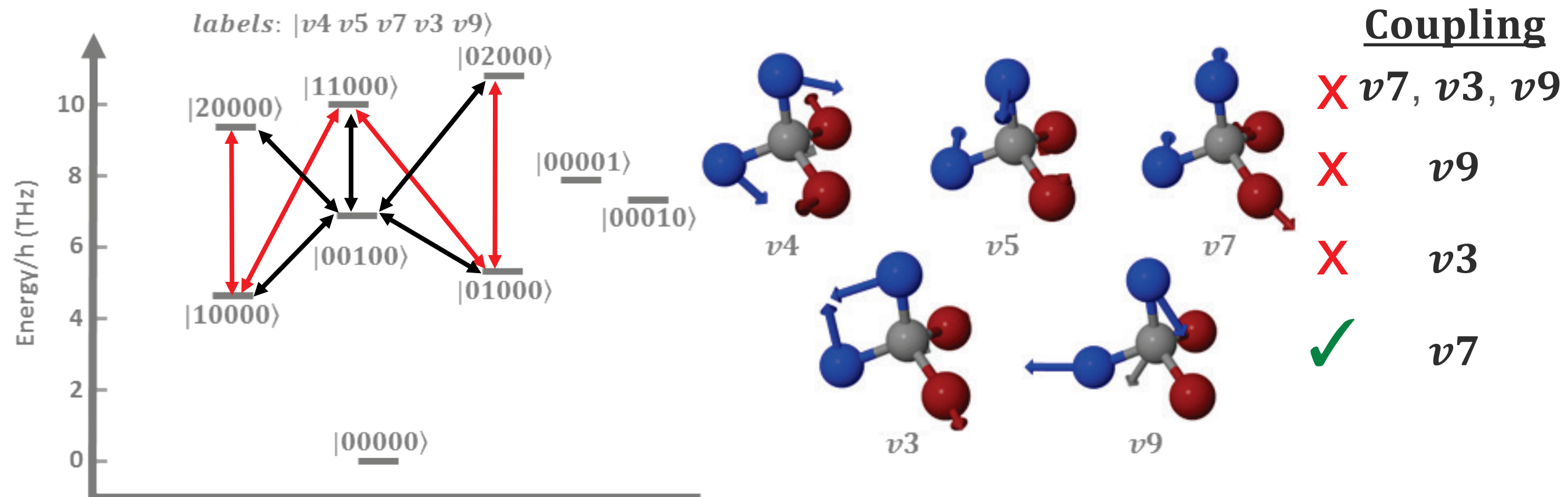
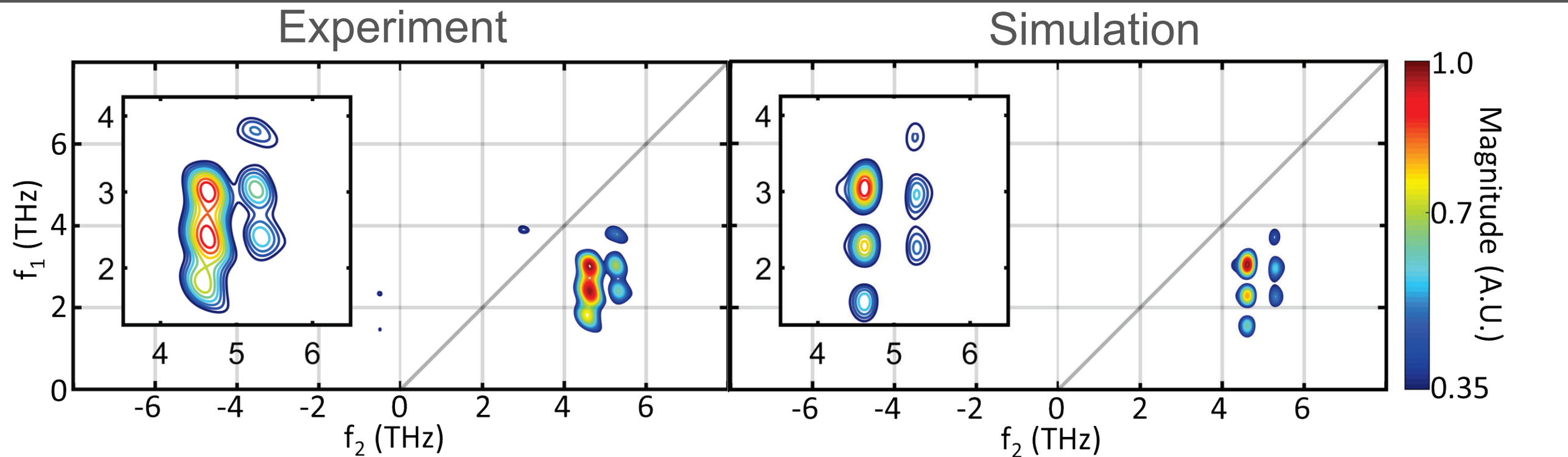
Liquid CBr_2Cl_2 : a more complex 2D spectrum

Experiment





Liquid CBr_2Cl_2 : a more complex 2D spectrum



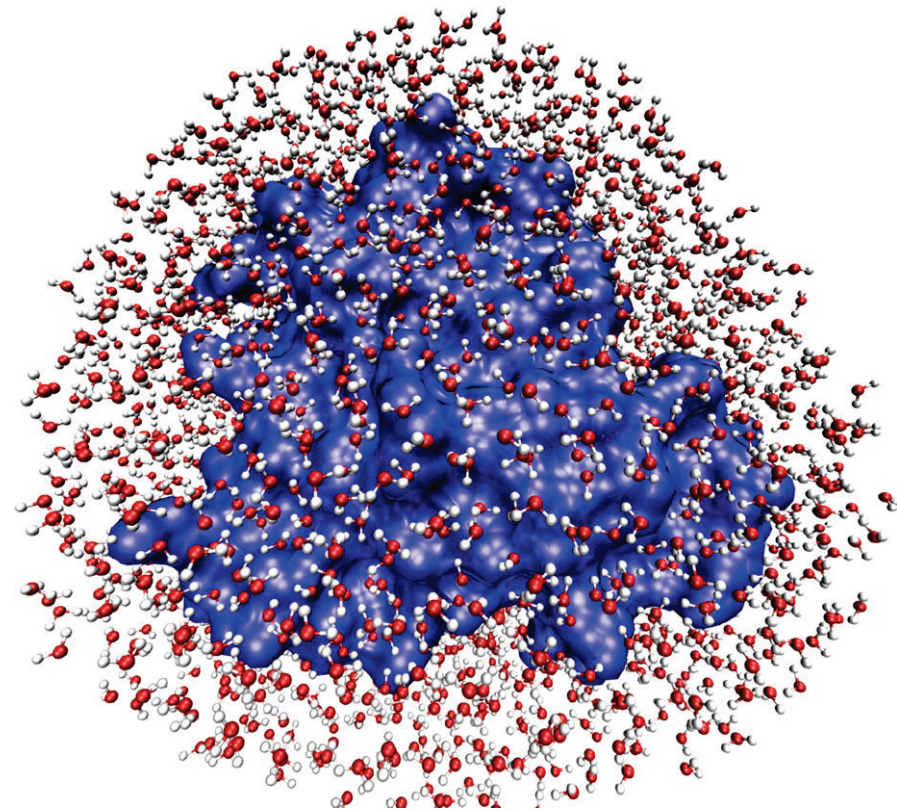
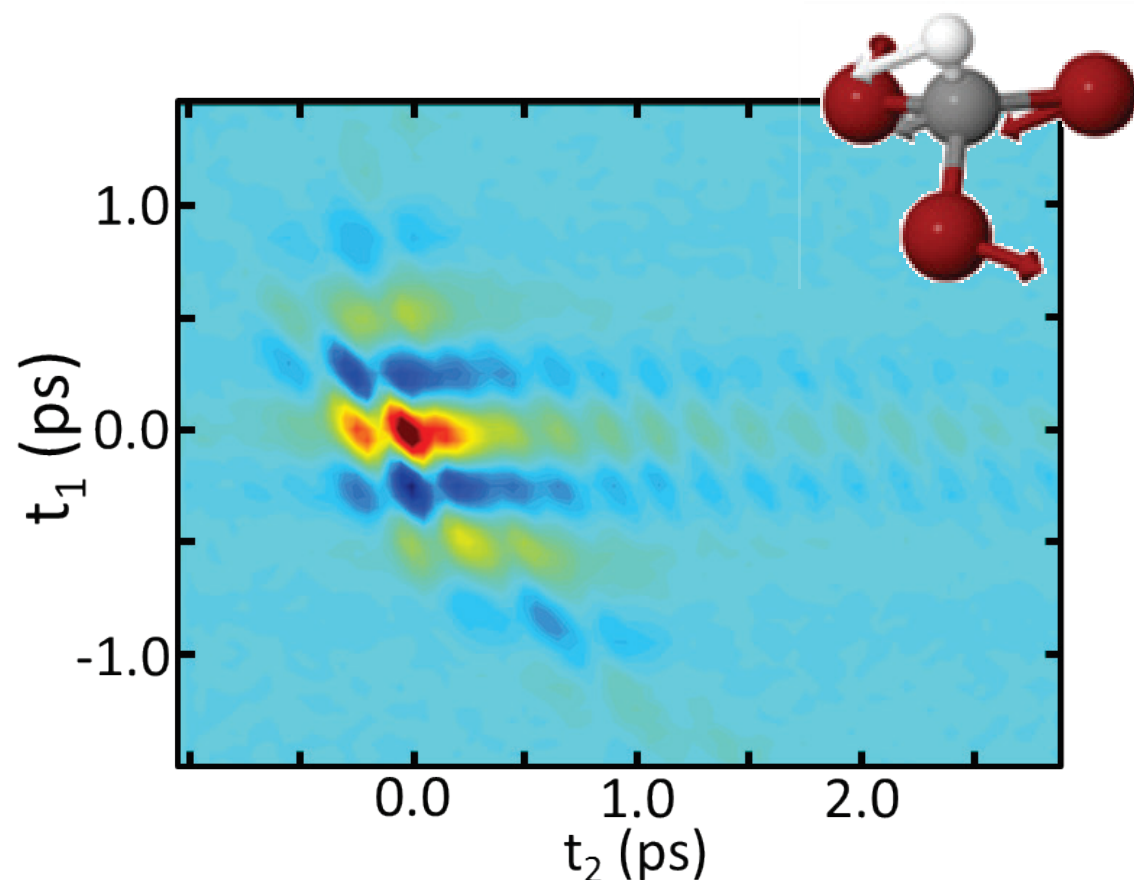


Conclusions and future directions

2D THz-THz-Raman is the first nonlinear 2D-THz spectroscopy of liquids.

It provides information on the coupling of thermally populated modes.

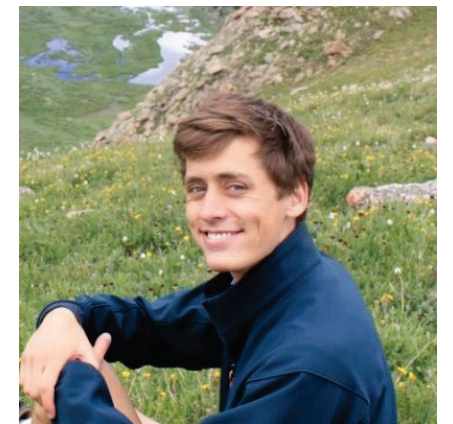
The next step is extending this technique to more complex systems.



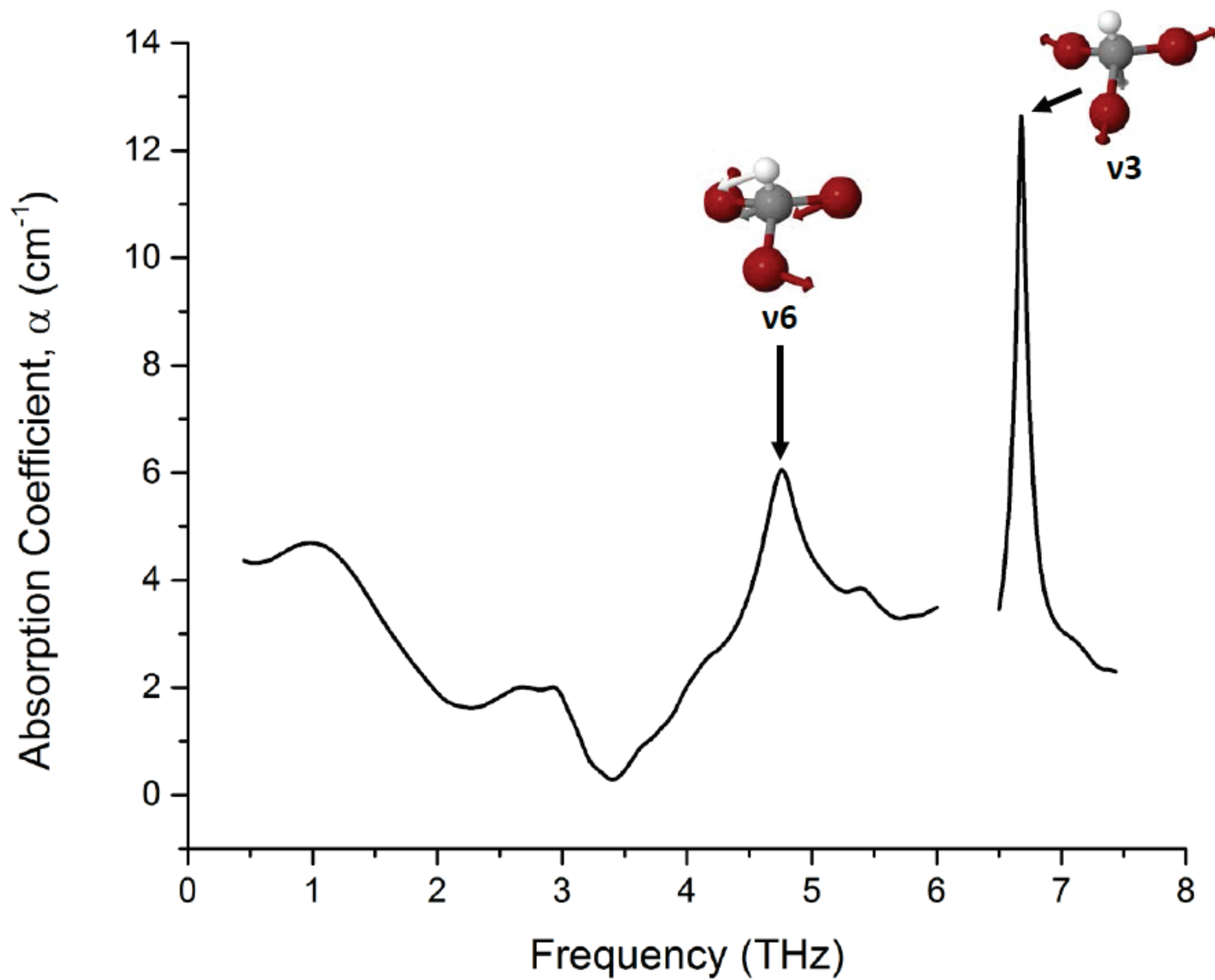
www.lsbu.ac.uk



Acknowledgements









THz-THz-Raman
This work



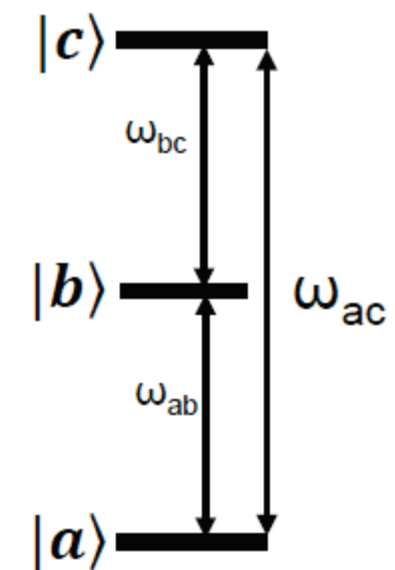
THz-Raman-THz
Savolainen et al. 2013



Raman-THz-THz
Savolainen et al. 2013

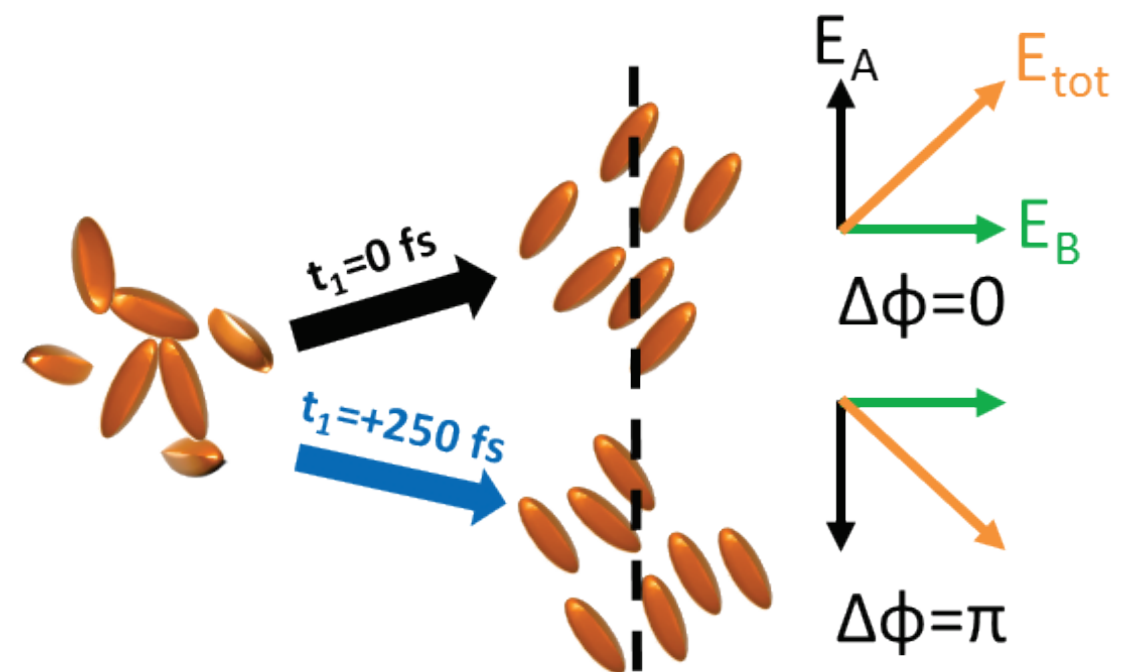
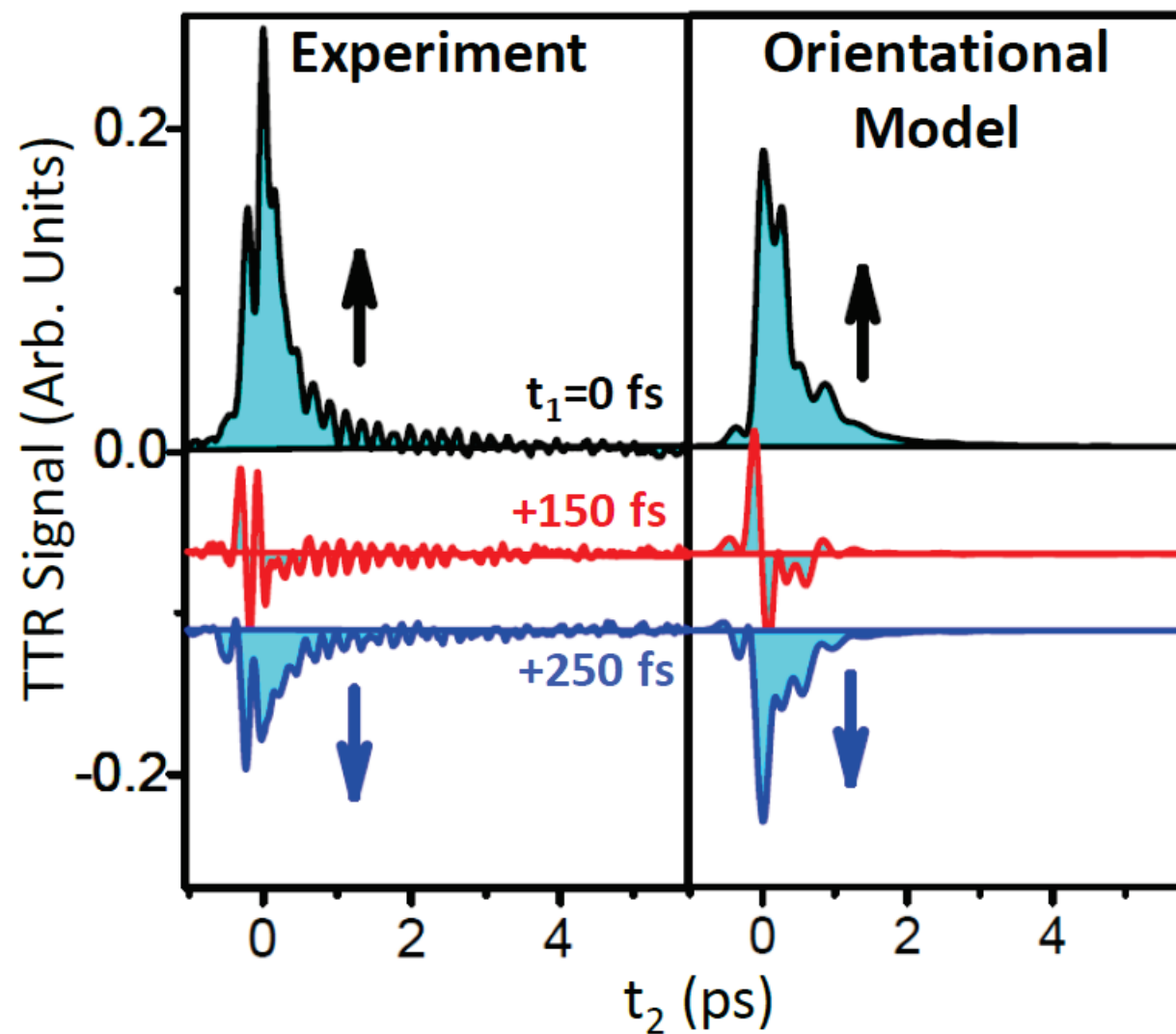
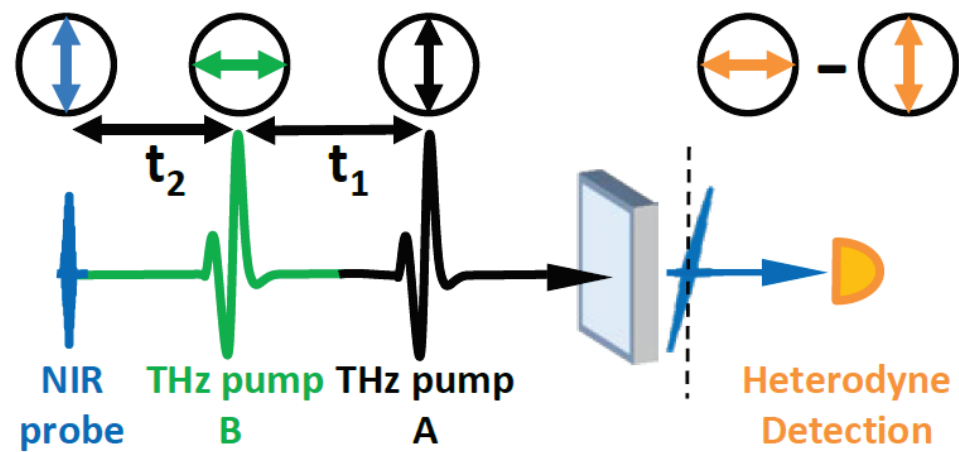


Raman-Raman-Raman
Tanimura and Mukamel 1993





Liquid CHBr_3 : the prototype system



Using assumption (i)
No assumptions

A Roadmap of 2D TTR Spectroscopy (+ c.c.)

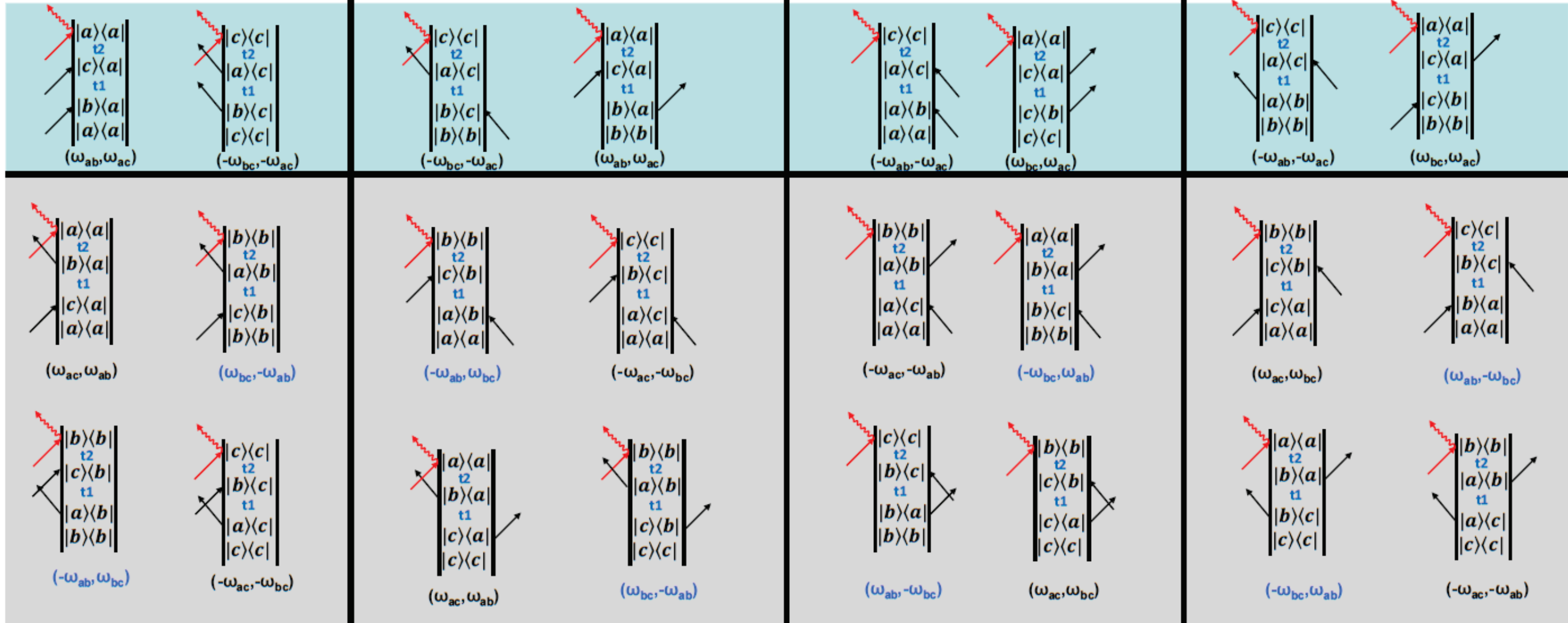
Labeling: (ω_1, ω_2)
Rephasing
Nonrephasing

$$\text{tr}\langle \Pi \mu_1 \mu_0 \rho_{eq} \rangle$$

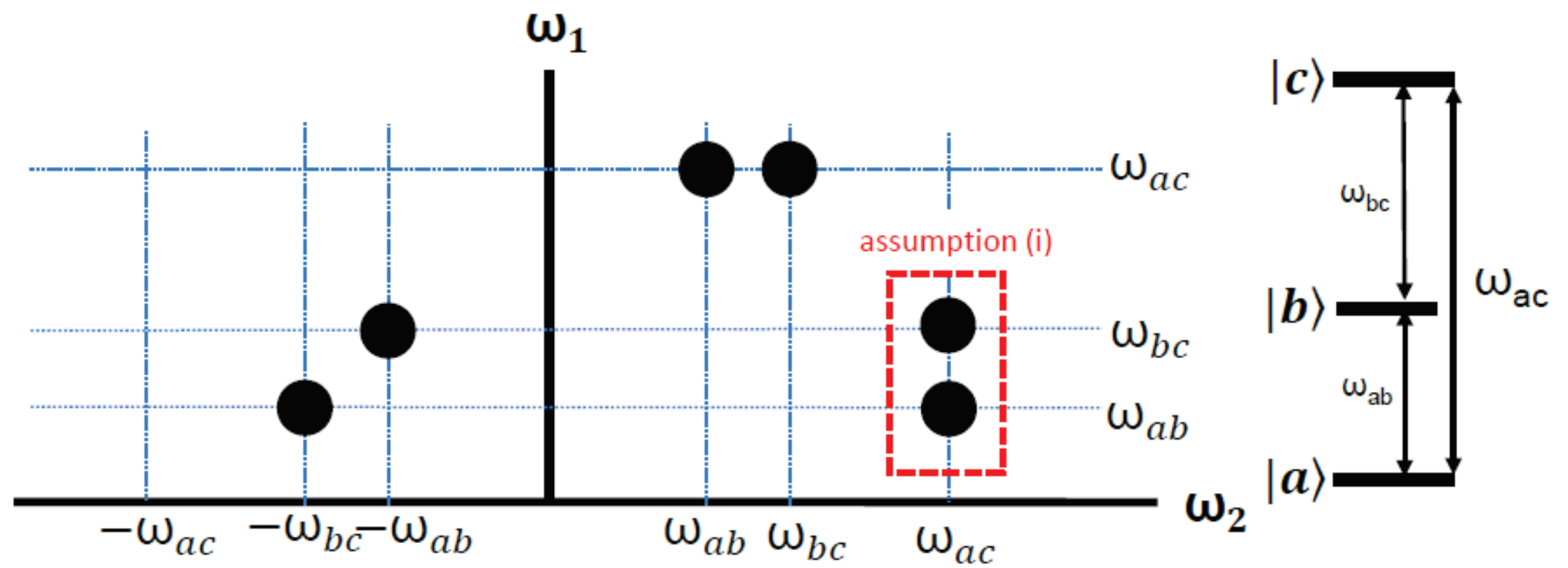
$$\text{tr}\langle \Pi \mu_1 \rho_{eq} \mu_0 \rangle$$

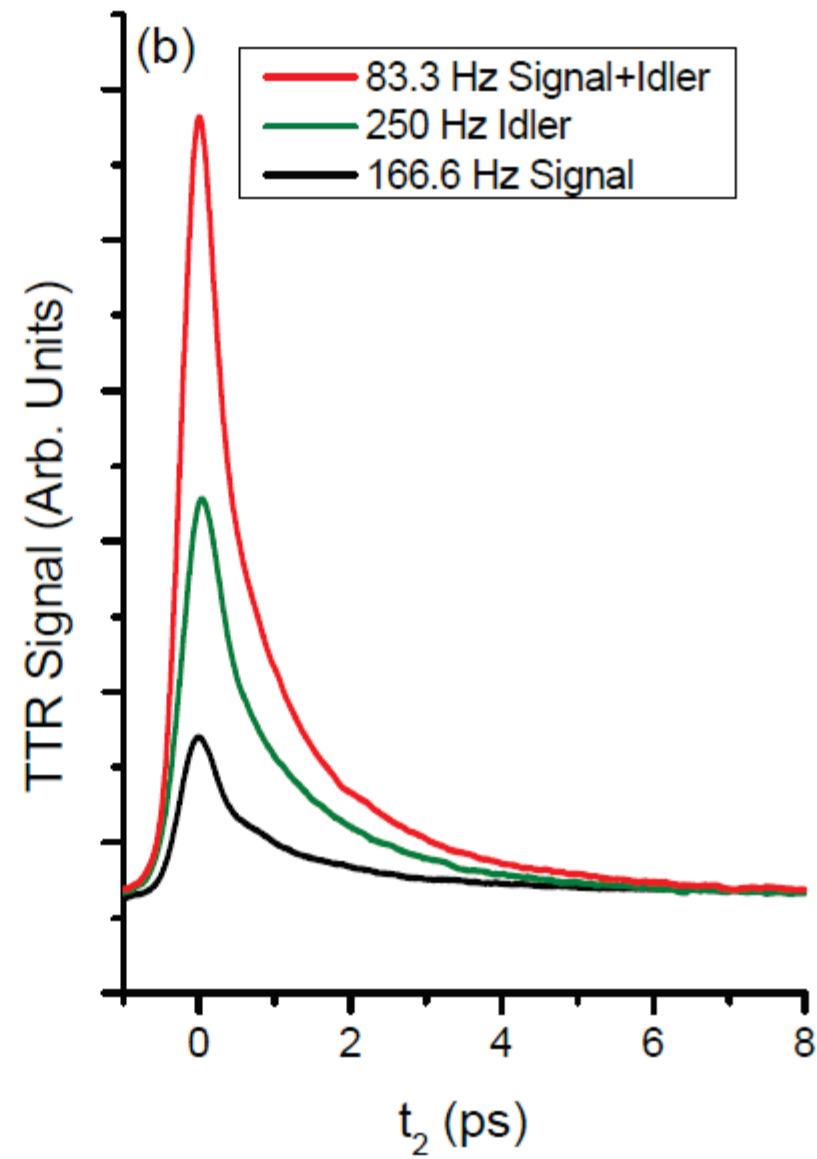
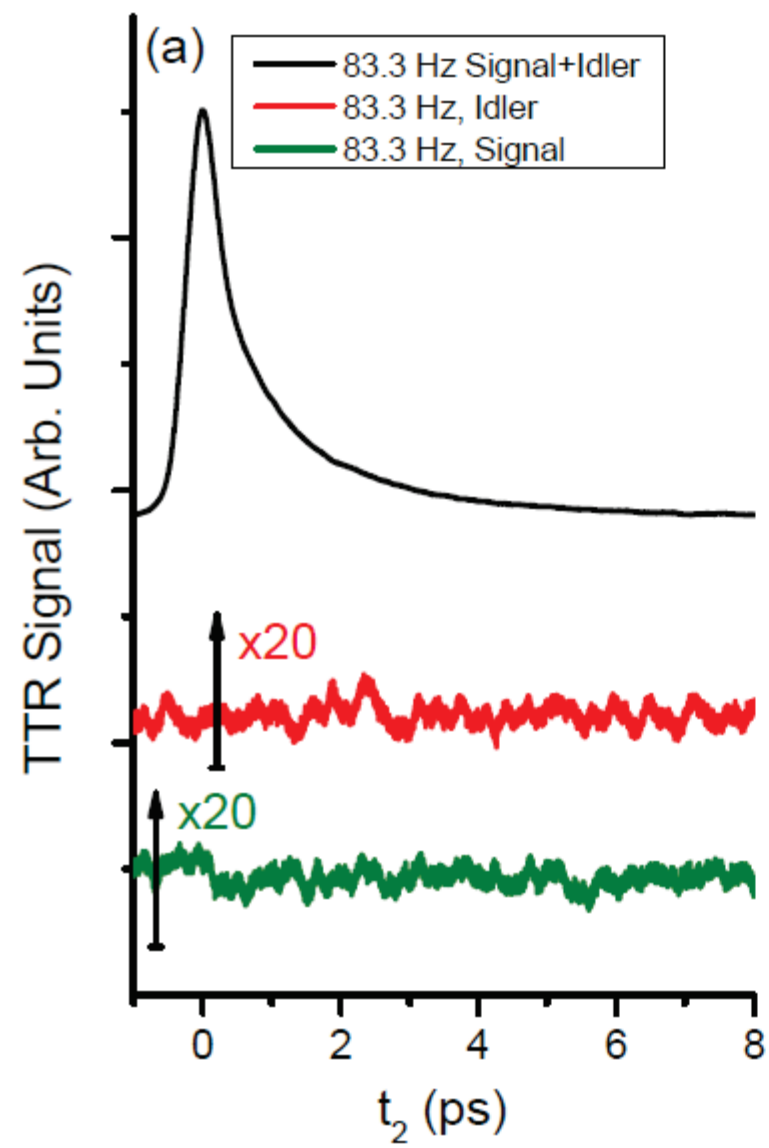
$$\text{tr}\langle \Pi \rho_{eq} \mu_0 \mu_1 \rangle$$

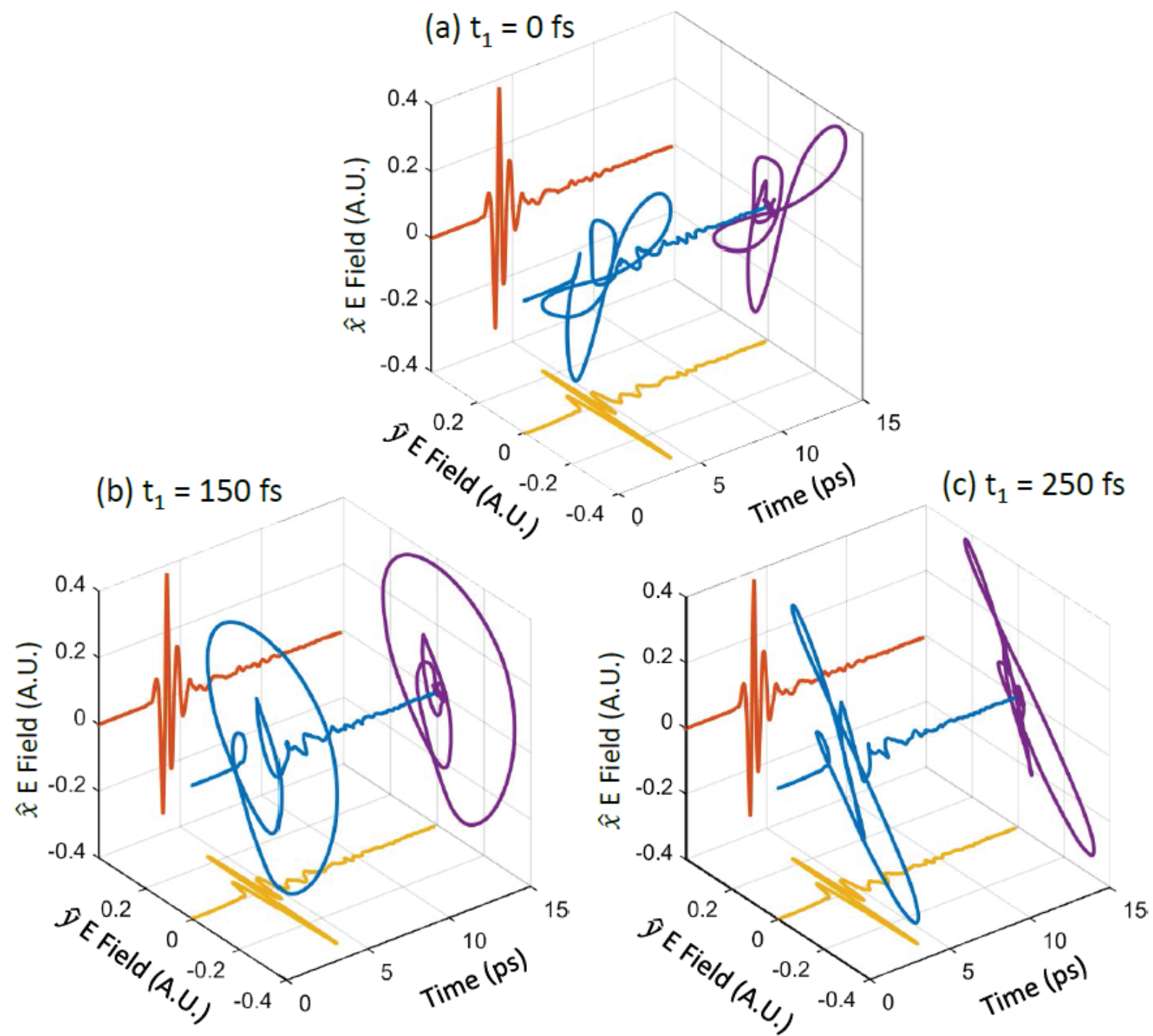
$$\text{tr}\langle \Pi \mu_0 \rho_{eq} \mu_1 \rangle$$



$$\begin{aligned}
 R^{(3)}(t_1, t_2) \propto & \mu_{ab} \mu_{bc} \Pi_{ac} (p_{ab} e^{-i\omega_{ab} t_1} e^{-i\omega_{ac} t_2} - p_{bc} e^{-i\omega_{bc} t_1} e^{-i\omega_{ac} t_2}) \\
 & + \mu_{ac} \mu_{bc} \Pi_{ab} p_{ac} e^{-i\omega_{ac} t_1} e^{-i\omega_{ab} t_2} - \mu_{ab} \mu_{ac} \Pi_{bc} p_{ab} e^{-i\omega_{ab} t_1} e^{+i\omega_{bc} t_2} \\
 & + \mu_{bc} \mu_{ac} \Pi_{ab} p_{bc} e^{-i\omega_{bc} t_1} e^{+i\omega_{ab} t_2} - \mu_{ac} \mu_{ab} \Pi_{cb} p_{ac} e^{-i\omega_{ac} t_1} e^{-i\omega_{bc} t_2} + c.c.
 \end{aligned}$$









$$\langle \Psi_a | \hat{\mu} | \Psi_b \rangle \neq 0 \Leftrightarrow \Gamma_a \otimes \Gamma_\mu \otimes \Gamma_b \supset A_1,$$

CHBr ₃		CCl ₄		CBr ₂ Cl ₂	
State	E	State	E	State	E
00⟩, A ₁	0.0	00⟩, A ₁	0.0	00000⟩, A ₁	0.0
10⟩, E	4.76	10⟩, E	6.51	10000⟩, A ₁	4.62
01⟩, A ₁	6.68	01⟩, F ₂	9.29	01000⟩, A ₂	5.25
20⟩, A ₁ + A ₂ + E	9.52	20⟩, A ₁ + A ₂ + E	13.0	00100⟩, B ₁	6.87
—	—	—	—	00010⟩, A ₁	7.25
—	—	—	—	00001⟩, B ₂	7.85
—	—	—	—	20000⟩, A ₁	9.24
—	—	—	—	11000⟩, A ₂	9.86
—	—	—	—	02000⟩, A ₁	10.5