Molecular Orientation echoes via concerted terahertz and near-IR excitations

Ran Damari[1,2], Amit Beer[1,2] ,Dina Rosenberg[1,2] and Sharly Fleischer[1,2]

Abstract

A new and efficient method for orientation echo spectroscopy is presented and realized experimentally. The excitation scheme utilizes concerted rotational excitations by both ultrashort terahertz and near-IR pulses and its all-optical detection is enabled by the Molecular Orientation Induced Second Harmonic method [2]. This method provides practical means for orientation echo spectroscopy of gas phase molecules and highlights the intriguing underlying physics of coherent rotational dynamics induced by judiciously-orchestrated interactions with both resonant (Terahertz) and nonresonant (NIR) fields.

Introduction

Laser-controlled rotational dynamics emerged from rotational coherence spectroscopy, a field aimed to extract rotational constants and structural data of molecules by monitoring their light-induced rotational dynamics. The field was primarily developed in order to induce anisotropic angular distributions within otherwise isotropic molecular ensembles (figure 1 ‘a’ and ‘b’). Anisotropic angular distributions are categorized as 'alignment' and 'orientation' with the inversion symmetry of the medium retained in the former or transiently lifted in the latter, respectively.

In recent years, vast efforts are put into obtaining molecular orientation that provides a more refined control over the angular distribution of molecules.
Here we demonstrate uniquely desirable rotational responses of polar gas molecules that are induced via judiciously-orchestrated rotational excitation by a terahertz (THz) and near-IR (NIR) pulses.

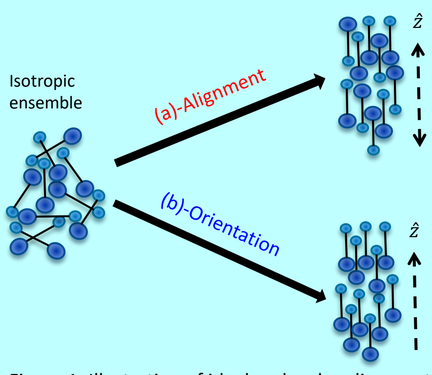


Figure 1: Illustration of ideal molecular alignment and orientation

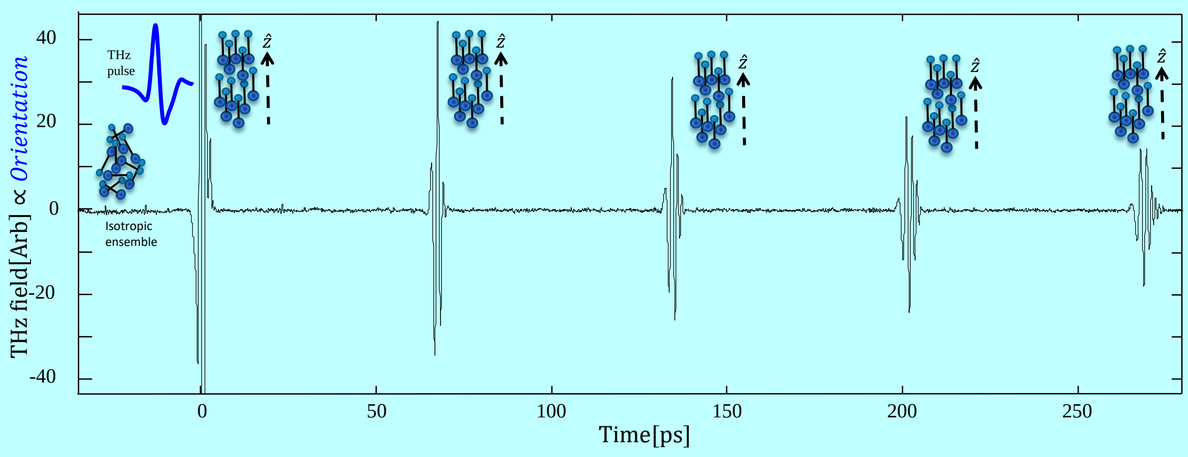


Figure 2: THz induced orientation signal of methyl iodide (20Torr, 300K). The signal decays with time due lose of rotational energy (intermolecular collisions and radiative decay)

Rephasing echoes

Two level echo scheme (NMR):

- Two magnetic pulses Δt apart
- 2nd pulse reverses phase accumulation
- Rephased echo appears Δt after the 2nd pulse
- Echo magnitude is time independent.

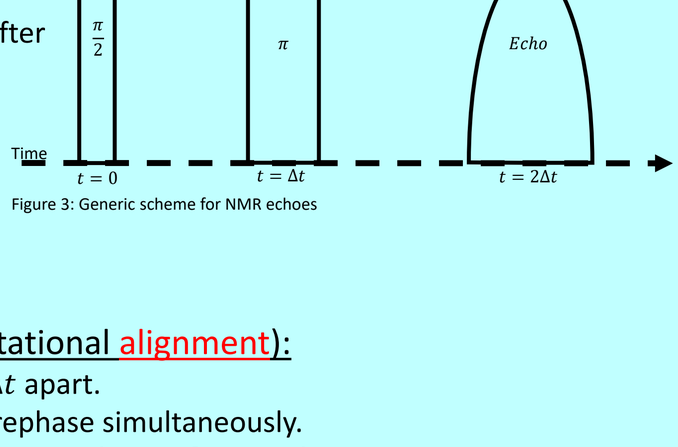


Figure 3: Generic scheme for NMR echoes

Multilevel echo scheme (Rotational alignment):

- Two identical optical pulses Δt apart.
- Many $J \rightarrow J \pm 2$ coherences rephase simultaneously.
- Rephased echo of many constructively interfering coherences.
- Due to interference of multiple interaction pathways, the echo has maximum rephasing efficiency value (~50%)

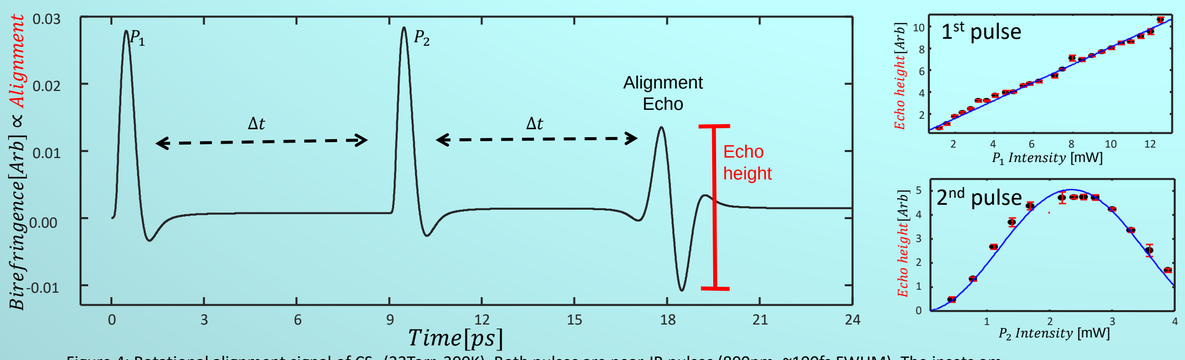


Figure 4: Rotational alignment signal of CS_2 (22Torr, 300K). Both pulses are near-IR pulses (800nm, ~100fs FWHM). The insets om the right depict the Echo height as a function of 1st and 2nd pulses, respectively.

Multilevel echo scheme (Rotational Orientation):

- Two identical THz pulses Δt apart.
- Many $J \rightarrow J \pm 1$ coherences rephase simultaneously.
- Linear dependence on 1st pulse
- Requires a double interaction with 2nd THz
  - Working in high vapor pressure
  - Large dipole moment limitation
  - Nontrivial required THz intensities

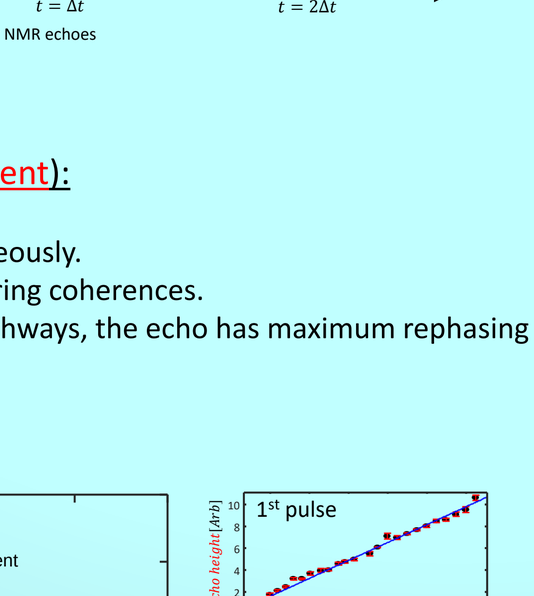


Figure 5: Acetnitril, 70Torr (vapor pressure), 300K, 3.92Debye.

Jian Lu, Yaqing Zhang, Harold Y. Hwang, +2, Benjamin K. Ofori-Okai, Sharly Fleischer, and Keith A. Nelson (2016)

THz-delay-NIR MOISH detection scheme

Near-Infrared (NIR, 800nm) pump:
- More efficient (linear interaction)
- Powerful (relative to current THz)
- Optically manageable.

NIR probe (MOISH)
- Solves geometrical problem
- Solves intensity problem
- Create Δk dephasing problem

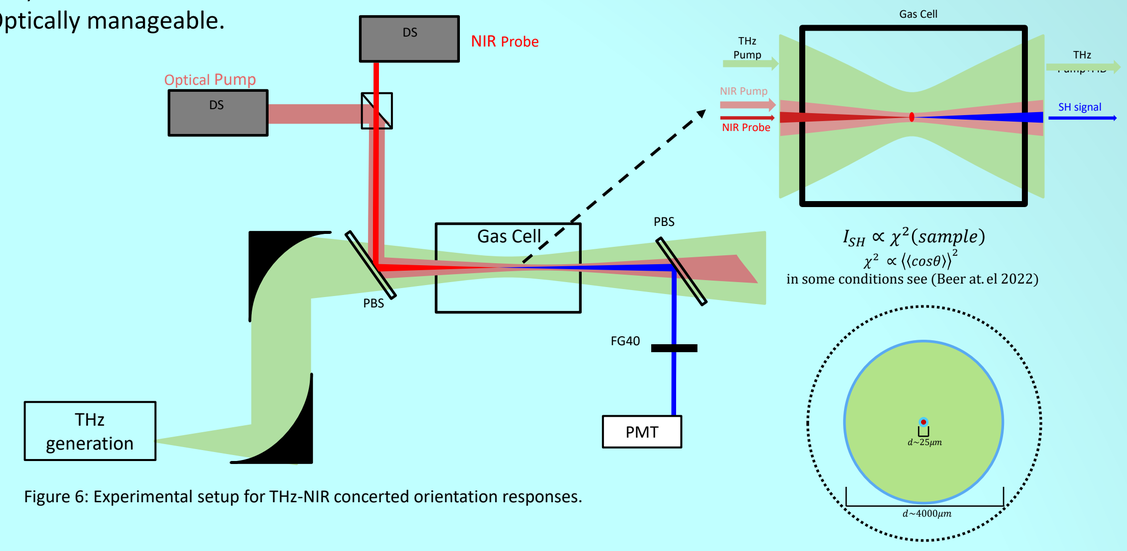


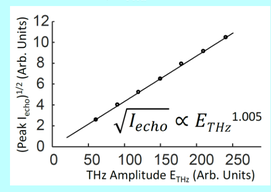
Figure 6: Experimental setup for THz-NIR concerted orientation responses.

THz-delay-NIR Orientation echo

MOISH Measurement (Molecular Orientation Induced SH,800nm)

- Single field-dipole interaction with 1st THz pulse
- Single RAMAN interaction with 2nd NIR pulse
- THz-NIR signals → small interaction length
- Minimal Δk effect
- $I_{SH\ of\ THz-NIR} \sim \chi^2_{eff} \sim \langle\langle cos\theta \rangle\rangle^2$

Single field-dipole interaction $\mu E_{THz} \cos\theta$



Single field-polarizability interaction $\frac{1}{4}\epsilon_{opt}^2 \Delta\alpha \cos^2\theta$

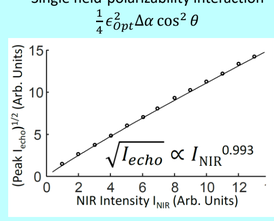
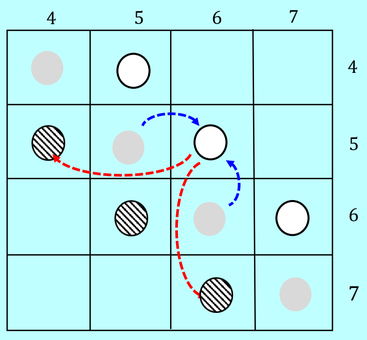


Figure 7: Time domain signal of THz induced orientation when affected by a second NIR pulse and recorded as the SH of a NIR probe. For further details see [3]

Density matrix inspired representation



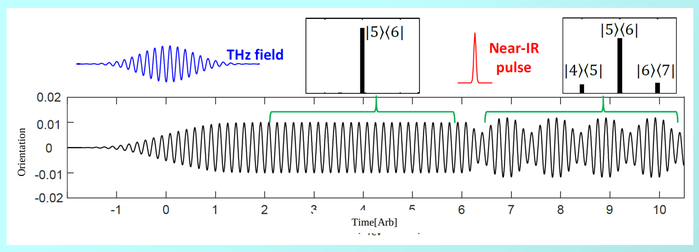


Figure 8: Left: 2D Density matrix representation describing the rotational transition pathways that lead to our observed orientation echo.
Right: Single rotational coherence simulation of a concerted THz-delay-NIR orientation response. The NIR pulse initiate the neighboring rephasing coherences.

In conclusion

we have demonstrated an efficient, all-optical excitation scheme for inducing orientation echo signals in gas phase molecular rotors. The detection of the orientation echo signal relies on the SH signal enabled by the lifted inversion symmetry of the medium upon orientation (MOISH) and emanate from the mutual interaction volume of the THz and NIR excitation pulses. The presented method provides new means for orientation echo spectroscopy which potentially unlocks a much broader range of gas pressures and molecular entities for study. It should be noted that the presented technique is applicable to linear and symmetric top molecular rotors, where dipole and stimulated Raman interactions drive a mutual rotational degree of freedom. Concerted THz- and NIR- induced rotations provide uniquely intriguing possibilities in three dimensional dynamics and coherent rotational control of asymmetric molecular rotors.

*[1] D. Rosenberg, R. Damari, S. Kallush, and S. Fleischer, "Rotational Echoes: Rephasing of Centrifugal Distortion in Laser-Induced Molecular Alignment," J. Phys. Chem. Lett. **8**(20), 5128–5135 (2017).*

*[2] A. Beer, R. Damari, Y. Chen, and S. Fleischer, "Molecular Orientation-Induced Second-Harmonic Generation: Deciphering Different Contributions Apart," J. Phys. Chem. A **126**(23), 3732–3738 (2022).*

[3] Orientation Echoes via Concerted Terahertz and Near-IR Ran Damari, Amit Beer, Sharly Fleischer 2022

Funding provided by