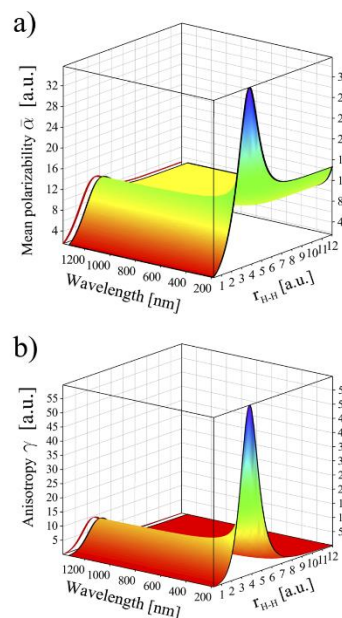


# Toward quantitative Raman spectroscopy

Henryk A. Witek, Ankit Raj, Yen-Bang Chao, Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, Hsinchu, Taiwan

Our goal is to standardize Raman spectroscopy by introducing simple molecular benchmark systems in order to establish absolute Raman intensity scale. This is achieved by computing accurate distance-dependent polarizability invariants of diatomic systems and averaging them over accurate rovibrational wave functions. The matrix elements determined in this fashion are used to calibrate the in-house built Raman spectrometer using the predicted intensity values of selected rovibrational Raman transitions. The calibrated spectrometer is subsequently used to determine the absolute Raman intensities of benchmark systems which are supposed to serve as a reference for calibration of the wide range of commercially available Raman spectrometers.

The current talk will mainly focus on theoretical aspects of the process described above. We will show that the calculations of polarizability invariants but for the simplest systems are exceedingly difficult and challenging due to the inherent shortcomings of the applicable wave functions. The computer programs for computing the rovibrational transition matrix elements over the polarizability tensor invariants for isotopes of molecular hydrogen are freely available at <https://github.com/ankit7540/H2-PolarizabilityMatrixElements>.



Dynamic (wavelength dependent)  
a) mean polarizability  $\bar{\alpha}$  and b) polarizability anisotropy  $\gamma$  of  $H_2$ , HD, and  $D_2$  as a function of internuclear separation.

- [1] A. Raj, H. Hamaguchi, and H. A. Witek, "Polarizability tensor invariants of  $H_2$ , HD, and  $D_2$ ", *J. Chem. Phys.* **148**, 104308 (11 pages) (2018).
- [2] A. Raj, H. A. Witek, and H. Hamaguchi, "Vibration–rotation interactions in  $H_2$ , HD and  $D_2$ : centrifugal distortion factors and the derivatives of polarisability invariants", *Mol. Phys.* **118**, e1632950 (13 pages) (2020).
- [3] A. Raj, C. Kato, H. A. Witek, and H. Hamaguchi, "Toward standardization of Raman spectroscopy: Wavenumber and intensity calibration using rotational Raman spectra of  $H_2$ , HD,  $D_2$  and vibration-rotation spectrum of  $O_2$  as primary standards", *J. Raman Spectrosc.* **51**, 2066–2082 (2020)
- [4] A. Raj, H. A. Witek, and H. Hamaguchi, "Determination of accurate absolute Raman cross-sections of benzene and cyclohexane in the gas phase", *Asian J. Phys.* **30**, 321–335 (2021).
- [5] A. Raj, C. Kato, H. A. Witek, and H. Hamaguchi, "Accurate intensity calibration of multichannel detectors using Raman intensity ratios", *J. Raman Spectrosc.* **52**, 2038–2050 (2021).
- [6] A. Raj, Y.-B. Chao, and H. A. Witek, "Testing the limitations of harmonic approximation in the determination of Raman intensities", *Mol. Phys.* e2069613 (2022).