

## Gas-phase Refractivity Measurement of Ordinary and Heavy Water

Patrick Egan<sup>1, S, C</sup>

<sup>1</sup>*National Institute of Standards and Technology (NIST), Gaithersburg, U.S.A.  
egan@nist.gov*

Water is one of the most studied substances, and yet gas-phase measurements of refractivity are rare. (Apparently, the sole measurement of gas-phase heavy water dates to Cuthbertson and Cuthbertson in 1936.) The reason gas-phase refractivity measurements are rare is because they are difficult. As a representative case: a  $10^{-4} \cdot (n - 1)$  accuracy target at 1 kPa vapor pressure is a  $2.3 \times 10^{-10}$  fractional uncertainty requirement. Consider an interferometer with a 0.1 m gas pathlength: achieving  $2.3 \times 10^{-10}$  fractional uncertainty translates to length metrology accurate within 23 pm---about one-eighth the diameter [1] of the water molecule!

The metrology challenge is worth undertaking, because gas-phase measurements of refractivity are especially valuable in the context computational chemistry. In extreme conditions, where experiment is difficult or nonexistent, computational chemistry can supplement measurement, and possibly extend the knowledge range of thermophysical quantities (e.g., as embodied in a reference equation of state). Precision measurements of molecular properties are an essential benchmark against which to build confidence in computational chemistry. For example, gas-phase measurements of water refractivity allow determination of the electronic polarizability, a property of a single molecule amenable to calculation. Agreement between calculation and measurement (for a well-controlled experiment at room-temperature) is the foundational criterion that establishes computational chemistry as an alternative to measurement at extreme conditions.

Work will be presented for optical measurements of gas-phase refractivity of ordinary water and heavy water. The apparatus is based on a Fabry-Perot cavity refractometer, covering the temperature range ( $293 < T < 433$ ) K and pressure  $p < 2$  kPa. The measurements suggest the IAPWS formulation [2] of gas-phase ordinary water overestimates the polarizability (refractivity) by 1.9 %, and incorrectly predicts the sign of the temperature dependence. By contrast, the measurements are in good agreement with recent ab initio calculation of the dipole polarizabilities [3].

### References:

1. A. H. Harvey, J. Hrubý, and K. Meier, "Improved and always improving: Reference formulations for thermophysical properties of water," *J. Phys. Chem. Ref. Data* 52, 011501 (2023). <https://doi.org/10.1063/5.0125524>
2. A. H. Harvey, J. S. Gallagher, and J. M. H. Levelt Sengers, "Revised formulation for the refractive index of water and steam as a function of wavelength, temperature and density," *J. Phys. Chem. Ref. Data* 27, 761-774 (1998). <https://doi.org/10.1063/1.556029>
3. G. Garberoglio, C. Lissoni, L. Spagnoli, and A. H. Harvey, "Comprehensive quantum calculation of the first dielectric virial coefficient of water," *J. Chem. Phys.* 160, 024309 (2024).