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Invited

SNAPS: Spectroscopic-network-assisted precision spectroscopy

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Frequency combs and cavity-enhanced optical techniques have revolutionized molecular spectroscopy. Their combination allows recording saturated Doppler-free lines with ultrahigh precision. As shown by Tóbiás *et al.*¹, the theory of spectroscopic networks² offers a powerful tool for the intelligent design and validation of such precision-spectroscopy experiments and the subsequent derivation of accurate rovibrational energy levels. The tool developed is called SNAPS: spectroscopic-network-assisted precision spectroscopy¹. The SNAPS procedure can be divided into four major phases: [I] preparation phase, where the SNAPS input is created, [II] selection phase, where the full set of possible target lines is generated, [III] measurement phase, where the list of target lines is reduced and then detected with a precision-spectroscopy setup, and [IV] evaluation phase, where the final paths and cycles are obtained and assessed. Phases II and IV are based on elements of network theory, while phase III is where the theoretical knowledge is turned into experimental information. It is advantageous to employ both network and quantum theory to facilitate the measurement campaign and to the full exploitation of the lines resolved.

Lines selected carefully *via* SNAPS have been detected, using a NICE-OHMS (noise-immune cavity-enhanced optical heterodyne molecular spectroscopy) apparatus, in the near-infrared window of 7000–7350 cm⁻¹, for H₂¹⁶O and H₂¹⁸O, benchmark systems of molecular spectroscopy, at kHz accuracy. The observation of 156 absorption lines of H₂¹⁶O in the near-infrared in saturation¹, augmented with extremely accurate literature lines to ensure overall connectivity, allowed the precise determination of the lowest *ortho*-H₂¹⁶O energy, set at 23.79436122(25) cm⁻¹. The same set of measurements yielded 160 pure rotational energy levels, all up to $J = 8$, on the ground, $(v_1 v_2 v_3) = (000)$, vibrational state with similar high accuracy, where v_1 , v_2 , and v_3 are quantum numbers associated with the symmetric stretch, bend, and antisymmetric stretch normal modes of H₂¹⁶O, respectively and J is the total rotational quantum number. The measurement of 71 newly observed lines³ allowed the determination of the relative energies for all of the 59 rovibrational states up to $J = 6$ within the $(v_1 v_2 v_3) = (200)$ vibrational parent of H₂¹⁶O. An experimental curiosity of this study is that for strong transitions an apparent signal inversion in the Lamb-dip spectra is observed; a novelty reserved to the NICE-OHMS technique. Similar measurements involving the (000) vibrational state allow the determination of all the pure rotational energies of H₂¹⁸O corresponding to J values up to 8⁴. Traversal of the (000) rotational energy levels *via* up and down jumps involving several vibrational bands is a novel approach, inspired by the network-theoretical view² of high-resolution spectroscopy.

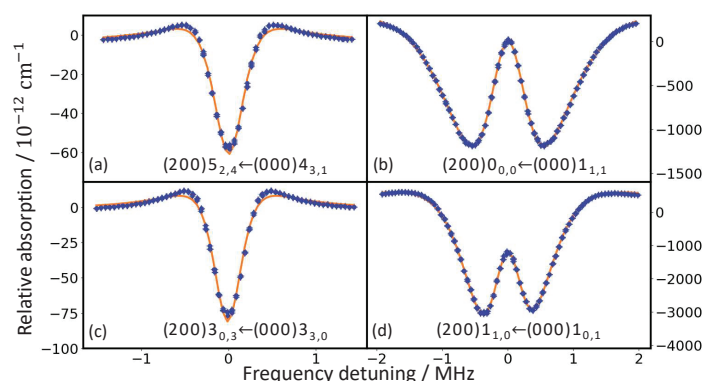


Figure 1: Spectral recordings of four Lamb-dip lines with their rovibrational assignments indicated. On panels (a)–(b) and (c)–(d), *para*- and *ortho*-H₂¹⁶O transitions are depicted, respectively. Note that the double-dip line profiles, depicted in panels (b) and (d), arise when the underlying transitions have larger Einstein- A coefficients.

¹R. Tóbiás, T. Furtenbacher, I. Simkó, A. G. Császár, M. L. Diouf, F. M. J. Cozijn, J. M. Staa, E. J. Salumbides, W. Ubachs, *Nat. Commun.* **11**, 1708 (2020).

²A. G. Császár, T. Furtenbacher, *J. Mol. Spectrosc.* **266**, 99 (2011).

³M. L. Diouf, R. Tóbiás, T. van der Schaaf, F. M. J. Cozijn, E. J. Salumbides, A. G. Császár, W. Ubachs, *Mol. Phys.* in press (2022).

⁴M. L. Diouf, R. Tóbiás, I. Simkó, F. M. J. Cozijn, E. J. Salumbides, W. Ubachs, A. G. Császár, *J. Phys. Chem. Ref. Data* **50**, 023106 (2021).