

Accurate spectroscopy of deuterium molecule

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The accuracy of the molecular spectroscopy on weak transitions (too weak to saturate) in molecules which cannot be cooled and trapped, is presently limited to the sub-megahertz level, without clear perspectives for further substantial improvements. We demonstrate a new method with the potential to achieve kilohertz-level accuracy. We bring the Doppler-regime measurements into the high-pressure region, where the signal-to-noise-ratio is much higher. The expected deterioration of accuracy by collision-induced systematics [1] is mitigated with *ab initio* line-shape and quantum scattering calculations [2]. We test our approach on a case of weak quadrupole transition in D₂, which is a benchmark system for testing quantum electrodynamics in molecules. We validate our methodology at the 400 kHz level by comparing our results with the best previous determination [3]. We demonstrate that our approach achieves higher accuracy despite much milder experimental requirements (in Ref. [3], the effective optical path was 20 times longer). For the same experimental apparatus, the accuracy of our approach will be at least one order of magnitude better. For the first time, we applied *ab initio* quantum scattering calculations to address the collisional line-shape effects [4, 5] in ultra-accurate spectra analysis collected at high pressures. The experimental and theoretical values of the 2-0 S(2) line position in D₂ reported here constitute the most precise comparison of the experimental and theoretical *ab initio* determinations of rovibrational splitting for any neutral molecule. We observe a 3.4 σ discrepancy, which, together with previously reported discrepancies [6], indicates that the theoretical accuracy is underestimated because of the uncalculated terms.

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