Dicke-narrowed spectroscopy of molecules confined in gas cells of sub-wavelength thickness

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Miniaturized atomic vapor cells of nanometric thickness have become promising platforms for fundamental measurements, metrology and quantum technologies. For example, nanometric cells have been used for exploring Dicke-type effects of confinement [1], measuring Casimir-Polder interactions, fabricating compact atomic clocks and probing collective effects. Extending these experiments to molecular gases is a fascinating prospect for applications in compact frequency referencing and for testing fundamental quantum electrodynamics using increasingly complex quantum objects. Towards this end, experiments have been performed with platforms such as hollow core fibers, tapered nanofibers and integrated waveguides. Moreover, selective reflection experiments with molecules have also been performed [2].

Here, we present our pioneering experiments probing molecular rovibrations of gases confined in micrometric cells, whose thickness is comparable to the excitation wavelengths. We work in two distinct regions of the electromagnetic spectrum, probing $\nu_1 + \nu_3$ resonances of acetylene at 1.530 µm, within the telecommunications wavelength range, as well as the ν_3 and ν_2 resonances of SF_6 and NH_3 respectively, in the mid-infrared fingerprint region around 10.55 µm. Thin-cell confinement allows us to explore and demonstrate Dicke-narrowing effects, probing molecules with linear sub-Doppler transmission spectroscopy. Our first experiment, reported recently in Nature Communications [3], uses a cell with a thickness that varies between 5.2–5.5 µm. This corresponds to 7λ/2 and λ/2 thickness for acetylene and SF_6 or NH_3 rovibrations respectively. We also report measurements in a second cell of thickness ranging from 600–1200 nm allowing us to explore tighter molecular confinement. The transmission spectra displaying sub-Doppler characteristics due to the coherent Dicke narrowing are analyzed by means of a theoretical model making specific assumptions about the physics and dynamics of confined molecules. In all the above measurements, the model reproduces exceptionally well the experimental data.

We focus our analysis on both the absolute signal amplitude and spectral lineshape. This allows us to confirm, within the limits of our precision, the hypotheses concerning the collisions with the cell-windows, the Maxwell-Boltzmann thermal distribution of velocities and the rotational redistribution (Boltzmann repartition function) of molecules after desorption from the wall. This is an important result, as the equilibrium conditions of confined gases have been put into question [4]. Furthermore, our analysis confirms that our spectroscopic technique can be used to determine molecular transition strengths and therefore enrich molecular databases. We demonstrate this by providing new data on the SF_6 greenhouse molecule for which databases are notoriously incomplete.

A major perspective resulting from this work is the measurement of Casimir-Polder interactions with molecules. For this purpose, we are currently building a new experiment to probe the strong HF rovibration at 2.5 µm. This experiment will allow us to probe strongly confined HF gas in a nanocell (100 nm thickness) and measure the effects of molecular orientation in Casimir-Polder interactions.

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