High resolution infrared measurements of dioxane isomers using Fourier transform and quantum cascade laser spectroscopies coupled to supersonic jet and long path cell

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Dioxines are volatile organic compounds considered as atmospheric pollutants. Among them, 1,4-dioxane ($C_4H_8O_2$) is extensively released in the environment.[1] The spectroscopic detection and quantification of 1,4-dioxane in sub ppbv levels is still a challenge to analytical methods and generate concerns that 1,4-dioxane in the environment has mostly gone undetected. There is also a fundamental interest in monitoring these molecules in simulation chambers (CHARME at LPCA) to study their reactivity with major oxidants but it requires knowledge of their rovibrational signatures through high-resolution experiments over a broad spectral range.

We report here a high resolution study of dioxane isomers on a wide infrared range (IR) combining the Jet-AILES set-up implemented at SOLEIL, and a room temperature long path cell, both coupled to a Fourier Transform Spectrometer (FTS), and the SPIRALES set-up available at MONARIS laboratory, a pulsed supersonic jet coupled to mid-IR quantum cascade lasers (QCL).[2]

In the case of 1,4 dioxane, high resolution IR spectroscopy turns to be the best alternative to determine ground state molecular parameters in the absence of permanent dipole moment.[3] In the fingerprint region, several bands of 1,4-dioxane were analyzed using mainly both jet-cooled spectroscopic set-ups. Reliable ground and excited-state (ES) molecular parameters could be derived from global rovibrational fits distributed over 4 vibrational excited states including all possible projections of the vibrational dipole moment with different selection rules, which strongly reduces the correlations between molecular parameters. Last, a combined HR millimeter-wave and jet-cooled-QCL and cell-FT IR spectroscopic study of the very expensive 1,3 dioxane isomer enabled to derive precise molecular parameters for the ground state and 6 vibrational states in the 950-1250 cm^{-1} range.

This present work focused about rovibrational analyses of dioxane isomers highlights the complementarity between supersonic jet set-ups and room temperature long path cells coupled to broadband FT and/or narrow band QCL infrared spectroscopies to characterize large molecules relevant for atmosphere science. [4]

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