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Near infrared cavity enhanced absorption spectra of atmospherically relevant ether-1, 4-Dioxane



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ABSTRACT

1, 4-Dioxane (DX) is a commonly found ether in industrially polluted atmosphere. The near infrared absorption spectra of this compound has been recorded in the region $5900\text{--}8230\text{ cm}^{-1}$ with a resolution of 0.08 cm^{-1} using a novel Fourier transform incoherent broadband cavity-enhanced absorption spectrometer (FT-IBBCEAS). All recorded spectra were found to contain regions that are only weakly perturbed. The possible combinations of fundamental modes and their overtone bands corresponding to selected regions in the measured spectra are tabulated. Two interesting spectral regions were identified as $5900\text{--}6400\text{ cm}^{-1}$ and $8100\text{--}8230\text{ cm}^{-1}$. No significant spectral interference due to presence of water vapor was observed suggesting the suitability of these spectral signatures for spectroscopic in situ detection of DX. The technique employed here is much more sensitive than standard Fourier transform spectrometer measurements on account of long effective path length achieved. Hence significant enhancement of weaker absorption lines above the noise level was observed as demonstrated by comparison with an available measurement from database.

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1. Introduction

1.1. 1, 4-Dioxane (DX)

One of the significant cyclic ether found in trace levels in the troposphere, 1, 4-Dioxane (DX), is widely used as a stabilizer in chlorinated organic solvents, such as 1, 1, 1-trichloroethane (TCA) [1]. DX is extensively used as an industrial solvent in pharmaceuticals and cosmetic paints [1]. It is also used as a wetting and dispersing agent in textile and dye industries [1]. It is not easily biodegradable and classified as a potential carcinogen by the US Environmental Protection Agency (EPA) [1–3] and by the International Agency for Research on Cancer (IARC) [2]. The major anthropogenic source of 1, 4-dioxane in the atmosphere is from its wide use as an industrial solvent. As per a 1985 US EPA report 90% of all DX manufactured was used as a stabilizer for chlorinated solvent [1]. Long term oral administration of DX is reported to cause tumors in liver and gallbladder of guinea pigs, and also in liver of the rats [2]. Because of high water solubility and low Henry constant it is difficult to extract DX from water thus making it a long-term hazard in contaminated atmosphere as well as in ground water [1]. Many US States are regulating DX in drinking water [1] and, recently, DX was added to the revised water quality standards in Japan [2].

1.2. Spectroscopic importance of DX

1, 4-Dioxane ($\text{C}_4\text{H}_8\text{O}_2$) has a chair conformation shown in Fig. 1 with a center of symmetry in the gas phase and is described by the D_{2h} point group. The thirty six normal modes of DX are distributed over four symmetry groups. The ten A_g and eight B_g vibrations are Raman-active, nine A_u and nine B_u are IR-active, and the first four observed normal modes in the A_u and B_u groups are degenerate [4]. Because of its known chair structure and high symmetry (D_{2h}), DX has been a probe for infrared spectroscopy for vibrational analysis [4]. In 1947 Ramsay reported all the selection rules for the fundamental vibrational modes of all symmetries of 1, 4-Dioxane [5]. In 1951, the vacuum ultraviolet spectrum of DX in the region $50,000\text{--}60,000\text{ cm}^{-1}$ was reported [6]. The $n\text{-}3s$ Rydberg photon transitions were studied using $2 + 1$ resonance enhanced multiphoton ionization spectroscopy [7]. These $n\text{-}3s$ transitions were intense, sharp and consisting of mainly Q branches [7]. The infrared spectra of DX and completely deuterated DX were reported together with their Raman spectra by Ellestad et al. [8]. They reported the spectra and its assignments (both in liquid and gas phases) in the region $80\text{--}4000\text{ cm}^{-1}$ [8]. In 1993, Brown et al. reported the first rotationally resolved high resolution near infrared band about 1260 cm^{-1} using diode laser spectroscopy [9]. They obtained accurate rotational parameter values for ground and upper states by analysis of one hundred and thirty six lines in the P, Q and R branches of this B type transition. Vibrational frequency of DX is calculated for both chair and twin twist conformation using ab-initio molecular orbital theory at the HF/6-31G* and BLYP/6-31G* levels [10]. DX was also used as a guest for producing Hofmann type clathrates for their vibrational and Raman spectral studies

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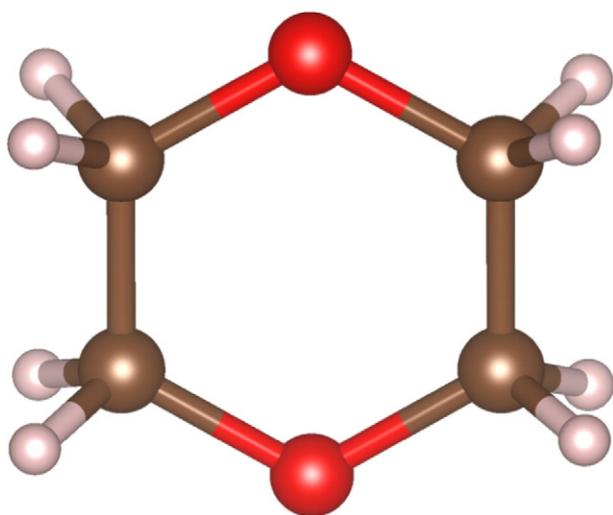


Fig. 1. Structure of DX.

[11]. Infrared spectra of the mixture of water and DX were used to study the state of water in organic compounds [12].

Since DX causes environmental contamination, its quantification and detection in trace levels has great importance in atmospheric pollution studies. Due to limited available laboratory data for spectroscopic characterization, DX has been an invisible contaminant in the atmosphere. The spectroscopic detection and quantification of DX in sub ppbv levels is still a challenge to analytical methods and generate concerns that DX in the environment has mostly gone undetected [3]. The US EPA proposed several analytical methods for DX analysis like 8260C, 8261, and 8270D [3]. The extraction and analysis of DX from water using solid-phase micro extraction coupled with gas chromatography have been reported in 2006 [1]. The gas phase in-situ detection of these compounds in the atmosphere is yet to be reported.

High resolution absorption measurements in the high ground state energies of molecules are experimentally difficult due to increasingly weak transitions and perturbations coming from vibrational overtones and combinations of fundamental modes in the near-infrared spectral region (NIR). Incoherent broadband cavity enhanced absorption spectroscopy (IBBCEAS) is a sensitive method for monitoring weak absorption lines of molecules in gaseous phase [13]. In this study, a versatile Fourier transform spectrometer (FTS) is coupled with IBBCEAS method [13–16] for recording NIR fingerprints of DX in the 5900–8220 cm^{-1} spectral region. Spectroscopic methods have been used for in-situ detection of many atmospheric trace pollutants in the recent past. For example, NIR spectral fingerprints have been used for in situ detection of trace gases [17,18] using tunable diode laser (TDL) technology. Sensitive laboratory measurements of DX spectrum like the ones presented here could help in identifying suitable signatures for development of similar spectroscopic instrumentation and could also contribute to spectroscopic databases like GEISA and PNNL.

DX has its important role as a target species in vibrational (Infrared) and rotational (Microwave) spectroscopy. So the spectral measurements reported here with high ground state energies are useful for molecular modeling scientists to develop new theoretical models for the ground state potential of DX. Measured spectra in this study were found to contain the regions that are weakly perturbed indicating the deviation from the harmonic approximations of the molecular models. Here we discuss the measured DX spectra in detail by comparing with spectra of water vapor. We present the interesting spectral ranges 5900–6400 cm^{-1} and 8100–8200 cm^{-1} where no spectral interference of water is present. These regions are potentially suitable for spectroscopic instrumentation for in-situ detection of DX in contaminated environment.

2. Experimental

All spectra have been measured using the IBBCEAS technique with a FTS detection scheme following previous studies in the method [13–16]. Light from a super continuum (SC) fiber laser (Fianium, SC-450, 2 W, 5 ps pulses with 80 MHz repetition) was spatially and spectrally filtered before entering an optical high finesse cavity (length $d = 644$ cm consisting of two dielectric mirrors; cc/pl, diameter 40 mm, $r = -600$ cm, reflectivity $R = 0.999$, Layertec GmbH). The light exiting the cavity was collected with an achromatic lens and guided with a multimode fiber (diameter 1 mm) into a FT spectrometer (Bruker, Vertex 80), where it was detected with an InGaAs photodiode at room temperature (a schematic of the experimental setup is depicted in Fig. 2).

This experimental method has significant advantage over the conventional single-path Fourier transform spectroscopy. The IBBCEAS technique has an advantage of detecting weaker lines of trace species because of enhanced sensitivity due to the increased effective path length through the sample provided by the resonator cavity. The effective path length becomes about 6.44 km in the 644 cm long optical cavity when a mirror pair having effective reflectivities of 0.999 is used. At the same time the FTS detection scheme enhances the resolution and spectral range of the conventional IBBCEAS setup, in which a dispersion spectrometer is traditionally used as detector where the resolution is limited by its grating. The main disadvantage of the FT-IBBCEAS technique is its relatively long scanning time necessary for the recording of measured spectra [14]. Cavity transmission spectra with (I) and without (I_0) the sample were recorded with a resolution of 0.08 cm^{-1} in the range 5900–8200 cm^{-1} from which absorption coefficients, α , were derived using [19].

$$\alpha = \left(\frac{I_0}{I} - 1 \right) \frac{(1 - R_{\text{eff}})}{d} \quad (1)$$

For that purpose the cavity was first evacuated to 1×10^{-5} Torr with a turbo pump, and then filled with DX at its vapor pressure at room temperature. Here R_{eff} is the effective reflectivity of the cavity, which is different from individual R values of the cavity mirrors specified by the manufacturer. Determining this effective reflectivity accurately over the spectral range of measurements specifies the calibration of the instrument. After aligning the cavity, $R_{\text{eff}}(\tilde{\nu})$ was determined by introducing a known amount of the calibration gas CO_2 ($P = 2$ Torr) into the cavity. The reflectivities at the center line positions $\tilde{\nu}_c$ of CO_2 are calculated from [15]

$$R(\tilde{\nu}_c) = 1 - \frac{S(\tilde{\nu}_c) N d}{\int_{\text{over line}} \left(\frac{I_0(\tilde{\nu})}{I(\tilde{\nu})} - 1 \right) d\tilde{\nu}} \quad (2)$$

and then interpolated over the spectral range with a second order polynomial. In Eq. (2) N [molecule cm^{-3}] denotes the number density of CO_2 (known to within $\sim 3\%$ error from pressure fluctuations) and S [cm molecule $^{-1}$] the line intensities of CO_2 , (known to within $\sim 10\%$ error) [20]. In order to achieve better signal to noise ratio (SNR) and improved sensitivity an integration time of 120 min was chosen for the measurements. The intensity measurements are known to within $\sim 5\%$ error. The detection limit for absorption coefficient was estimated to 8×10^{-8} cm^{-1} (corresponding to a measurement sensitivity of ~ 200 parts per trillion volumes (pptv) of DX at STP conditions).

DX was used as purchased without further purification (1,4-dioxane (anhydrous)), $\text{C}_4\text{H}_8\text{O}_2$, 99.8% and degassed by numerous freeze–pump–thaw cycles. Anhydrous solvents were not additionally dried and the natural contamination with vestiges of water does not exceed 0.02%, as per the manufacturer's datasheet

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