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## Absorption spectrum of nitrous acid for the $\nu_1+2\nu_3$ band studied with continuous-wave cavity ring-down spectroscopy and theoretical calculations

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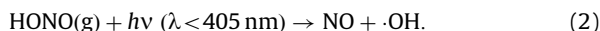
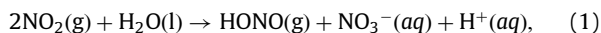
### ABSTRACT

We present the high resolution absorption measurements of gaseous HONO at room temperature using continuous-wave cavity ring-down spectroscopy in the near-infrared region between 6017 and 6067  $\text{cm}^{-1}$  at a resolution of 1 pm ( $0.037 \text{ cm}^{-1}$ ). For the *trans*-HONO isomer an extensive analysis of the  $\nu_1+2\nu_3$  combination band  $6045.8089 \text{ cm}^{-1}$  was performed starting from the results of a previous study for the  $1^1$  and  $3^1$  vibrational states [Guilmot J-M, Godefroid M, Herman M. Rovibrational parameters for *trans*-nitrous acid. J Mol Spectrosc 1993;160:387–400]. The present combination band is perturbed because of the existence of several dark states of HONO which could not be identified unambiguously. The rotational constants achieved for the  $1^1 3^2$  state deviate slightly from the values which are predicted from the rotational constants achieved in the previous studies for the  $1^1$  and  $3^1$  vibrational states of *trans*-HONO.

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### 1. Introduction

Nitrous acid (HONO) is an important photochemical precursor of the hydroxyl radical. Nitrogen dioxide, criteria tropospheric pollutant produced from anthropogenic nitric oxide emissions during photochemical smog events, decays via direct solar photolysis and in association with OH during daytime. It is slowly oxidized by ozone at night [1], and hydrolyzed into HONO, the leading precursor of OH at sunrise, via reaction (1) on cloud and fog droplets:



Several spectroscopic studies of HONO were performed to better understand its spectral features and intramolecular dynamics. Nitrous acid is a  $\text{C}_s$ -type planar molecule, and at room temperature, the *trans*-HONO isomer is approximately two times more abundant than the *cis* form [2]. The equilibrium structures of *trans*-HONO, and, to a lesser extent of *cis*-HONO, were determined using experimental methods and *ab initio* calculations ([3–6] and references therein). For the ground vibrational state accurate rotational and centrifugal distortion constants were determined for both *trans*- and *cis*-HONO [7] by combining the results of these far-infrared measurements with microwave experimental data [8]. Nitrous acid has six vibrational modes [9,10] which are listed in Table 1 for the *trans*- and *cis*-isomers of HONO.

Perrin et al. [11] performed high resolution Fourier-transform infrared (FTIR) analysis of the  $\nu_5$  and  $\nu_6$  bands of

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**Table 1**

Vibrational modes and band origins for the *cis*- and *trans*-isomers of nitrous acid.

	Mode		$\nu$ (cm <sup>-1</sup> )	
			<i>cis</i> -HONO	<i>trans</i> -HONO
$\nu_1$	$a'$	O–H stretch	3426.218 <sup>a</sup>	3590.77035 <sup>a</sup>
$\nu_2$	$a'$	N=O stretch	1640.517 <sup>a</sup>	1699.76015 <sup>a</sup>
$\nu_3$	$a'$	OH bend	~1261 <sup>b</sup>	1263.2071 <sup>a</sup>
$\nu_4$	$a'$	O–N stretch	851.9431 <sup>a</sup>	790.11706 <sup>a</sup>
$\nu_5$	$a'$	ONO bend	609.224 <sup>c</sup>	595.62003 <sup>c</sup>
$\nu_6$	$a''$	Torsion	639.74320 <sup>c</sup>	543.87971 <sup>c</sup>

<sup>a</sup> From Guilmot et al. [10,12,14].

<sup>b</sup> From McGraw et al. [9].

<sup>c</sup> From Perrin et al. [11].

*trans*-HONO (at 543 and 595 cm<sup>-1</sup>, respectively) and of the  $\nu_6$  band of *cis*-HONO (at 638.5 cm<sup>-1</sup>), and for both isomers the strong A- and B-type Coriolis interactions linking the {5<sup>1</sup>,6<sup>1</sup>} interacting levels were accounted for during the energy levels calculations.

Using numerous high resolution FTIR spectra measured in the 400–12 000 cm<sup>-1</sup> spectral range, several studies lead to a complete set of rotational and vibrational parameters for the  $\nu_i$  ( $i = 1$ –6) fundamental bands of *trans*-HONO, together with the  $\nu_i$  ( $i = 1, 2, 4, 6$ ) bands of *cis*-HONO [10–14]. As far as the overtones or combination bands are concerned, only the  $2\nu_1$  band of *trans*-HONO located at 7016.789 cm<sup>-1</sup> was investigated in details. [10]. It has to be mentioned that several of these bands are noticeable perturbed. For the first low frequency bands,  $\nu_5$  and  $\nu_6$  [11], the strong A- and B-type Coriolis interactions linking the {5<sup>1</sup>,6<sup>1</sup>} interacting levels were accounted for during the energy levels calculations for both the *trans*- and *cis*-HONO isomers. Unfortunately, for the bands located at higher frequencies, the resonances were not considered because the scheme of resonance is very complicated, and this is due of the existence of numerous low frequency modes (see Table 1). In addition, a vibrational analysis was performed for several overtones or combination bands, which are the  $2\nu_2$ ,  $\nu_1+\nu_4$ ,  $\nu_1+\nu_3$ ,  $\nu_1+2\nu_3$ ,  $\nu_2+\nu_4$ ,  $3\nu_1$  and  $4\nu_1$  bands of *trans*-HONO, located at 3372.10, 4378.30, 4829.64, 6045.81, 10280.5 and 13385 cm<sup>-1</sup> [10,15] and the  $\nu_2+\nu_4$ ,  $2\nu_2$ ,  $\nu_1+\nu_4$ ,  $2\nu_1$  bands of *cis*-HONO located at 2492.95, 3257.97, 4281 and 6664.4 cm<sup>-1</sup>, respectively [14,15]. It has to be mentioned that the proposed vibrational assignments in Refs. [10,14] were validated carefully by band contour simulations for most of the assigned vibrational bands. Indeed, the band shape depends on the vibrational dependence of the rotational constants in the upper vibrational states. Using the results of these investigations, a complete set of rovibrational parameters, including the vibrational dependence of the rotational constants and equilibrium rotational parameters was achieved for *trans*-HONO [10]. For *cis*-HONO, for which only several fundamental bands were investigated in detail, only some of the rovibrational parameters could be determined [14].

Cavity ring-down spectroscopy (CRDS) is one of the sensitive laser spectroscopic absorption techniques, which

have been utilized for high resolution spectroscopy [16]. In the present study, we have analyzed the  $\nu_1+2\nu_3$  band of *trans*-HONO in details using the CRDS technique in the near-infrared region between 6017 and 6067 cm<sup>-1</sup> with a narrow band near-infrared continuous-wave (CW) laser. As mentioned above, the band center of this very weak band has already been identified by Guilmot et al. [10]. However, this band was too weak in FTS spectra to be analyzed in details.

## 2. Experimental

The experimental setup used in the present study is similar to that described in our previous studies [17]. The output laser beam (Santec, TSL-210 V, <1 pm wavelength scan increment resolution, 0.01 cm<sup>-1</sup> line width) was deflected by an acousto-optical modulator (Isomet) and directed into an optical cavity that consisted of two high reflectivity mirrors (Los Gatos Research, Reflectivity >0.9999) with a separation of 60 cm. One of the two mirrors was incorporated in a tube type piezoactuator for cavity length modulation with a rate of about 200 Hz. For measurements at room temperature, the mirrors were set at the ends of the cavity. The mirrors were set inside of the cell as described previously [17]. The transmitted light from the cavity was detected with an InGaAs photodiode (Hamamatsu Photonics, G5851-11) attached by a pre-amplifier (NF, SA220F5). When the transmitted beam reached a threshold level, the deflected beam was switched off by the acousto-optical modulator and the light stored within the cavity started to ring-down. In the presence of an absorbing species, the light intensity within the cavity is given by the expression

$$I(t) = I_0 \exp(-t/\tau) = I_0 \exp(-t/\tau_0 - \sigma Nct), \quad (3)$$

where  $I_0$  and  $I(t)$  are the light intensities at time 0 and  $t$ , respectively,  $\tau$  the cavity ring-down time in the presence of an absorbing species,  $\tau_0$  the cavity ring-down time without the absorber present (typically 2  $\mu$ s), and  $c$  the velocity of light.  $N$  and  $\sigma$  are the concentration and absorption cross section of the absorbing species, respectively. The exponential decay data were digitized with an analog-to-digital converter (National Instruments, model 5122, 100 MHz, 14 bits). Our LabVIEW program averaged the profile of several ring-down wave forms, for which individual ring-down decay curves except for the initial part of the decay were fitted to a single-exponential function. Twenty one ring-down events were averaged for each spectral data point, and typically 12 000 data points were measured in one scan with line resolutions equal to 1 pm, thus, a complete scan took about 200 min.

HONO was produced by introducing a mixture of H<sub>2</sub>O (20 Torr) with O<sub>2</sub> (150 Torr) into a glass bulb, and then NO until the total pressure became 620 Torr, leading to the chemical equilibrium between NO+NO<sub>2</sub>+H<sub>2</sub>O and 2HONO. After reaching a stable concentration under dark conditions, the mixture gas was flowed into the CRDS cavity cell at total pressure 6 Torr. The partial pressure of nitrous acid is estimated to be about 7500 ppm at room temperature using the equilibrium constant at 300 K [18]. In this estimation, other minor equilibrium reactions such as

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