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## High-resolution spectrum of the $v_9$ band and reinvestigation of the $v_8$ band of *cis*-CH<sub>3</sub>ONO $\stackrel{_{\scriptstyle \frown}}{\sim}$

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#### ABSTRACT

The infrared spectrum of methyl nitrite CH<sub>3</sub>ONO has been recorded at a spectral resolution of 0.003 cm<sup>-1</sup> using a Fourier-transform spectrometer Bruker IFS125HR. The  $v_8$  band of the *cis* isomer has been reinvestigated in the 780–880 cm<sup>-1</sup> spectral range to complete the study made by Goss et al. (2004) [3] and to fit the internal rotor splittings. The BELGI-IR program, which enables us to treat an isolated infrared band for asymmetric molecules containing one internal methyl rotor has been used for the analysis and predictions of spectra. Finally 1036 lines (913 A-type and 123 E-type lines for  $I \le 50$  and  $K_a \le 28$ ) have been assigned for the *cis* isomer and fitted with a standard deviation of 0.00047  $\text{cm}^{-1}$ .

Furthermore, for the first time, the v<sub>9</sub> band of *cis*-CH<sub>3</sub>ONO was investigated in the  $540-660 \text{ cm}^{-1}$  spectral range and rather large internal rotation splittings were also observed at higher *I* values. For the  $v_9$  band, the effective approach performed with the BELGI-IR program allowed us to analyze and reproduce 682 lines up to J = 50 and  $K_a = 18$ with a standard deviation of 0.00051 cm<sup>-1</sup>. The multiple vibration-rotation-torsion interactions, which are likely to occur between the excited  $v_9=1$  and  $v_8=1$  states and the torsional manifolds are discussed.

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#### 1. Introduction

Methyl nitrite is produced by biomass burning in the atmosphere and in the processes of photochemical oxidation of volatile organic compounds (VOCs). It is formed in the atmosphere by the reaction of methoxy radical

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 $(CH_3O^{\bullet})$  with nitric oxide radical (NO<sup> $\bullet$ </sup>), but during the day, it is rapidly photolysed and reforms these radicals [1]:  $CH_3ONO + hv(\lambda \le 440 \text{ nm}) \rightarrow CH_3O^{\bullet} + NO^{\bullet}$ 

(1)

Since methoxy and nitric oxide radicals are important intermediates in photochemical air pollution, methyl nitrite can act as a night-time reservoir molecule for the so-called aged-smog phenomenon [2]. However, in contrast to HONO, methyl nitrite has not yet been detected in the atmosphere. Indeed its weak concentrations and its short atmospheric lifetime do not facilitate its detection. On the other hand, no line-list or absorption cross-sections of CH<sub>3</sub>ONO are available in the infrared (IR) region, to our knowledge. Only one previous high resolution study of cis-CH<sub>3</sub>ONO in the infrared has been published so far by Goss et al. in 2004 [3]. Very recently, the ground and first torsional states of the cis-isomer of CH<sub>3</sub>ONO

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were reinvestigated quite completely for  $J \le 65$  and  $K_a \le 48$  in the microwave, millimeter-wave and far-infrared range [4]. Microwave (MW) investigations of the *trans*-isomer, however, are so far limited to a few very low *J* transitions [5].

Methyl nitrite exists as a mixture of a cis- and a transisomers in a ratio of vapor pressures  $p_{\text{trans}}/p_{\text{cis}}$  of about 0.59 at 298 K [6], so that absorption bands of roughly similar magnitude for both isomers are observed in the room temperature gas phase IR and MW spectra. From the temperature dependence of intensities of rotational transitions in the MW spectrum [7], from infrared bands in the gas phase [8], or from cold matrix environments [9]. the cis-isomer was determined to be more stable than the *trans*-isomer by about 300 cm<sup>-1</sup>. The *cis*-isomer is a rather asymmetric top ( $\kappa$ =-0.75) with a very high torsional potential barrier hindering the internal rotation of the methyl group  $(V_3 = 726.58 \ (16) \ \text{cm}^{-1})$  [4]. The presence of this high torsional barrier leads to rather small splittings of the rotational A and E energy levels, which are observed in the ground and excited torsional state  $v_t = 0$  and 1 of the *cis*-CH<sub>3</sub>ONO. The *trans*-isomer, on the other hand, is a near-prolate molecule with  $\kappa = -0.98$ , and has a much lower value for the barrier to internal rotation ( $V_3 \approx 10 \text{ cm}^{-1}$ ) leading to large internal splittings that cannot be described by high-barrier internal rotation approximations [5] and are much more difficult to model. As a consequence of the presence of the two isomers and the existence of the large-amplitude internal rotation motion, the infrared spectrum of methyl nitrite is thus very dense and its analysis is therefore expected to be rather complicated.

In 2004, Goss et al. [3] have reported for the first time a high resolution analysis of the  $v_8$  (A') band corresponding to the NO stretching mode of the *cis*-isomer of CH<sub>3</sub>ONO. The band center lies at 841.29 cm<sup>-1</sup>, in a good spectral range for an atmospheric detection, and presents an intense and narrow Q-branch. The  $v_9$  band (A') which corresponds to the bending of the ONO bond, lies around 628 cm<sup>-1</sup> and is also of potential interest for atmospheric detection because the spectral features of the two isomers are quite well separated.

In our previous work on the fundamental state of the *cis*-CH<sub>3</sub>ONO [4], we determined the value of the internal potential barrier height ( $V_3$ ) to be 726.58 (16) cm<sup>-1</sup>. This relatively high barrier leads to internal rotation splittings between A and E type transitions whose magnitude depends on the *J* and  $K_a$  values. For the 1<sub>0,1</sub>-O<sub>0,0</sub> transition for example this A–E splitting in the ground torsional state of the *cis*-CH<sub>3</sub>ONO is about 40 kHz and about 8 MHz for the 40<sub>15,25</sub>-39<sub>15,24</sub> transition.

In the absence of any perturbation with other vibrational states, similar values for the potential barrier hindering internal rotation in the excited vibrational  $v_8=1$  and  $v_9=1$  states are expected if those states are indeed "isolated". We would thus expect that the A–E internal rotation splitting will not be observable or barely observable in the infrared spectrum (at least for the  $v_t'=0 \leftarrow v_t''=0$  cold band), at the resolution reported by Goss et al. (i.e. 0.0015 cm<sup>-1</sup> or 45 MHz). Surprisingly, those authors did observe about 150 larger internal rotation splittings in their spectrum of the  $v_8$  band [3]. These splittings occur for transitions characterized by quantum numbers between  $4 \le l \le 47$  and  $0 \le K_a \le 13$ and present a magnitude of  $0.001-0.005 \text{ cm}^{-1}$ (30-150 MHz). In their fit Goss et al. decided to exclude all the lines showing internal rotation splittings and used a Watson-type Hamiltonian to analyze and reproduce the rest of the data. Their study includes 634 transitions (all belonging to a-type transitions) reproduced with a standard deviation of 0.00044 cm<sup>-1</sup> [3]. When they tried to include the internal rotation splittings, Goss et al. also could not progress in the analysis when they tried to include only the frequency of the A lines (which they assumed was the higher frequency component for each doublet). They also tried to fit the frequency of the center of gravity for these internal rotation split transitions as 1/3 ( $v_A + 2v_F$ ), but this treatment substantially degraded the quality of the fit. So in their prediction a single line is generated between the two components A and E as the result of the treatment by a Watson-type Hamiltonian.

As mentioned also in Ref. [3], we believe that the presence of such internal rotor splittings, amplified compared to those of the fundamental vibrational state, is indicative of perturbations between different vibration–rotation–torsion states close in energy. This phenomenon has already been observed for other molecules containing an internal rotor like acetaldehyde  $CH_3CHO$  [10–14] or methanol  $CH_3OH$  [15–19], which have been extensively studied in the infrared spectral range. So far however no global theoretical treatment involving vibration–rotation–torsion interactions allowed us to reproduce the internal rotation splittings in asymmetric rotor molecules within experimental accuracy in this spectral range.

It should be noticed that a number of studies of smallamplitude vibrations embedded in the torsional bath of symmetric-top molecules have been published, for CH<sub>3</sub>CD<sub>3</sub> [20], CH<sub>3</sub>CF<sub>3</sub> [21], CH<sub>3</sub>SiH<sub>3</sub> [22], CH<sub>3</sub>SiD<sub>3</sub> [23] and CH<sub>3</sub>CH<sub>3</sub> [24] for example. These studies have achieved least-square fits of better quality than for asymmetric rotors. Some of the reasons, as pointed out in Ref. [14] for this are that (i) CH<sub>3</sub>XY<sub>3</sub> molecules are symmetric tops by symmetry, so the vibration-rotation interactions destroying the validity of the K quantum number are much smaller than in an asymmetric rotor like acetaldehyde or methyl nitrite (ii) in CH<sub>3</sub>XY<sub>3</sub> molecules the direction of the methyl top axis coincides with the direction of the symmetric top axis, and so there is no competition between internal rotation and overall rotation for the choice of the K-quantization axis (z-axis) and this competition is often causing "labeling" problems for asymmetric top molecules and making the assignments difficult (iii) CH<sub>3</sub>XY<sub>3</sub> molecules have permutation-inversion groups ( $G_{18}$  for  $XY_3 \neq CH_3$  and  $G_{36}$  for  $XY_3 = CH_3$ ) larger than the G<sub>6</sub> group appropriate for CH<sub>3</sub>ONO. The selection rules for the CH<sub>3</sub>XY<sub>3</sub> symmetric-top molecules are thus much stricter for allowed perturbations, and thus in general they have fewer perturbations than asymmetric internal rotors.

In the present paper, we have decided to test the global "Rho-Axis-Method (RAM)" approach implemented in the BELGI code [25,26], which involves a whole set

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