



Reinvestigation of the microwave and new high resolution far-infrared spectra of *cis*-methyl nitrite, CH₃ONO: Rotational study of the two first torsional states

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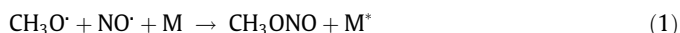
ABSTRACT

The first far-infrared high resolution absorption measurement of the *cis*-methyl nitrite molecule has been recorded in the range 15–400 cm⁻¹ using the synchrotron AILES beamline radiation at SOLEIL with a resolution of 0.0011 cm⁻¹. First assignments for the pure rotational transitions (15–65 cm⁻¹) belonging to the ground $v_t (=v_{15}) = 0$ and first $v_t = 1$ excited torsional state are based on measurements from previous studies performed in the 13–40 GHz spectral range, as well as on new millimeter-wave measurements performed at Lille in the spectral range 75–465 GHz. A few measurements and remeasurements in the 1.8–13 GHz were also performed using the chirped FT-MW spectrometer located in North Texas. The pure rotational transitions in the far-infrared and in the microwave spectral range belonging to the two first torsional states have been globally fitted using the RAM (“Rho Axis Method”) dealing with the rotation–torsion Hamiltonian and implemented in the BELGI code. A total of 708 and 713 microwave transitions ($6 \leq J \leq 40$, $K_a^{max} \leq 23$) belonging to the ground torsional state $v_t = 0$ and 1 have been fitted with root-mean-square (rms) deviations of 37.4 kHz and 32.3 kHz respectively, and 3170 pure rotational transitions in the far-infrared range ($12 \leq J^{max} \leq 65$, $0 \leq K_a^{max} \leq 48$) belonging to $v_t = 0$ and 1 have been fitted with a rms deviation of 0.00017 cm⁻¹, using 35 parameters. Since in the far-infrared spectral range, the A–E internal rotor splittings have not been observed for the transitions belonging to the torsional ground $v_t = 0$ state of the *cis*-methyl nitrite species, another fit was performed on those lines, using a Watson type Hamiltonian for comparison.

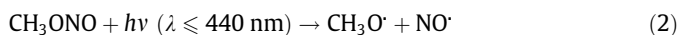
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1. Introduction

Methyl nitrite (CH₃ONO) is an important species in atmospheric chemistry where it is produced by biomass burning and in the processes of photochemical oxidation of volatile organic compounds (VOCs). It is formed in the atmosphere by the reaction of methoxy radicals (CH₃O[•]) with nitric oxide radical (NO[•]):



During the day, its rapid photolysis reforms these radicals [1]:



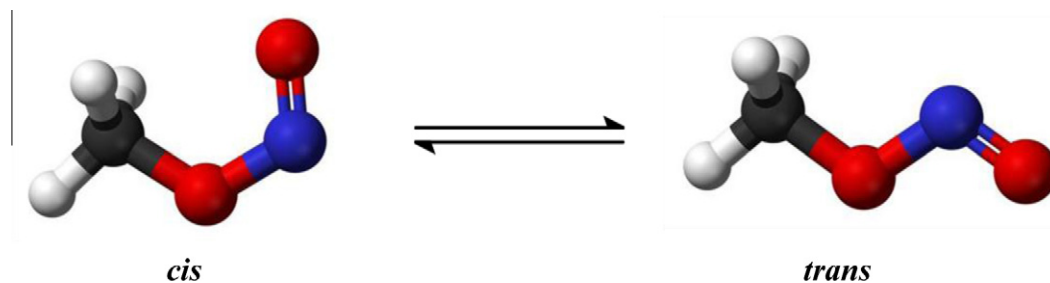
Since the methoxy radical and the nitric oxide radical are important intermediates in photochemical air pollution, methyl nitrite can act as a night-time reservoir molecule for the so-called aged-smog phenomenon [2].

The methyl nitrite ultraviolet absorption spectrum, its photo-fragmentation products and their internal energy distribution have been extensively studied in the laboratory (e.g. [3–6]), but only scarce information is available in the high resolution infrared and microwave regions.

Methyl nitrite exists as a mixture of *cis* and *trans* rotational isomers as shown hereafter:

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^1H MR measurements of the *cis* \rightleftharpoons *trans* equilibrium determined the thermodynamic parameters to be $\Delta H_{\text{trans-cis}} = 4.18$ kJ/mol and $\Delta S_{\text{trans-cis}} = 9.62$ J/mol K [7]. This results in a ratio of pressure vapors $p_{\text{trans}}/p_{\text{cis}} = 0.59$ at 298 K and thus absorption bands of roughly similar magnitude for both isomers are observed in the room temperature gas phase IR and MW spectra. Similarly, from the temperature dependences of relative intensities of rotational transitions in the MW spectrum [8], from infrared band in the gas phase [9], and from cold matrix environments [10], the *cis* isomer was determined to be more stable than the *trans* isomer by 3.76, 3.13 and 3.5 kJ mol $^{-1}$ (i.e. an average value of 298 cm $^{-1}$) respectively. *Ab-initio* calculation also confirmed that the *cis*-methyl nitrite is more stable than the *trans* isomer with a barrier to the *cis*-*trans* isomerisation of 3786 cm $^{-1}$ [11].

Besides its thermodynamic and kinetic interests, the structural parameters of this compound are also very interesting. The microwave spectrum of methyl nitrite was first investigated in 1968 by Gwinn et al. [12] and they reported the values of dipole moments ($\mu_a = 1.66$ D and $\mu_b = 1.20$ D for the *cis* isomer). A complete r_s structure of both isomers was then calculated by Turner et al. [13] who used microwave data of nine isotopic species for the *cis*-methyl nitrite and of six isotopic species for the *trans*-methyl nitrite. Their assignments for the normal species cover up transitions in the 12–40 GHz spectral range up to $J = 6$ and up to $J = 4$ for the *cis* and *trans* isomers respectively. Turner et al. also determined the internal rotation barriers of the methyl group for both isomers. They confirmed that 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 ($V_3 = 2090$ cal/mol = 731 cm $^{-1}$) leading to small splittings of the rotational energy levels (called A and E levels). For the *trans* isomer which is a near-prolate rotor with $\kappa = -0.98$, they reported a much lower value for the barrier to internal rotation ($V_3 = 29$ cal/mol = 10 cm $^{-1}$) than that previously reported by Gwinn et al. [12]. For the *trans*-methyl nitrite isomer, the low internal rotation barrier leads to much larger internal rotation splittings than for the *cis* one, and these splittings cannot be analyzed using the traditional effective Hamiltonians valid for rigid or semi-rigid asymmetric top molecules only.

In 1980, Ghosh et al. [8] extended the measurements for the *cis* isomer to the 12–40 GHz spectral range. They reported assignments for 42 A and 27 E-type transitions up to $J = 20$ belonging to the fundamental torsional state $\nu_t (= \nu_{15}) = 0$. For these ground state transitions, various components arising from quadrupole moment of the nitrogen nucleus were observed. Quadrupole coupling constants were determined more precisely than those provided by Gwinn et al. ($\chi_{aa} = 1.443(81)$ MHz, $\chi_{bb} = -4.874(76)$ MHz, $\chi_{cc} = 3.431(80)$ MHz), allowing the authors to derive hypothetical unsplit line centers for all measured rotational transitions. Thirty-one hypothetical centers frequencies of the A species up to $J = 20$ were finally included in their fit to determine a set of rotational and centrifugal distortion constants with a standard deviation of 110 kHz, much larger than the measurement accuracy estimated by the authors to be 20 kHz for isolated lines. Gosh

et al. also investigated vibrationally excited states. Thirteen A and E-type transitions in the first torsional excited state $\nu_t = 1$, and twelve A and E-type transitions in the second excited methyl torsional states $\nu_t = 2$ were assigned up to $J = 3$. The internal rotation parameters of the methyl group in the *cis*-methyl nitrite were adjusted using the high barrier approximation and the so-called “internal axis” or Woods method [14]. In this method, each torsional state $\nu_t = 0, \nu_t = 1, \dots$, are treated separately with separated least squares fits for each of the ground and excited states. For the ground state, only the barrier, V_3 , was varied whereas the moment of inertia of the methyl top, I_y , and the direction cosines of the methyl top relative to the principal a axis were kept constant at the values reported from the structure determination [13].

Beside the internal rotation parameters, the centrifugal distortion constants were determined by a fit of the A lines for the torsional ground state using a Hamiltonian for asymmetric rotor according to the Watson asymmetric A reduction [8].

Even for the ground torsional state, the observed-calculated values obtained by Ghosh et al. were rather large, reaching 0.6 MHz for high J values, probably because the Woods code did not allow them to float higher order terms in the Hamiltonian. In addition to the methyl group excited torsional states, Ghosh et al. also assigned a small number of transitions (up to $J = 3$) belonging to the first and second excited state of the NO torsion ν_{14} mode of the *cis*-CH $_3$ ONO (located at 269(16) cm $^{-1}$ following their low-resolution infrared study [15]) and belonging to the ground state of the CON deformation ν_{10} mode (located around 346 cm $^{-1}$ [15]) but for those low J transitions, the A–E internal rotor splittings were not resolved. Finally still in this paper, Ghosh et al. also provided the relative intensity measurements for three lines of the *cis* isomer and two for the *trans* one, leading to the determination of the energy difference between the *trans* and *cis* isomers to be 314 cm $^{-1}$, close to the value found by Gwinn et al. [12] (275 cm $^{-1}$).

In the infrared and far-infrared spectral range several low resolution studies were performed [15–20]. In 1981, Ghosh and Günthard assigned all the fundamental modes of both the *cis* and *trans* isomers between 300 and 4000 cm $^{-1}$. Using hot band progressions they determined that the ν_{14} mode should lie around 269(16) cm $^{-1}$ and the ν_{15} mode ($\nu_t = 1-0$) should lie around 147(7) cm $^{-1}$ for the *cis* species [15]. These values are quite different compared to the values estimated from the relative peak intensity measurements in the microwave analysis to be 210(31) cm $^{-1}$ for ν_{14} [8] and 170 cm $^{-1}$ for the torsional $\nu_t = 1-0$ band [13] respectively. The values for the *trans*-methyl nitrite are even more uncertain because the highly complicated low-lying (nearly-free) methyl torsion mode makes the simulation of the infrared band contours really difficult (or impossible) to realize. Turner et al. [13] estimated the value for the ν_{14} band center of the *trans* isomer to be around 230 ± 30 cm $^{-1}$, but no value for the torsional ν_t band center of this isomer was given. The far-infrared region from 10 to 300 cm $^{-1}$ was recorded at low resolution in 1982 [17], but the *trans*-methyl nitrite presents such a difficult spectrum to analyze due to its very low internal rotation barrier that no reliable assignments were

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