

# The structure and molecular parameters of camphene determined by Fourier transform microwave spectroscopy and quantum chemical calculations



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## ABSTRACT

Camphene ( $C_{10}H_{16}$ ) is a bicyclic monoterpene of atmospheric interest. The structure of the unique stable conformer was optimized using density functional theory and *ab initio* calculations. The rotational spectrum of camphene was recorded in a supersonic jet expansion with a Fourier transform microwave spectrometer over the range 2–20 GHz. Signals from the parent species and from the ten  $^{13}C$  isotopomers were observed in natural abundance. The rotational and centrifugal distortion parameters were fitted to a Watson's Hamiltonian in the A-reduction. Complex line-shapes resulting from a magnetic interaction associated with the pairs of hydrogen nuclei in the methylene groups was observed and modeled. The rotational constants were used together with equilibrium structure to determine the  $r_0$  and the  $r_m^{(1)}$  gas-phase geometries of the carbon skeleton. The present work provides the first spectroscopic characterization of camphene in the gas phase.

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## 1. Introduction

The emission of biogenic volatile organic compounds (BVOCs) from plants has strong relevance for plant physiology, plant ecology and atmospheric chemistry [1]. Camphene ( $C_{10}H_{16}$ ), also named 2,2-dimethyl-3-methylenebicyclo[2.2.1]heptane, is one of several BVOCs emitted in the atmosphere by natural sources [2]. It is one of many products of common plants from Mediterranean regions affected by forest fires [3]. It is also one of the major monoterpenes emitted from *Pinus koraiensis* [4] and it has been identified as one of various monoterpenes emitted from scots pine stumps tree [5].

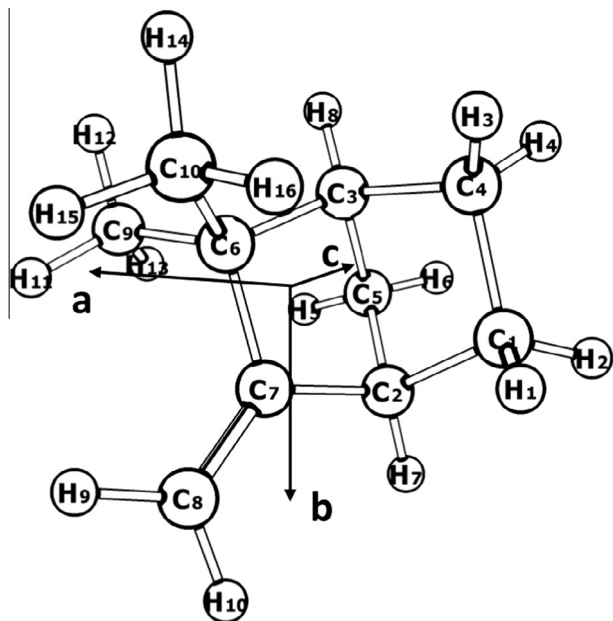
BVOCs such as isoprene ( $C_5H_8$ ) and monoterpenes ( $C_{10}H_{16}$ , i.e.  $\alpha$ -pinene,  $\beta$ -pinene, camphene, and sabinene), and their oxidation products may form atmospheric aerosols, which are liquid or solid particles suspended in air. Aerosols play a key role in many environmental processes. Indeed they affect the Earth's radiation balance by scattering the solar radiation and by acting as cloud condensation nuclei. They also participate in heterogeneous chemical reactions in the atmosphere. They finally have considerable effects on health [6,7].

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Regarding physical chemistry, the ozone initiated chemistry is generally believed to lead to the formation of Criegee intermediates. Ozonolysis reactions of bicyclic monoterpenes is a current subject of investigation, using quantum chemistry calculations. Recently this reaction mechanism was theoretically investigated by Oliveira and Bauerfeldt on four monoterpenes typically emitted into the atmosphere:  $\alpha$ -pinene,  $\beta$ -pinene, camphene, and sabinene [8]. The first step of the Criegee mechanism is the cycloaddition of ozone to the double bond of these unsaturated species, and it is believed to be rate determining in the complete mechanism [8]. A good knowledge of the structure of these monoterpenes is a pre-requisite to model their kinetics.

In the present work, we have studied camphene in the gas phase. The spectroscopic information available on gas phase  $C_{10}H_{16}$  monoterpenes are rather scarce [9]. Meanwhile the rotational spectrum of camphor ( $C_{10}H_{16}O$ ), which is one oxidation product of camphene, has been studied in detail by Kisiel and co-workers by rotational spectroscopy and quantum calculations, allowing the determination of precise structural parameters [10]. In the present work, we have investigated the structural properties of camphene, using the same approach. Camphene is a bicyclic hydrocarbon which is characterized by the proximity of the two methyl groups near the carbon-carbon double bond ( $C_7C_8$ ), as depicted in Fig. 1. It is a rigid cage and as such it is presenting only one stable conformer. At first the rotational spectrum was predicted from the structure optimized using density functional



**Fig. 1.** Equilibrium geometry of camphene, calculated at the MP2/aug-cc-pVTZ level, and the numbering of all atoms. The principal axis system is also presented.

theory (DFT) and *ab initio* calculations. A supersonic expansion coupled to a Fourier-transform microwave (FTMW) spectrometer was used to observe the rotational spectrum of the main species as well as of all the ten  $^{13}\text{C}$  isotopomers in natural abundance, despite the small dipole moment of camphene. In addition a complex line-shape was observed on several lines. It was associated with the spin-spin magnetic interaction between hydrogen nuclei, and modeled accurately by considering only the hydrogen pairs of the three methylene groups. The molecular parameters were obtained by fitting the observed transitions to a standard Watson Hamiltonian. Structural parameters have been obtained, with the support of quantum calculations.

## 2. Quantum chemical calculations

The quantum chemical calculations were performed using the Gaussian 09, Rev. D.01, software package (G09) [11]. The structure of camphene (Fig. 1) was optimized using *ab initio* calculations at the MP2 level of the theory (Møller–Plesset second order perturbation theory) [12], with the Dunning’s correlation consistent triple-zeta aug-cc-pVTZ basis set with added polarization functions [13] in order to obtain an equilibrium structure which could be compared with the experimental structural parameters.

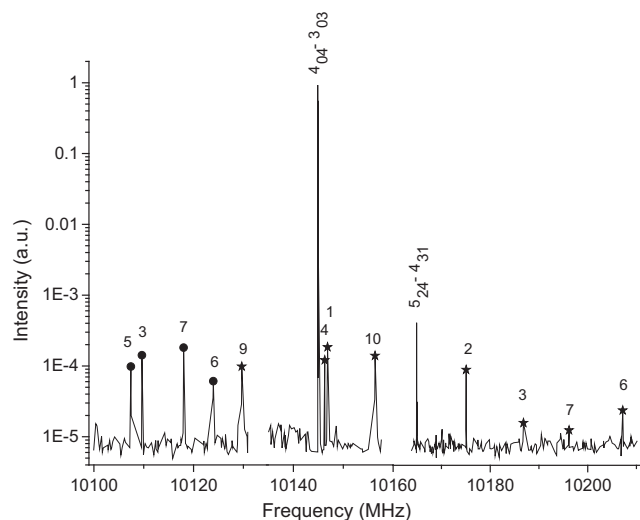
The molecular parameters and the harmonic force field have also been evaluated using the B3LYP density functional [14,15], with the Pople split-valence triple-zeta basis set augmented with diffuse and polarization functions on all atoms (the 6-311+G (2df,p) basis set) [16]. The principal rotational constants ( $A$ ,  $B$ ,  $C$ ), and the quartic centrifugal distortion parameters ( $\Delta_J$ ,  $\Delta_{JK}$ ,  $\Delta_K$ ,  $\delta_J$ ,  $\delta_K$ ) have been calculated for the main species, as well as the electric dipole moment components. It turned out that camphene is a prolate asymmetric rotor with a Ray’s value of  $\kappa = -0.415$ . The calculated dipole moment value is rather small (0.7 D), which is not surprising since camphene is a hydrocarbon, and a- and b-type transitions with weaker c-type transitions are expected.

The two methyl groups are attached to the same carbon atom ( $\text{C}_6$ ). Therefore the steric hindrance between the two groups should limit internal rotations or present a sufficiently high barrier that no internal rotation splitting should be observed. No further calcula-

tion was found useful, regarding the experimental observed signals in the centimeter-wave range.

## 3. Experimental details

The pure rotational spectrum (2–20 GHz) of camphene was recorded using the Fourier transform microwave spectrometer coupled to a molecular beam (MB-FTMW) in Lille [17]. Camphene ( $\geq 96\%$  purity) was purchased from Sigma–Aldrich and used without further purification. The solid camphene (which has a melting point around 48–52 °C) was heated at 343 K in a reservoir in order to be vaporized. Neon at a stagnation pressure of 3 bars was used as carrier gas and mixed with camphene. The mixture was introduced into a Fabry–Pérot cavity through a 1 mm diameter pinhole with a pulsed nozzle at a repetition rate of 1.5 Hz. Microwave power pulses of 2  $\mu\text{s}$  duration were used to polarize the molecules which were injected co-axially to the optical axis of the cavity. The Free-Induction Decay (FID) signal was detected and digitized at a repetition rate of 120 MHz. FID signals were accumulated in order to obtain a good S/N ratio. About thirty and a few hundred FID signals were accumulated in the low resolution scan mode and in the high resolution measurement mode, respectively. After a fast Fourier transformation of the time domain signals, lines were observed as Doppler doublets. The central frequency of each line was determined by averaging the frequencies of the two Doppler components. The spectral resolution is dependent on the chosen number of data points. In our case, the uncertainty of the measurements is estimated to be better than 1 kHz for the parent molecules signals (0.92 kHz high resolution mode) and better than 2 kHz for the  $^{13}\text{C}$  isotopomers (1.8 kHz high resolution mode). By optimizing the temperature in order to minimize the decomposition of camphene, spectra were left with strong signals associated with the parent molecule, and weak signals associated with the isotopomers ( $^{13}\text{C}$ ). An optimum signal was obtained at a reservoir temperature of 343 K. A portion of the rotational spectrum, in the scan mode, is shown in Fig. 2. As explained hereafter, more than one hundred R lines of the parent species were measured, in the high resolution mode, up to  $J = 8$  and  $K_a = 5$  (47 a-type, 48 b-type and 19 c-type transitions were fitted). The quantum number values



**Fig. 2.** A portion of the spectrum of camphene showing pure rotational lines associated with the main species  $^{12}\text{C}_{10}\text{H}_{16}$ . Transitions are identified by the  $J_{K_aK_c}$  values. The rotational lines of singly substituted  $^{13}\text{C}$  isotopomers are also shown, with the identity of the substituted  $^{13}\text{C}$  atom in the molecule (1–10), for the 4<sub>04</sub>-3<sub>03</sub> (black circles) and 4<sub>14</sub>-3<sub>03</sub> (black asterisks) lines. The low resolution scan mode of the MB-FTMW spectrometer was used. Intensity is in arbitrary unit.

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