



Microwave, infrared, and Raman spectra, r_0 structural parameters, conformational stability, and vibrational assignment of allyl thiol

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ABSTRACT

FT-microwave spectrum of allyl thiol, $\text{H}_2\text{C}=\text{CHCH}_2\text{SH}$, has been recorded, and 19 transitions have been assigned for the most abundant isotopologue of Gg conformer, and the rotational constants have been determined; $A = 20,041.439$ (4), $B = 2795.830$ (1), $C = 2701.084$ (1). From the determined microwave rotational constants and *ab initio* MP2(full)/6-311+G(d,p) predicted structural values, adjusted r_0 parameters are reported with distances (Å): $r_{\text{C}=\text{C}} = 1.343$ (3), $r_{\text{C}-\text{C}} = 1.496$ (3), $r_{\text{C}-\text{S}} = 1.827$ (3) and angles ($^\circ$) $\angle_{\text{CCC}} = 123.4$ (5), $\angle_{\text{CCS}} = 112.5$ (5), and $\tau_{\text{C}_\gamma\text{C}_\beta\text{C}_\alpha\text{S}} = 118.7$ (5). Variable temperature (-55 to -100 °C) infrared spectra (3600 – 400 cm^{-1}) were recorded of allyl thiol in liquid xenon and the Gg conformer was determined to be the most stable form. The enthalpy differences relative to the Gg form are for Cg 120 ± 9 cm^{-1} (1.44 ± 0.11 kJ/mol), for Gg' 337 ± 34 cm^{-1} (4.03 ± 0.41 kJ/mol), and for Gt 360 ± 36 cm^{-1} (4.31 ± 0.43 kJ/mol). The relative amounts present at ambient temperature are Gg 52 \pm 1%, Cg 29 \pm 1%, Gg' 10 \pm 1%, and Gt 9 \pm 1%. The conformational stabilities have been predicted from *ab initio* calculations with many basis sets up to aug-cc-pVTZ and the predicted stabilities are in agreement with the experimentally determined order. Vibrational assignments are reported with support by *ab initio* predictions and results are discussed.

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1. Introduction

Mono-substitution at the 3-position of propene, i.e. substituted allyl molecules, results in *cis* and *gauche* conformers where there has been considerable controversy concerning which conformer is the more stable rotamer. For example where the substitution is a methyl group (1-butene), the vibrational data clearly indicates that the more stable form is the *cis* conformer with an enthalpy difference of 64 ± 10 cm^{-1} (0.76 ± 0.12 kJ/mol), from variable temperature infrared spectra of rare gas solutions [1]. However, from the analysis of electron diffraction data, it was concluded [2], that the *gauche* conformer was the more stable form. Also, we have found that *ab initio* calculations may not give the correct conformer stability. For example *ab initio* calculations [3], at the MP2 level with a variety of basis sets with diffuse functions predict the *gauche* conformer to be the more stable form of 3-fluoropropene

(allyl fluoride), $\text{CH}_2=\text{CHCH}_2\text{F}$, whereas the experimental results [4,5] clearly show the *cis* conformer to be the more stable rotamer.

When the substituent is an asymmetric rotor such as an OH, SH, NH_2 or PH_2 group there is the possibility of five different stable conformers with *cis* and *gauche* conformations around the C–C bond and *trans* and *gauche* conformations around the C–O (S, N, P) bond (Fig. 1). Only two of the five possible conformations of allyl alcohol (2-propene-1-ol) have been identified from microwave studies [6–9]. The conformers are designated according to the relative position of the alcohol group (C = *cis* or G = *gauche*) to the double bond (rotation around the C–C bond) and the second one (t = *trans*, g = *gauche*, g' = *gauche'*) to the relative position of the OH rotor, i.e. rotation around the O–C bond. In two earlier microwave studies [6,8] only assignments were made for the *gauche*–*gauche* (Gg) conformer (or –ac, sc) but many lines were observed for a second form. In the most recent microwave study [9] lines which had been observed were assigned for the second conformer to be the *cis*–*gauche* (Cg) form. It was estimated that the two forms had nearly the same energy and these investigators planned to obtain more details on the conformational energies from rotational spectra. To the best of our knowledge such studies have not been reported.

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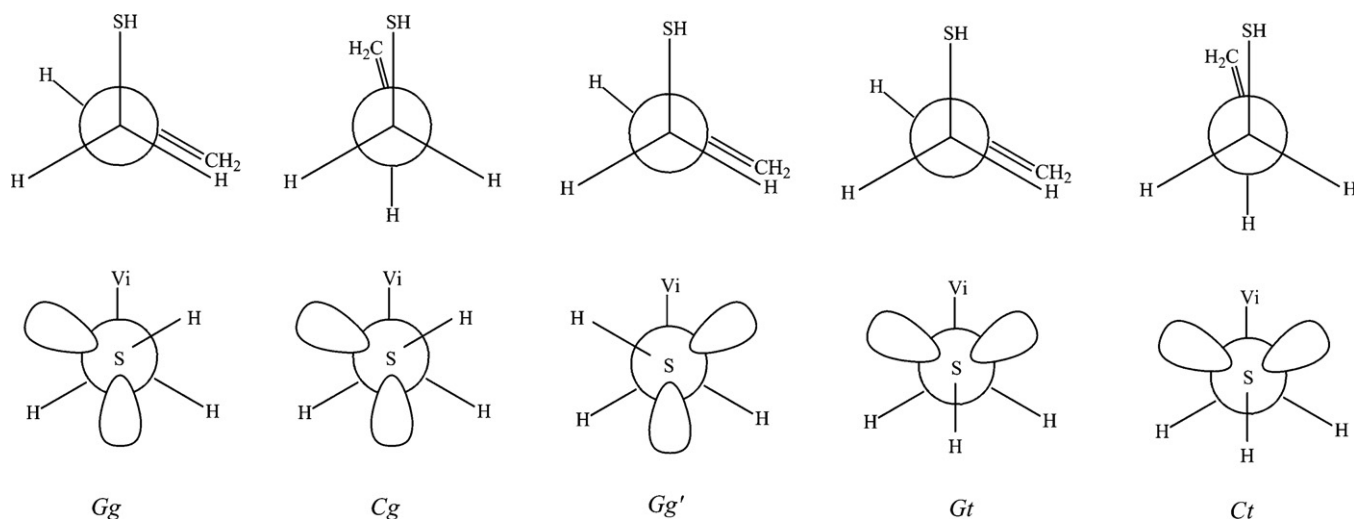


Fig. 1. Possible stable conformers of allyl thiol.

However from an earlier electron diffraction investigation [10] the authors reported the concentrations to be $57 \pm 6\%$ Cg and 43% Gg forms.

Since there was considerable uncertainty which of the two identified conformers of allyl alcohol was the more stable species as well as little scientific information on the other three possible conformers, we [11] carried out variable temperature (-55 to -145°C) studies of the infrared spectra (4000 – 50 cm^{-1}) of the alcohol dissolved in liquid krypton and/or liquid xenon. From these data four of the five possible stable conformers were identified and their relative stabilities determined. The enthalpy differences have been determined between the most stable Gg conformer and the second most stable rotamer, Cg, to be $135 \pm 14\text{ cm}^{-1}$ ($1.62 \pm 0.1\text{ kJ/mol}$), and the third most stable conformer is Ct $260 \pm 46\text{ cm}^{-1}$ ($3.11 \pm 0.6\text{ kJ/mol}$), with the fourth most stable conformer Gt $337 \pm 75\text{ cm}^{-1}$ ($4.03 \pm 0.9\text{ kJ/mol}$). This experimentally determined order is consistent with the order of stability predicted by *ab initio* calculations $Gg > Cg > Ct > Gt > Gg'$. No evidence was obtained for the fifth conformer Gg' which is predicted by most of the *ab initio* calculations to be less stable by an enthalpy difference of more than 500 cm^{-1} than the Gg form. The percentage of each conformer at ambient temperature was estimated to be Gg ($54 \pm 2\%$), Cg ($28 \pm 2\%$), Ct ($8 \pm 2\%$) and Gt ($11 \pm 3\%$).

As a continuation of these conformational stability studies of mono substituted allyl molecules we have turned our attention to allyl thiol (mercaptan), $\text{H}_2\text{C}=\text{CHCH}_2\text{SH}$, where again five possible conformations could be present. We have recorded variable temperature spectra in xenon solutions to identify the less stable conformers not identified by a microwave study [12] as well as the vibration investigation where all of the vibrations were assigned to one conformer [13].

From the microwave study [12] only the dihedral CCCS angle ($124 \pm 3^\circ$) and the gauche angle (50°) of the SH group were obtained from the six determined rotational constants with the remaining parameters estimated from the corresponding parameters of 3-fluoropropene [14] and methyl mercaptan [15]. Although there were a very large number of microwave lines measured the centrifugal distortion constants were not obtained which possibly could make a difference in the values of the rotational constants which are necessary for obtaining all of the structural parameters. Therefore we carried out FT-microwave studies to determine the distortion constants and obtain more accurate structural parameters.

Also to aid in identifying vibrations for additional conformers and to assign fundamentals for the less stable conformers for use in determining the enthalpy differences we have utilized *ab initio* calculations. We obtained the harmonic force fields, infrared intensities, Raman activities, depolarization ratios, and vibrational frequencies from MP2 6-31G(d) *ab initio* calculations with full electron correlation. Additionally MP2(full) *ab initio* and Density Functional Theory (DFT) calculations by the B3LYP method have been carried out with a variety of basis sets up to aug-cc-pVTZ as well as with diffuse functions to predict the conformational stabilities. The results of these spectroscopic, structural, and theoretical studies of allyl thiol are reported herein.

2. Experiments

The sample of allyl thiol was purchased from Alfa Aesar, Shore Road, Heysham, Lancashire, United Kingdom with an estimated purity of 70%. The sample was further purified by a low-temperature, low-pressure fractionation column and the purity of the sample was verified from the infrared spectra of the gas.

Microwave spectra of the sample were recorded by using a “mini-cavity” Fourier-transform microwave spectrometer [16,17] at Kent State University. The Fabry–Perot resonant cavity is established by two 7.5-inch diameter diamond-tip finished aluminum mirrors with a 30.5-cm spherical radius. The Fabry–Perot cavity resides inside a vacuum chamber formed by a 6-way cross and a 15-inch long, 8-inch diameter extension tube. The two cavity mirrors are nominally separated by 30 cm.

The sample was entrained in a 70:30 Ne–He carrier gas mixture at 2 atm and expanded into the cavity to attain 4K using a reservoir nozzle [17] made from a modified Series-9 General Valve. The reservoir nozzle is mounted in a recessed region of the mirror flange, external to the vacuum chamber, and the expansion passes through a 0.182-inch diameter hole into the resonant cavity. The center of the expansion is offset from the center of the mirror by 1 inch.

The sample is irradiated by microwave radiation generated by an Agilent Technologies E8247C PSG CW synthesizer; details of the irradiation and heterodyne detection circuitry can be found in Ref. [18]. The vacuum system can accommodate pulse repetition rates of up to 15 s^{-1} while maintaining a pressure below 10^{-4} Torr, and the instrument can scan 450 MHz in 6 h while averaging 100 shots per scan segment. The frequencies for the measured transitions in the region of 10,500–22,000 MHz are listed in Table 1

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