



Microwave spectra and conformational studies of ethylamine from temperature dependent Raman spectra of xenon solutions and ab initio calculations



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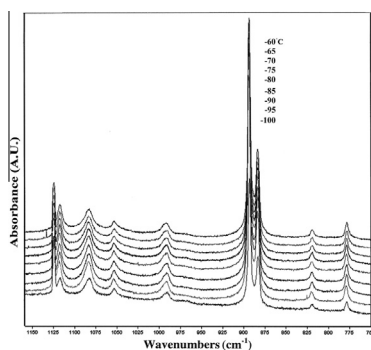
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HIGHLIGHTS

- Vibrational data indicate the presence of two conformers.
- The enthalpy difference going from the trans form to the gauche form is $62 \pm 6 \text{ cm}^{-1}$.
- Structural parameters have been determined for both conformers.
- Ab initio calculations have been performed for both forms.

GRAPHICAL ABSTRACT



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ABSTRACT

FT-microwave spectroscopy was carried out where the trans conformer was identified to be the most stable conformer. Variable temperature (-60 to -100 °C) studies of the Raman spectra (4000 – 50 cm^{-1}) of ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$ dissolved in liquefied xenon have been carried out. From these data both conformers have been identified and their relative stabilities obtained. The enthalpy difference has been determined to be $62 \pm 6 \text{ cm}^{-1}$ ($0.746 \pm 0.072 \text{ kJ mol}^{-1}$) with the trans conformer the more stable form. The percentage of the gauche conformer is estimated to be 60% at ambient temperature. The conformational stabilities have been predicted from ab initio calculations with the Møller–Plesset perturbation method to the second order (MP2(full)) and the fourth order (MP4(SDTQ)) as well as with density functional theory by the B3LYP method by utilizing a variety of basis sets. Vibrational assignments have been made for the observed bands which have been predicted by MP2(full)/6-31G(d) ab initio calculations which includes harmonic force fields, frequencies, infrared intensities, Raman activities and depolarization ratios for both conformers. The results are discussed and compared to the corresponding properties of some similar molecule.

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Introduction

The determination of the conformational stability of amine molecules have provided some interesting challenges for scientists over the years. Of particular interest is the ethylamine molecule, where there have been several studies reported the conformational stabilities. One of the first studies that was reported of ethylamine [1] indicated the presence of both trans and gauche conformers which had not been experimentally determined, but from this study the conformational stability between the two conformers was not reported. From another latter study [2] the gauche conformer was reported as slightly favored by 182 cm^{-1} (0.52 kcal/mol) than the trans form from ab initio predictions. Within a few years, the gauche–trans rotational isomerism of ethylamine in the vapor phase was studied [3] by the analysis of the far infrared spectra of $\text{CH}_3\text{CH}_2\text{ND}_2$ and $\text{CH}_3\text{CD}_2\text{ND}_2$. The gauche form was reported as being more stable than the trans conformer and a difference of 104 cm^{-1} of the potential energy minima was obtained. Another study was reported in 1975 [4] where the predicted energy difference between the potential energy minima of the gauche form and the trans conformation to be 207 cm^{-1} (0.592 kcal/mol) with the trans conformer the more stable form in the Raman spectra of the gas. During the same year an infrared absorption spectra of eight isotopic ethylamine molecules in the vapor phase were studied [5] and a difference of about 230 cm^{-1} was obtained between the potential energy minima of the trans and gauche conformations with the trans form the more stable conformer. Nevertheless after a decade later, an energy difference of both (gauche–trans) conformers has been estimated to be $100 \pm 10\text{ cm}^{-1}$ [6] from the intensity changes of the NH_2 wagging modes observed on changing the nozzle temperature in the matrix formation. From a microwave investigation study [7] the enthalpy difference of $100 \pm 50\text{ cm}^{-1}$ was obtained with the trans form as the more stable conformer. This value is comparable with the energy difference value obtained from the investigation reported in Ref. [6] but it had a much larger uncertainty value. Hamada et al. [8] examined the enthalpy difference between the two conformers by an electron diffraction study where it was reported that the trans form is more stable than the gauche conformer by 107 cm^{-1} (306 cal/mol) with a large uncertainty of 200. The abundance of the trans conformer was reported [8] to be 46(10)%. The most recent study reported on the ethylamine conformational stability investigation [9] was from a Fourier transform infrared spectra of noble gas solution where it was reported that the enthalpy difference was $54 \pm 4\text{ cm}^{-1}$ ($0.65 \pm 0.05\text{ kJ/mol}$) with the trans conformer the more stable form. From the reported studies up to this time, there is still a question of which conformer is the more stable form and what the enthalpy difference is between them. These uncertainties of the more stable form and the value of the enthalpy difference between them as well as the structural parameters of this important molecule provide a very clear reason for again investigate this molecule. Therefore, microwave and conformational stability investigations have been initiated to answer conclusively the questions of the more stable conformer and the enthalpy difference.

In order to obtain a confident determination of the conformational enthalpy differences, an investigation of the Raman spectra ($4000\text{--}50\text{ cm}^{-1}$) of ethylamine, $\text{CH}_3\text{CH}_2\text{NH}_2$ dissolved in liquefied xenon was carried out. Also to aid in identifying vibrations for conformers and to assign fundamentals for the less stable conformer for determining the enthalpy differences ab initio calculations have been utilized. The harmonic force fields, infrared intensities, Raman activities, depolarization ratios, and vibrational frequencies were predicted from MP2(full)/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 energy difference and the conformational stabilities. The results of these microwave, spectroscopic, structural, and theoretical studies of ethylamine are reported herein.

Experimental and theoretical methods

The sample of ethylamine was purchased from Sigma–Aldrich Chemical Co., with stated purity of $\geq 98\%$ and the sample was used without further purifications.

The microwave spectra were recorded by a “mini-cavity” Fourier transform microwave spectrometer [10,11] 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 4 K by using a reservoir nozzle [10] 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 was irradiated by microwave radiation generated by an Agilent Technologies E8247C PSG CW synthesizer. The details of the irradiation and heterodyne detection circuitry can be found in Ref. [11]. 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 Raman spectra ($4000\text{--}50\text{ cm}^{-1}$) of the sample dissolved in liquefied xenon (Fig. 1) at nine different temperatures (-60 to $-100\text{ }^\circ\text{C}$) was recorded on a Trivista 557 spectrometer consisting of a double $f=50\text{ cm}$ monochromator equipped with a 2000 lines mm^{-1} grating, a $f=70\text{ cm}$ spectrograph equipped with a 2400 lines mm^{-1} grating, and a back-illuminated LN₂-cooled PI Acton Spec-10:2 kB/LN 2048 \times 512 pixel CCD detector. For all experiments, the 514.5 nm line of a 2017-Ar S/N 1665 Spectra-Physics argon ion laser was used for Raman excitation, with the power set to 0.8 Watt. Signals related to the plasma lines were removed by using an interference filter. The frequencies were calibrated by using Neon emission lines, and depending on the setup used, are expected to be accurate within 0.4 cm^{-1} . The experimental set-up used to investigate the solutions has been described before [12,13]. A home-built cell for liquids was equipped with four quartz windows at right angles were used to record the spectra. The infrared and Raman bands chosen as fundamentals along with their proposed assignments and depolarization values are listed in Tables 1 and 2, respectively.

The LCAO–MO–SCF restricted Hartree–Fock calculations were performed with the Gaussian-03 program [14] by using Gaussian-type basis functions. The energy minima with respect to nuclear coordinates were obtained by the simultaneous relaxation of all geometric parameters by the gradient method of Pulay [15]. Several basis sets as well as the corresponding ones with diffuse functions were employed with the Møller–Plesset perturbation method [16] to the second order (MP2(full)), as well as with the density functional theory by the B3LYP method. The predicted conformational energy differences are listed in Table 3.

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