



The weak fundamental NH-stretching transition in amines



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ABSTRACT

Absolute intensities of NH-stretching fundamental and overtone transitions of gas phase aniline, methylamine, ethylamine, cyclopropylamine, methylethylamine, diethylamine and pyrrolidine have been measured with long path length conventional absorption spectroscopy. To support the assignments of NH-stretching transitions, transition frequencies and intensities were calculated with the local mode model using *ab initio* calculated local mode parameters and dipole moment functions obtained at the CCSD(T)-F12a/VDZ-F12 level of theory. For aniline, the absolute intensities of the NH-stretching transitions show the typical decrease of approximately an order of magnitude for each successive vibrational excitation. For methylamine, ethylamine, cyclopropylamine, methylethylamine, diethylamine and pyrrolidine, the observed absolute intensities of the fundamental NH-stretching transition is weak and of similar strength or even weaker than the corresponding first overtone transition. Characteristic for the amines with a normal fundamental intensity is a conjugated double bond next to the amine group.

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1. Introduction

The intensities of vibrational XH-stretching ($X = C, N, O$ or S) transitions typically decrease with approximately an order of magnitude for each successive vibrational excitation [1–3]. Exceptions to this general trend have been reported only for a few molecules [4,5] for example the fundamental CH-stretching transition of chloroform [1,6,7]. Previously, a study of absolute intensities of NH-stretching transitions of dimethylamine (DMA) and pyrrole (PY) showed that the fundamental NH-stretching intensity of DMA was weaker than that of the first NH-stretching overtone, whereas the NH-stretching intensity of PY followed the typical trend for intensities [5]. The intensity of a vibrational transition depends on the transition dipole moment. Thus, the dipole moment function along the NH-stretching displacement coordinate was found to explain the weak fundamental NH-stretching transition of DMA [5].

Here, we study a range of amines to investigate whether weak fundamental NH-stretching transitions are more general and associated with any molecular characteristics. We have determined absolute intensities from spectra of $\Delta\nu_{\text{NH}}=1-3$ transitions of gas phase aniline (AN), methylamine (MA), ethylamine (EA), methylethylamine (MEA), diethylamine (DEA) and pyrrolidine (PLD) as well as the $\Delta\nu_{\text{NH}}=1-2$ transitions of gas phase cyclopropylamine (CPA).

All $\Delta\nu_{\text{NH}}=1-3$ transitions were recorded with Fourier-transform infrared (FTIR) spectroscopy. Due to MAs and EAs relative high vapor pressures, absolute intensities of the $\Delta\nu_{\text{NH}}=4-5$ transitions were also obtained with UV/vis/NIR spectroscopy. In addition, the $\Delta\nu_{\text{NH}}=4$ transitions of MA, EA, MEA, DEA and PLD were recorded with intracavity laser photoacoustic spectroscopy. We compare the present measurements with the previous results obtained for PY, DMA and CPA [4,5]. Assignment of the observed NH-stretching transitions is guided by calculated vibrational frequencies from a local mode model with dipole moment functions and local parameters obtained at the CCSD(T)-F12a/VDZ-F12 level of theory. The local mode model has previously been successful in predicting vibrational transitions frequencies and intensities [5,8–10].

2. Theory and Calculations

2.1. Optimization Procedure

Stable conformers of AN, MA, EA, MEA, DEA, PLD and CPA were identified with Spartan'10 [11]. In Spartan'10, conformer searches were run with molecular mechanics and the Merck molecular force field (MMFF) followed by geometry optimizations at the B3LYP/6-31+G(d) level of theory. This approach has been shown to provide relative energies in good agreement with higher level coupled cluster calculations [12].

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The B3LYP [13,14] geometries with abundances > 8% were subsequently re-optimized using the CCSD(T)-F12a [15,16] method and the VDZ-F12 [17] basis set with the geminal exponent set to 0.9. Except for CPA, all CCSD(T)-F12a/VDZ-F12 optimizations were run with Molpro 2010.1 [18]. For CPA, the CCSD(T)-F12a/VDZ-F12 optimization was run with Molpro 2012.1 [19]. Threshold criteria of energy = 1×10^{-7} a.u., gradient = 1×10^{-5} a.u. and step size = 1×10^{-5} a.u. were used in all CCSD(T)-F12a/VDZ-F12 optimizations.

2.2. Local Mode Model

NH-stretching transition frequencies and intensities of MEA, DEA and PLD were calculated with a one-dimensional anharmonic oscillator local mode model [20,21]. In this model, the NH-stretching

transition is considered as isolated, where coupling to the additional molecular vibrations are neglected. This is a fair treatment of the NH-stretching vibration, which has previously been illustrated for DMA where the calculated $\Delta v=1-3$ NH-stretching frequencies and intensities were within 9 cm^{-1} and a factor of 1.5, respectively, of the observed values [5]. The NH-stretching vibration is described by a Morse oscillator with energy levels [22]:

$$\frac{E_v}{hc} = \left(v + \frac{1}{2}\right) \tilde{\omega} - \left(v + \frac{1}{2}\right)^2 \tilde{\omega}x, \quad (1)$$

where the frequency, $\tilde{\omega}$, and the anharmonicity, $\tilde{\omega}x$, are determined from the second, third and fourth order derivatives of a

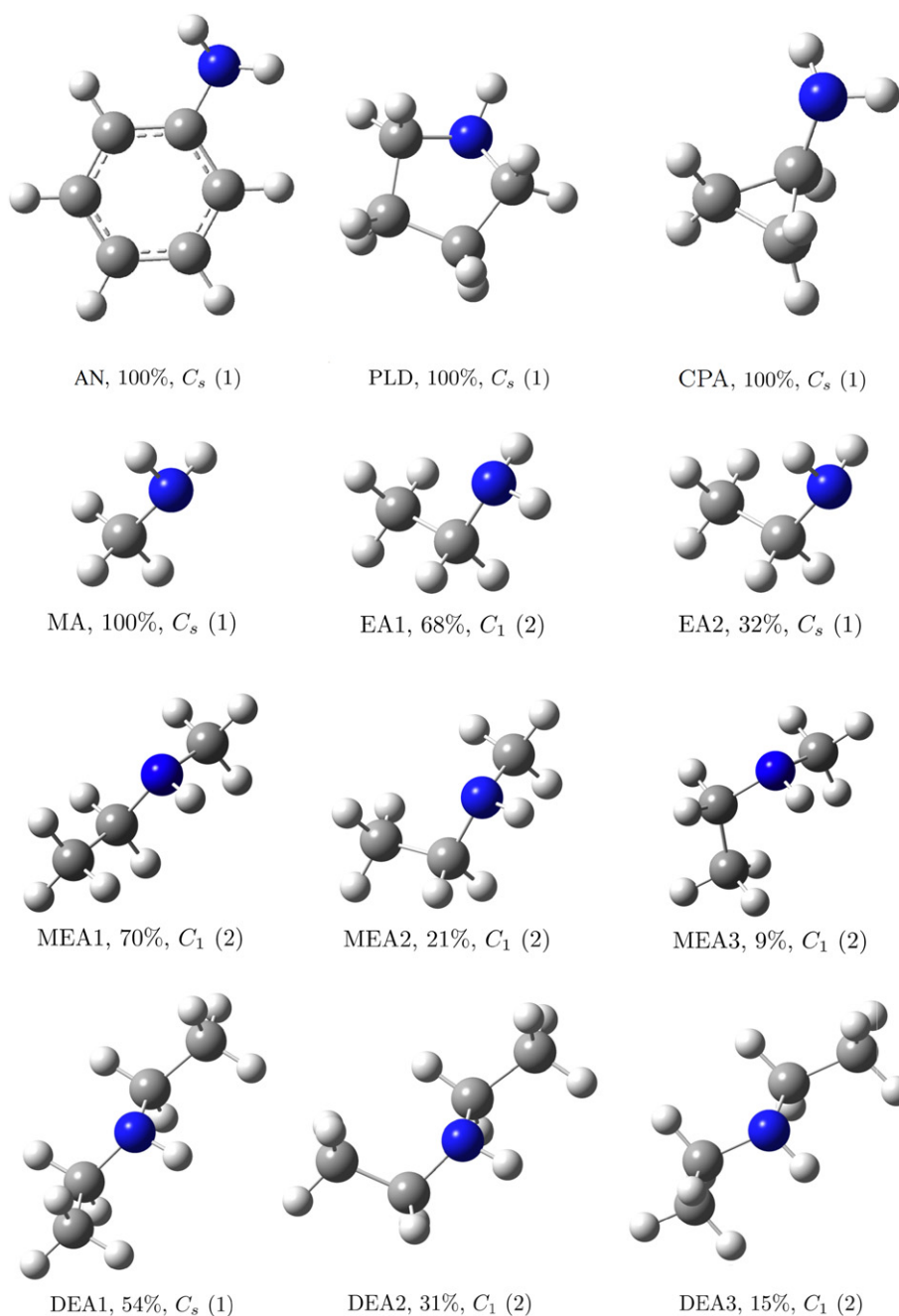


Fig. 1. CCSD(T)-F12a/VDZ-F12 optimized conformers of aniline (AN), pyrrolidine (PLD), methylamine (MA), ethylamine (EA), cyclopropylamine (CPA), methylethylamine (MEA) and diethylamine (DEA) with Boltzmann distributions corrected for structural degeneracies according to symmetry factors.

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