

Molecular Structure and Vibrational Analysis of N, N-Dimethylaniline Based on DFT Calculations

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Abstract: The FT-IR and FT-Raman spectra of the N, N-Dimethylaniline (NNDMA) was recorded in the range 4000–400 cm^{-1} and 3500–100 cm^{-1} , respectively. Theoretical information on the optimized geometry, harmonic vibrational frequencies, Infrared and Raman intensities were obtained by means of density functional theory (DFT) using standard B3LYP/6-311++G** level. This information was used in the assignment of the various fundamentals. Comparison of the simulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the vibrational modes.

Keywords: Normal coordinate analysis; FT-IR and FT-Raman spectra; Density functional theory, First-order hyperpolarizability.

1. Introduction

N,N-Dimethylaniline (NNDMA) is an organic chemical compound, a substituted derivative of aniline. It consists of a tertiary amine, featuring dimethylamino group attached to a phenyl group. This oily liquid is colourless when pure, but commercial samples are often yellow. It is an important precursor to dyes such as Crystal violet. NNDMA is a key precursor to commercially important triarylmethane dyes such as Malachite green and Crystal violet. NNDMA serves as a promoter in the curing of polyester and vinyl ester resins. NNDMA is also used as a precursor to other organic compounds. The aim of this work is to check the performance of the B3LYP density functional force field for simulation of the FT-IR and FT-Raman spectra of NNDMA with the use of the large B3LYP/6-311+G** basis sets, and comparing the effect of simpler and more elaborate versions of scaling, while paying attention to ensuring correct band assignments.

2. Experimental Details

The compound NNDMA was purchased from Lancaster Chemical Company USA, with a stated purity of 99% and it was used as such without further purification. The FT-Raman spectrum of NNDMA was recorded using 1064nm line of Nd:YAG laser as excitation wave length in the region 3500–100 cm^{-1} with FT-Raman module accessory. The FT-IR spectrum of the title compound was recorded in the region 4000–400 cm^{-1} on Perkin Elmer Spectrophotometer. The spectrum was recorded at room temperature with a scanning speed of 30 $\text{cm}^{-1}\text{min}^{-1}$ and the spectral width of 2.0 cm^{-1} .

3. Computational methods

All the calculations were performed using the 3-parameter hybrid functional (B3) for exchange part and the Lee-Yang-Parr (LYP) [1] correlation function, with 6-311++G** as the basis set using the Gaussian 03 suite of program. The vibrational modes were assigned by means of visual inspection using the GAUSS VIEW program. The analysis for the vibrational modes of NNDMA is presented in some detail in order to better

describe the basis for the assignments. From the basic theory of Raman scattering Raman activities calculated by Gaussian 03 program.

4. Result and Discussion

4.1. Geometrical Structure

The molecular structure of NNDMA having C_s point group symmetry. The most optimized geometry is performed at B3LYP/6-311++G** basis set of NNDMA molecule with atoms numbering scheme shown in Fig.1. The optimized bond length and bond angles of the title compound which are calculated using DFT (B3LYP) method with 6-311++ G** basis set.

4.2. Assignments of spectra

A detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, a full set of 68 standard internal coordinates containing 14 redundancies were defined. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendation of Pulay *et al* [2,3]. The theoretically calculated DFT force fields were transformed to this later set of vibrational coordinates and used in all subsequent calculations. When using computational methods to predict theoretical normal vibrations for relatively complex polyatomic, scaling strategies are used bring computed wave numbers. For the DFT method employed in this work the simplest limiting scaling strategy was used.

In order to reproduce the observed wave numbers, refinement of scaling factors were applied and optimized via least-square refinement algorithm which resulted is an average difference between the experimental and SQM wave numbers for 6-311++G** basis set. The vibrational assignments in the present work are based on the DFT/6-311++G** frequencies, Infrared intensities, Raman activities as well as characteristic group frequencies. The 54 normal modes of NNDMA are distributed among the symmetry species as $\sqrt{\text{vib}}=37A'(\text{in-plane})+17A''$ (out-of-plane). Assignments were made through visualization of the atomic displacement representations for each vibration, viewed through GAUSSVIEW [4] and matching the predicted normal wave numbers and intensities with experimental data. The observed experimental FT-IR and FT-Raman spectra and theoretically predicted IR and Raman spectra at DFT and B3LYP levels are shown in Fig.2 and Fig.3 respectively.

C-C vibrations

The bands between $1400\text{--}1650\text{ cm}^{-1}$ in benzene derivatives are assigned to C-C stretching modes [5]. Accordingly, in the present study, the carbon-carbon vibrations of the title compound are observed at 1509 , 1577 and 1578 cm^{-1} in the FT-IR spectrum and 1520 cm^{-1} in the FT-Raman.

C-H vibrations

The aromatic structure shows the presence of C-H stretching vibrations around 3000 cm^{-1} . In NNDMA these modes were observed at 3074 , 3063 , 3027 , 2984 and 2996 cm^{-1} . A number of spikes observed throughout the broad absorption is indicative of Fermi resonance. In benzene-like molecule C-H in-plane bending vibrations are observed in the region $1000\text{--}1300\text{ cm}^{-1}$ and are usually weak. The C-H out-of-plane bending modes arise in the region $600\text{--}900\text{ cm}^{-1}$ [6]. In the present study, the bands observed at 1168 , 1231 , 1216 and 1360 cm^{-1} in NNDMA were assigned to C-H in-plane bending vibrations. The C-H out-of-plane bending modes for NNDMA are also assigned within characteristic region.

Ring vibrations

Due to aromatic ring vibrations, NNDMA absorb strongly in the region $1635\text{--}1300\text{ cm}^{-1}$ [7, 8]. In the present study the peaks observed at 1672 , 1637 , 1578 , 1558 , 1500 , 1472 , 1444 , 1385 and 1372 cm^{-1} were assigned to ring stretching vibrations. The ring deformation vibrations were observed at 1131 , 704 , 554 , 516 , 473 and 288 cm^{-1} for NNDMA. For most of the remaining ring vibrations, the overall agreement is satisfactory. Small changes in frequencies observed for these modes are due to the changes in force constant/reduced mass ratio resulting mainly due to the extents of mixing between ring and substituent group vibrations.

Carbon–nitrogen vibration

The IR and Raman bands observed between 1444 and 1229 cm^{-1} , in the title compounds have been assigned to C-N stretching vibrations [9]. The in-plane and out-of-plane bending vibrations assigned in this study are also supported by the literature [10]. For the title compounds a pure mode cannot be expected for this vibration since it falls in a complicated region of the vibrational spectrum.

CH₃ vibration

The CH₃ stretching and bending modes appear to be quite pure group vibrations. Considering the assignment of CH₃ group frequencies, one can expect that nine fundamentals can be associated to each CH₃ group, namely the symmetrical $\nu_s(\text{CH}_3)$, and asymmetrical $\nu_a(\text{CH}_3)$, in-plane stretching modes; the symmetrical $\alpha_s(\text{CH}_3)$ and asymmetrical $\alpha_a(\text{CH}_3)$, deformation modes; the in-plane rocking and out-of-plane rocking and twisting bending modes. The asymmetric stretching and asymmetric deformation modes of the methyl group is expected to be depolarised for A' symmetry species. The infrared bands observed at 2804 cm^{-1} is assigned to $\nu_s(\text{CH}_3)$. The FT-IR in plane bending and Raman out-of-plane bending are assigned to 1229 , 1195 cm^{-1} , respectively. The assignment of the band at 282 cm^{-1} of IR is attributed to the torsion CH₃ [11].

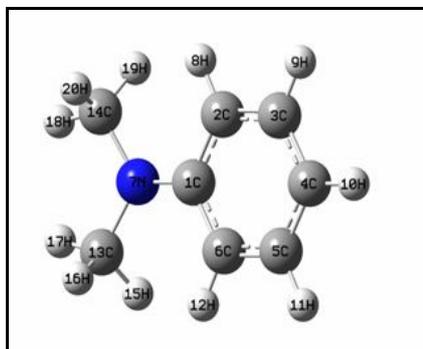


Fig. 1. The optimized molecular structure of NNDMA

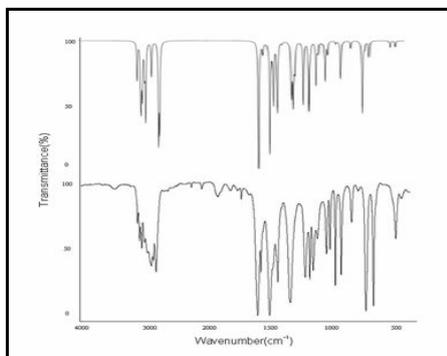


Fig. 2 FT-IR spectra of NNDMA (a) Observed (b) Calculated with B3LYP/6-311+G**

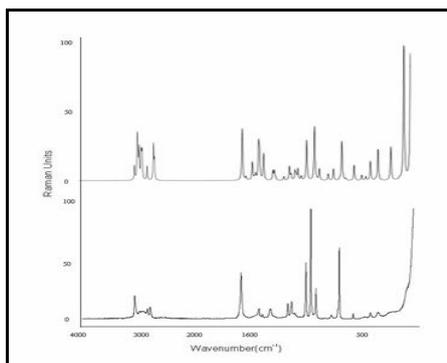


Fig. 3. FT-Raman spectra of NNDMA (a) Observed (b) Calculated with B3LYP/6-311+G**

5. Conclusions

IR and Raman Spectra were obtained for NNDMA, in which all of the expected 54 normal modes of vibration were assigned. The optimized molecular geometry, force constants and vibrational frequencies were calculated using DFT techniques in the B3LYP approximation. Taking the observed frequencies as a basis corresponding to the fundamental vibrations, it was possible to proceed to a scaling of the theoretical force field. The resulting SQM force field served to calculate the potential energy distribution, which revealed the physical nature of the molecular vibrations, and the force constants in internal coordinates, which were similar to the values obtained before for related chemical species.

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