



# Normal coordinate analysis of pyridine and its $C_{2v}$ $^2H$ -isotopomers. A new approach



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## ABSTRACT

The vibrational spectra of pyridine and its  $C_{2v}$  deuterated isotopomers were reconsidered by means of density functional theory (DFT) methods. The B3LYP level, with 6–311++G\*\* and cc-pVTZ basis sets, is used for geometrical optimization and calculations of harmonic vibrational wavenumbers. Furthermore, the anharmonic vibrational wavenumbers were also calculated at the B3LYP/6-311++G\*\* level. The calculated internal coordinates were used to perform complete normal coordinate analysis (NCA) and potential energy distribution (PED) calculations for pyridine and its  $^2H$ -isotopomers.

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## 1. Introduction

It is a goal of spectroscopic chemist to find a reliable method for precise description of molecular vibrational spectra. The description of vibrational spectra is based on normal coordinate analysis (NCA) and calculating the potential energy distribution (PED) of each vibrational normal mode. Three main methods have been applied for this purpose; (a) classical method [1], based on GF matrix calculations. In this method, the precise knowledge about the geometry and force constants governing the vibrational spectra of the molecule are very important. The geometry may be obtained from x-ray diffraction, neutron diffraction, or microwave spectroscopy and force constant will be estimated from known force constants of similar chemical bonds. (b) Force constants will be calculated by *ab initio* or DFT approaches and then calculated force fields will be used to obtain the GF matrix [2,3]. (c) The internal (displacement) coordinates for each normal mode are obtained directly from *ab initio* or DFT calculations [4–6]. Then by appropriate combinations of internal coordinates it is possible to

calculate the symmetry coordinates. By calculating the contributions of symmetry coordinates in each normal mode, the PED of the normal modes will be obtained. The last method has not been used previously for aromatic compounds. In this work, the last method will be applied on the pyridine and its deuterated derivatives.

In the present work, the vibrational spectra of pyridine and its  $C_{2v}$  deuterated isotopomers will be investigated. Pyridine and its derivatives have been extensively studied from the spectroscopic point of view, mainly due to their presence in many chemicals of high interest in a variety of biomedical, agricultural, and industrial fields. These compounds are found as the active ingredients of many drugs and are widely distributed in nature; for example, vitamin B6, nicotine, nicotinamide, chloroquine (antimalarial drug), serve as good anesthetic agents, and are widely used in preparation of drugs for certain brain disease [6–11].

The vibrational spectra of pyridine have been extensively studied over the past 60 years [2,3,12–44].

The IR spectra of pyridine in the gas phase [13,15–18,22,23], as well as liquid phase [13,15–18,21–23] and its Raman spectra in the gas phase [20] and liquid phase [13,15–21] are reported. The PED of vibrational spectra for pyridine and its deuterated analogues have also been reported [8,10,18].

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## 2. Experimental

Pyridine and  $d_5$ -pyridine were purchased from Sigma-Aldrich and used without further purification.

The IR spectra were recorded on a Bomem B-154 Fourier Transform Spectrophotometer in 4000–600  $\text{cm}^{-1}$  region. The spectra were collected with resolution 2  $\text{cm}^{-1}$  by coadding the results of 15 scans.

The Far-IR spectra in the region 600–100  $\text{cm}^{-1}$  were obtained using a Thermo Nicolet Nexus 870 FT-IR spectrometer equipped with a DTGS/polyethylene detector and a solid substrate beam splitter. The spectra were collected with a resolution of 2  $\text{cm}^{-1}$  by coadding the results of 64 scans.

The Raman spectra were recorded employing a 180° back-scattering geometry and a Bomem MB-154 Fourier transform Raman spectrometer. It was equipped with a ZnSe beam splitter and a TE cooled InGaAs detector. Raleigh filtration was afforded by a set of two holographic technology filters. The spectra were collected with a resolution of 2  $\text{cm}^{-1}$  by coadding the results of 1500 scans. The laser power at the sample was 300 mW.

## 3. Method of analysis

All theoretical computations were performed within the framework of DFT using the Gaussian 09 [45] software system. Geometry optimization of pyridine is achieved at the B3LYP level [46–48], using 6-311++G\*\* and cc-pVTZ basis sets. The B3LYP/6-311++G\*\* level was also utilized for calculating the Raman activity of vibrational frequencies [49]. In order to obtain more accurate vibrational transition frequencies, anharmonic frequency calculations [50,51] were also performed at the B3LYP/6-311++G\*\* level.

A normal coordinate analysis was carried out to provide a complete assignment of the fundamental vibrational wavenumbers for pyridine and its  $C_{2v}$  deuterated isotopomers. The procedure for calculating the displacement (internal coordinate) and symmetry coordinates for each normal mode are described elsewhere [4,6,52].

Three constraints should be applied in calculation of symmetry coordinates contributions in normal modes. First, the number of symmetry coordinates should be  $3N-6$  ( $3N-5$  in linear molecules). Second, the sum of contributions percent of all symmetry coordinate,  $S_i$ , in each normal mode should be normalized to 100%.

$$\sum_{i=1}^{3N-6} S_i^{qj} = 100 \quad (1)$$

Which,  $S_i^{qj}$  is contribution of  $i$ th symmetry coordinate in the  $j$ th normal mode. Third, sum of contribution of each symmetry coordinate percent over all normal modes should be also normalized to 100%.

$$\sum_j S_i^{qj} = 100 \quad (2)$$

The symmetry coordinates used for calculation of PED of the vibrational normal modes of pyridine are those defined by Wiberg et al. [2] (hereafter WWWC) and Szfran and Koput [3] (hereafter SK), except for out of plane vibrational modes. Since in out of plane vibrational modes several atoms may be displaced, any definition of dihedral angles depending on the other atoms may cause severe errors in calculations of PEDs. Therefore, the out of plane movement of each atom (H, C, or N) will be calculated with respect to the equilibrium position of all other skeletal atoms.

Using this data, it is possible to calculate the relative vibrational

amplitude for each internal coordinate in the normal modes and obtain the changes in bond lengths, bond angles, and dihedral angles (internal coordinates). The full sets of 38 standard internal coordinates containing 11 redundancies for pyridine, are defined in Table 1. From these internal coordinates, a non-redundant set of local symmetry coordinates was constructed by a suitable linear combination of internal coordinates (see Table 1). These symmetry coordinates were then normalized over all 27 normal coordinates. The contributions of each symmetry coordinate in all normal modes must be unity (100%) and sum of the contributions of all symmetry coordinates in each normal mode should also be unity (100%).

According to the  $C_{2v}$  symmetry for the pyridine and its considered isotopomers molecules, the  $3N - 6 = 27$  vibrational modes can be classified among the symmetry species as follows:

$$\Gamma_{\text{vib}} = 10A_1(\text{IR and R active}) + 3A_2(\text{R active}) + 5B_1(\text{IR and R active}) + 9B_2(\text{IR and R active}).$$

In addition to PED calculations, vibrational assignments for the pyridine ring are also given in the Wilson notation [53] used for vibrational modes of benzene ring.

## 4. Results and discussion

The optimized geometry and atom numbering are shown in Fig. 1.

By combining the results of GaussView 5 program [54] with symmetry considerations and potential energy distribution (PED) the vibration descriptions were made with a high degree of accuracy. Vibrational assignments are based on comparison of calculated and observed Raman and IR frequencies and intensities.

### 4.1. $d_0$ -pyridine

The observed and calculated vibrational wavenumbers of  $d_0$ -pyridine are given in Table 2. In Table 3 the calculated PED of  $d_0$ -pyridine normal modes are compared with the corresponding values previously reported by Wiberg et al. (WWWC) [2] and Szfran and Koput (SK) [3]. The observed and stimulated IR and Raman spectra for  $d_0$ -pyridine are shown in Figs. 2 and 3, respectively.

#### 4.1.1. Band assignments

The vibrational wavenumbers of pyridine in the gas and liquid phases are not much different [20]. As it is shown in Table 2, there are several discrepancies between the reported assignments with each other and also with our calculated results. Those band assignments which are not in agreement with our results are highlighted as bold and italic entries in Table 2 and the corresponding tables related to the pyridine isotopomers.

The IR spectrum of  $d_0$ -pyridine, in the liquid phase, indicates four medium weak bands at 3078, 3054, 3033, and 3025  $\text{cm}^{-1}$  and a weak band at 3001  $\text{cm}^{-1}$ . According to our calculation results, these bands are assigned to  $\nu_{20b}$ ,  $\nu_2$ ,  $\nu_{13}$ ,  $\nu_{7b}$ , and  $\nu_{20a}$ , respectively. However, some authors considered a weak band at about 3090  $\text{cm}^{-1}$  as  $\nu_2$  vibrational band [2], whilst, some others considered the 3057  $\text{cm}^{-1}$  band for  $\nu_2$ . The 3057  $\text{cm}^{-1}$  IR band, which its corresponding Raman band is strong and polarized [13,21], is assigned to  $\nu_2$ . This assignment is in agreement with that given in Refs. [15,20,29,40]. DiLella et al. [16] considered the 3057  $\text{cm}^{-1}$  band as superposition of  $\nu_2$ ,  $\nu_{13}$ , and  $\nu_{20a}$ . Walters et al. [22], Pongor et al. [25], and Kumar et al. [23] assigned a band at about 3080–3087  $\text{cm}^{-1}$  to  $\nu_2$ . WWWC [2] assigned a band at 3073  $\text{cm}^{-1}$  to  $\nu_2$ . By considering the IR and Raman intensities and predicted anharmonic wave numbers, the 3031  $\text{cm}^{-1}$  band is assigned to  $\nu_{13}$ , which is in agreement with the Ureña et al. [13] assignment. This band is assigned by Wilmshurst and Bernstein (WB) [15], Corrsin

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