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Anharmonic vibrational spectra and mode-mode couplings analysis of 2-aminopyridine

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Vibrational spectra of 2-aminopyridine (2AP) have been analyzed using the vibrational self-consistence field theory (VSCF), correlated corrected vibrational self-consistence field theory (CC-VSCF) and vibrational perturbation theory (VPT2) at B3LYP/6-311G(d,p) framework. The mode-mode couplings affect the vibrational frequencies and intensities. The coupling integrals between pairs of normal modes have been obtained on the basis of quartic force field (2MR-QFF) approximation. The overtone and combination bands are also assigned in the FTIR spectrum with the help of anharmonic calculation at VPT2 method. A statistical analysis of deviations shows that estimated anharmonic frequencies are closer to the experiment over harmonic approximation. Furthermore, the anharmonic correction has also been carried out for the dimeric structure of 2AP. The fundamental vibration bands have been assigned on the basis of potential energy distribution (PED) and visual look over the animated modes. Other important molecular properties such as frontier molecular orbitals and molecular electrostatics potential mapping have also been analyzed.

1. Introduction

Pyridine and their derivatives, a class of heterocyclic compounds, have attracted considerable interest due to their wide applications in pharmacology and industries [1,2]. Specifically, 2AP shows great biological importance because it is an intermediate in the manufacturing of various important drugs like antihistamines, piroxicam, ciclopirox olamine, diphenlpyramide, methaqualone, propiram fumarate, pyrilamine, triprolidine, and zomepirac [3]. Among various effective spectroscopic methods, vibrational spectroscopy (FTIR and Raman) techniques are highly sensitive and these are helpful in the elucidation of structural as well as dynamical properties for the molecular system [4]. The experimental vibrational spectroscopy, combined with quantum chemical calculations, has become popular in the interpretation of complex spectra efficiently. The harmonic vibrational studies of 2AP [5–7] and its dimer structure [8–9] have been investigated earlier. To the best of our knowledge, the vibrational studies beyond the harmonic approximation using VSCF and CC-VSCF method and anharmonic coupling integral of the molecule have not been carried out elsewhere. The anharmonic simulation results show close approximation with experiment over the harmonic one. Generally, the theoretical treatment of vibrational spectra of the polyatomic molecules is restricted to harmonic oscillator approach. Such treatment is useful for semirigid molecules and shows limited accuracy for molecules having floppy vibrations with strong anharmonic effect. Therefore, it is necessary to consider anharmonic approximation in computing potential energy surface for the molecule. The vibrational second order perturbation (VPT2) approach implemented by Barone [10] is usually employed to account the anharmonic corrections. Vibrational self-consistent field (VSCF) method is also an efficient method for anharmonic vibrational calculations, which provides excellent results [11]. Furthermore, the correlation corrected vibrational self-consistent field (CC-VSCF) method uses the second order perturbation theory (PT2) and shows more accurate results than the VSCF method within separable approximation [12,13]. Many researchers have reported anharmonic coupling integral using VSCF and CC-VSCF method [14–16].

The present study has been focused on the vibrational analysis of 2-aminopyridine using anharmonic force field calculations. The anharmonic corrections of the vibrational frequencies have been performed using VPT2, VSCF and CC-VSCF levels of theory. The coupling interaction based anharmonic corrections at CC-VSCF level provide insight into energy flow between different modes of vibration. The anharmonic calculation is not only directly used for the PES but also can provide information about energy flow between vibrational modes. Therefore, magnitudes of the two-mode coupling are also computed. Moreover, the combination and overtone bands have been accounted in the FTIR spectrum with the help of anharmonic calculation at VPT2 level.

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2. Experimental Methods

The solid sample of the title compound was obtained from Sigma-Aldrich Chemical Co., USA and used as such for spectral measurements. FTIR spectrum of the 2AP was recorded in the region 4000-400 cm^{-1} using KBr pellet technique on Tensor 37 (Bruker) spectrophotometer at a resolution of 2 cm^{-1}.

3. Computational Details

In the VSCF method, the analysis of anharmonic interaction comprises coupling between different modes of vibration [11,12]. The VSCF algorithm is based on the approximation of separability and the total vibrational wave function is described by a product of single mode wave functions.

$$\Psi_n(Q_1,\ldots\ldots\ldots Q_N)=\prod_{j=1}^{N}\Psi_j^{(n)}(Q_j) \tag{1}$$

Additionally, the potential is represented as a sum of terms that include the single mode and mode-mode interaction potentials [17].

$$V\,(Q_1,\ldots\ldots\ldots\ldots Q_N)=\sum_{j=1}^{N}V_j^{dig}(Q_j)+\sum_{i}\sum_{j>i}V_{ij}^{coup}\,(Q_{i,}Q_j) \tag{2}$$

where the potential due to the pair of interactions is defined by

$$V_{ij}^{coup}(Q_{i,}Q_j)=V\,(0,\ldots Q_{i,}\ \ .\ \ldots Q_{j,.}\ .\ .\ .\ ..0)-V_j^{dig}\,(Q_j\,)-V_i^{dig}(Q_i) \tag{3}$$

To calculate the magnitude of mode-mode coupling between modes pairs, the coupling potential terms can be presented as a quartic force field (QFF) [18]

$$V_{ij}^{QFF}(Q_{i,}Q_j)=\ C_{ijj}Q_iQ_j^2+C_{iij}Q_i^2Q_j+C_{ijjj}Q_j^3Q_i+\ C_{iiij}Q_jQ_i^3 \\ +C_{iijj}Q_i^2Q_j^2 \tag{4}$$

where Q_i and Q_j are normal coordinates; the coefficients C_{ijj}, C_{iij},C_{ijjj},C_{iiij} and C_{iijj} are estimated by numerical differentiation of analytical Hessian. The method is implemented in Gamess-US package [19]. The first order correction of mode-mode coupling integral between modes pairs in the ground state can be presented as

$$CI=C_{iijj}<0|Q_i^2Q_j^2|0> \tag{5}$$

Table 1
Comparison of the geometrical parameters of monomer and dimer of 2AP.

Bond lengths (A°)	B3LYP/6-311G(d,p)		Bond angles (°)	B3LYP/6-311G(d,p)	
	Monomer	Dimer		Monomer	Dimer
N1-C3	1.339	1.347	C3-N1-C7	117.93	118.39
N1-C7	1.336	1.338	C3-N2-H12	113.95	119.22
N2-C3	1.381	1.361	C3-N2-H13	117.52	118.13
N2-H12	1.009	1.024	H12-N2-H13	115.11	117.21
N2-H13	1.008	1.005	N1-C3-N2	116.15	117.36
C3-C4	1.409	1.416	N1-C3-C4	122.46	121.09
C4-C5	1.384	1.379	N2-C3-C4	121.35	121.09
C4-H8	1.084	1.084	C3-C4-C5	118.39	119.05
C5-C6	1.397	1.399	C3-C4-C8	120.42	119.85
C5-H9	1.085	1.084	C5-C4-C8	121.19	121.10
C6-C7	1.389	1.385	C4-C5-C6	119.57	119.72
C6-H10	1.083	1.082	C4-C5-H9	119.90	119.84
C7-H11	1.087	1.087	C6-C5-H9	120.53	120.43
			C5-C6-C7	117.5	117.26
			C5-C6-H10	121.68	121.85
			C7-C6-H10	120.81	120.89

$$CI=C_{iijj}\left(\frac{\hbar}{2\omega_i}\right)\left(\frac{\hbar}{2\omega_j}\right) \tag{6}$$

where $|0\rangle$ is the ground state harmonic oscillator wave function [14].

The optimized structural parameters were calculated using DFT method at B3LYP/6-311G (d,p) level and harmonic vibrational analysis was performed at the same level of theory. The suitable uniform scaling factor (0.9679) was used to correct harmonic frequencies [20]. The anharmonic vibrational frequencies were computed using VPT2 approach implemented in Gaussian 09 software [10,21] as well as by VSCF and CC-VSCF theory implemented into Gamess-US software package [19]. All fundamental modes of vibrations were assigned on the basis of potential energy distribution (PED) using Gamess-US program [22] and visual inspection of the atomic displacements for each normal mode. The simulated IR spectra were plotted in Lorentzian line shape with FWHM at 6 cm^{-1}. The calculations of harmonic and anharmonic frequencies were also performed for possible hydrogen bonded dimer structure of the molecule using B3LYP/6–311(d,p) method.

4. Results and Discussion

4.1. Vibrational Analysis

The structure of 2AP was optimized to achieve a stable structure (minimum energy) and followed by vibrational calculation. The

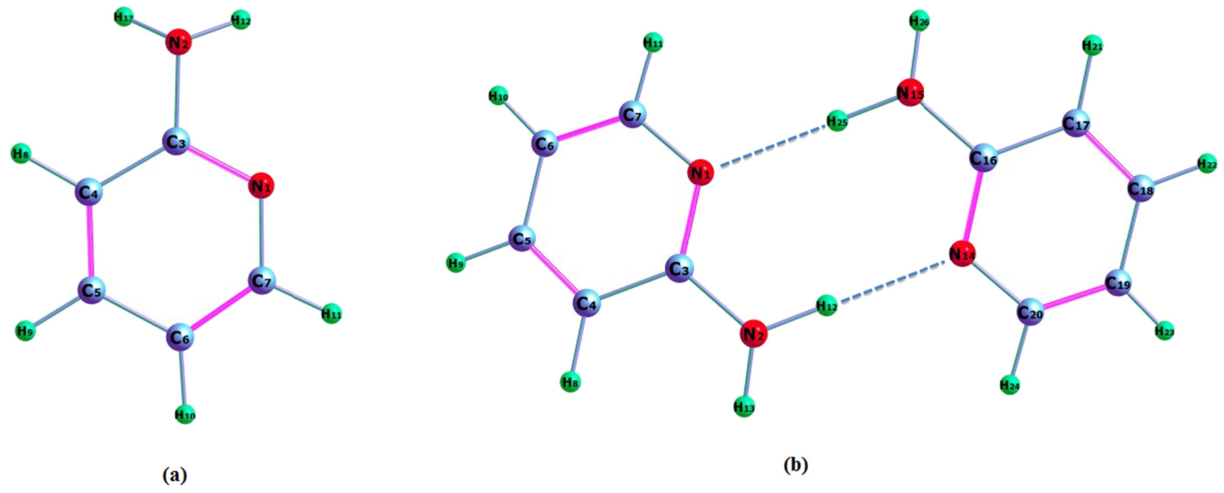

Fig. 1. (a) Optimized geometry of 2AP for monomer with numbering scheme (b) Optimized dimer structure of 2AP molecule with intermolecular interaction and labelling of atoms.