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Vibrational studies of benzene, pyridine, pyridine-N-oxide and their cations

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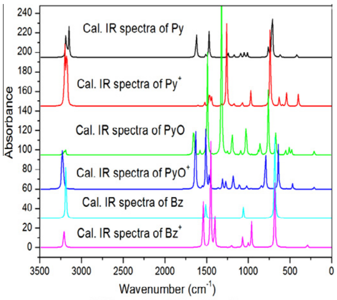
HIGHLIGHTS

- Pyridine is one of the building blocks of a large number of biologically important molecules.
- N–O moiety possesses a unique functionality of acting effectively as a push electron donor and a pull electron acceptor.
- Pyridine is used as a precursor to agrochemicals and pharmaceuticals.
- Due to removal of electron all the fundamentals are affected in pyridine/pyridine-N-oxide.

GRAPHICAL ABSTRACT

The computed IR spectra for the Bz, Bz^+, Py, Py^+, PyO and PyO^+ molecules were carried out using the Gaussian-03 software at the B3LYP/6-311++G** level.



Cal. IR spectra of Py, PyO, Bz and their cations

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ABSTRACT

IR and Raman spectra of pyridine and pyridine-N-oxide have been recorded and analyzed. The optimized molecular geometries, APT charges and vibrational characteristics for benzene, pyridine, pyridine-N-oxide and their cations have been computed using DFT method. Due to attachment of O atom at N site or removal of electron all the modes are affected in magnitudes. However, significant changes are noticed in their IR intensities, Raman activities and depolarization ratios of the Raman bands in going from pyridine to its N-oxide or in going from neutrals to their cations. It is interesting to note that in going from benzene to benzene cation charge redistribution takes place to reduce the symmetry from D_{6h} to D_{2h}. The calculated frequencies have been correlated with the experimental frequencies for the pyridine and pyridine-N-oxide molecules.

Introduction

Pyridine (Py) is basically a heterocyclic organic compound with the chemical formula C_5H_5N and is structurally related to benzene, with one C–H fragment replaced by a nitrogen atom. The Py ring occurs in many important compounds including azines and vitamins, niacin and pyridoxal. It is used as a precursor to agrochemicals and pharmaceuticals and is also an important solvent and reagent. Py is one of the building blocks of a large number of biologically important molecules. The chemistry and applications of pyridine compounds have recently received much attention due to their usefulness as synthetic intermediates and their biological importance. The N–O moiety of pyridine N-oxides possesses a unique functionality of acting effectively as a push electron donor and as a pull electron acceptor group. The frequencies of the normal vibrations and the intensities of the bands in the IR and Raman spectra of pyridine N-oxide and three of its isotopomers are calculated with the DFT method with 6-311+G (d, p) basis set by Berezin [1]. Vibrational analysis of Py, pyridinium, pyridinyl radical and 1,4-dihydroxy Py molecules were studied by Lee and Masel [2]. The surface-enhanced Raman scattering (SERS) spectra of pyridine

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have been studied and interpreted on the basis of a resonant charge transfer mechanism by Arenas et al. [3].

The pressure dependences of the internal Raman-active modes of solid Py and Py-d$_5$ in both the crystalline and glassy phases as well as of the complexes Zn(Py)$_2$Cl$_2$, Ni(Py)$_2$Cl$_2$, and Ni(Py)$_4$Cl$_2$ were reported by Heyns and Venter [4]. The depolarized Rayleigh spectra of aqueous Py have been studied by Wang et al. [5]. Crystal structures of Py and Py trihydrate were studied by Mootz and Wussow [6]. The complete harmonic vibrational force fields, diagonal and semidiagonal cubic force fields for Py were computed by Pongor et al. [7]. Low temperature calorimetry, comparative ebulliometry, flow calorimetry, combustion calorimetry values, entropy, heat capacity and heat of formation of Py in the ideal gaseous state and vibrational assignments of Py and its derivatives were studied by McCullough et al. [8].

Vibrational spectra of nitrogen-containing six-membered heterocyclic compounds i.e., Py, pyridazine, pyrimidine, pyrazine and sym-triazine were studied by Todorovskii and Plotkin [9]. Thermodynamic property of Py was studied by Chirico et al. [10]. The IR spectra of Py and its derivatives in the liquid and vapor states have been obtained by Wilmshurst and Bernstein [11]. IR spectrum of Py with metal ion was studied by Perelygin and Klimchuk. [12]. Radical production in the radiolysis of liquid Py and vibrational spectra of Py and some radicals were studied by Laverne et al. [13]. Raman spectra of Py and 2-chloropyridine were studied by Kagel [14]. Infrared spectra in the liquid and gas phases as well as Raman spectra in the liquid phase have been recorded and analyzed for $-d_0$, $-d_5$ and ^{15}N isotopomers of Py was determined by Ureña et al. [15]. Structure and vibrational spectra of Py and its isotopomers were studied by Szafran and Koput [16].

The vibrational spectra of pyridine betaine and partially deuterated pyridine betaine were calculated and compared with the experimental data by Szafran and Koput [17]. Vibrational frequency shift induced by protonation on Py was also studied using ab initio molecular orbital calculation by Ajito et al. [18]. The high-resolution FT-IR spectra of Py-h$_5$ and Py-d$_5$ have been obtained by Wong and Colson [19]. Time developments of SERS of Py, pyrimidine, pyrazine and cyanide adsorbed on Ag electrodes were studied by Dornhaus et al. [20]. Electronic absorption spectrum of the pyridine-N-oxide (PyO) molecule in the gas phase was studied by Berezin et al. [21] Combination band intensities of C–H out-of-plane vibrations for Py and its deuterium derivatives in CS$_2$ solution were determined by Yamamoto et al. [22]. The IR and Raman spectra of methyl-3 pyridine were simplified by Gandolfo and Zarembowitch [23]. The in-plane Urey–Bradley type force field of Py has been refined by Suzuki [24]. Matrix isolation studies of lewis acid complexes of Py were studied by Ault [25]. In-plane and out-of-plane vibrational modes assignments of PyO were made by Bist et al. [26,27]. Crystal structure of PyO was studied by Űlkű et al. [28].

Dissociation of Py cation was investigated by Gridelet et al. using retarding field technique up to an internal energy of 4 eV above the reaction threshold internal energies [29]. Vibrational spectra of benzene radical were studied by some workers [30–35] in the past, however, neither the molecular structures nor the vibrational spectra of the PyO$^+$ was studied earlier. Vibrational spectra of the pyridine cation (Py$^+$) in the electronic ground state have been measured in several intermediate states (0^0, 16b$_0^2$, 16b$_0^4$, 6a$_0^1$, 6b^1, 16a$_0^1$, 10a$_0^1$ and 12^1) by Mass-Analyzed Threshold Ionization spectroscopy [36].

In the present article, we have measured and analyzed the IR and Raman spectra of Py, PyO and their cations in light of the DFT calculations for structures and vibrational spectra of these molecules. All these results have been compared with the corresponding quantities for benzene (Bz) and its cation (Bz$^+$).

Computational details

All the calculations for the Py, PyO, singly charged cation of Py (Py$^+$) and singly charged cation of PyO (PyO$^+$) were carried out using the Gaussian-03 [37] software at the B3LYP/6-311++G** level. The atomic numbering and labeling schemes are shown in Fig. 1 for Py, PyO, Bz and their cations.

For the PyO molecule the initial geometrical parameters were taken from the work of Űlkű et al. [28] and calculations were performed using the RHF method employing the 6-31+G* basis set. The optimized geometries at the RHF/6-31+G* level were taken as the input structures for the calculations at the B3LYP/6-31+G* level. Similarly, the optimized geometries at the B3LYP/6-31+G* level were used as the input structures for the calculations at the B3LYP/6-31++G** level. Finally, the optimized geometries at the B3LYP/6-31++G** level were used as the starting geometries for the calculations at the B3LYP/6-311++G** level.

The computed IR and Raman spectra for the Bz, Bz$^+$, Py, Py$^+$, PyO and PyO$^+$ molecules are shown in Figs. 2 and 3 respectively.

For the cations of Py, Bz and PyO the input structures were taken from the optimized geometries at the B3LYP/6-311++G** level for the neutral species and the calculations were performed using the B3LYP method with the 6-311++G** basis set by taking charge 1 and multiplicity 2. The DFT calculations were carried out to compute the optimized molecular geometries, APT charges and fundamental vibrational frequencies along with their corresponding intensities of the IR bands, Raman activities and depolarization ratios of the Raman bands for the neutrals (Bz, Py and PyO) as well as their cations. The geometries were optimized by minimizing the energies with respect to all the geometrical parameters without imposing any molecular symmetry constraints.

Experimental

IR spectra

The Py compound is found in liquid phase at the room temperature whereas the PyO compound is hygroscopic and is found in colorless solid phase at room temperature. These compounds were purchased from the Sigma–Aldrich Chemical Co. (USA). To record their FTIR spectra the Perkin Elmer RX1 spectrometer was used in the spectral range 400–4000 cm^{-1} with the following parameters:

- scans – 200;
- resolution – 4 cm^{-1};
- gain – 50.

The recorded IR spectra of the Py and its N-oxide molecules are reproduced in Fig. 4.

Raman spectra

The Raman spectra of both the compounds were recorded on a Jobin Yvon Raman-HR spectrometer in the spectral range 50–4000 cm^{-1}. The radiation (λ = 4880 Å) from an Ar$^+$ laser was used as the exciting source. During the recording of the Raman spectra the following parameters were used:

- scanning speed – 100 cm^{-1}/min;
- resolution – 1 cm^{-1};
- power of the laser beam, on the sample, 500–600 mW;
- PMT voltage – 800 V.

The Raman spectra for Py and its N-oxide are given in Fig. 5.