



# Vibrational spectra, normal coordinate analysis, and hydrogen bond investigation of pyridinium perchlorate



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## ABSTRACT

The IR and Raman spectra of pyridine perchlorate salt (PyHClO<sub>4</sub>) have been recorded in the 4000–300 and 3200–200 cm<sup>-1</sup> regions, respectively. The structure and vibrational spectra of pyridine salt have been investigated by means of *ab initio* and density functional theory (DFT) calculations. To examine the efficiency of basis sets in predicting the vibrational spectra of ClO<sub>4</sub><sup>-</sup> ion, several basis sets were used with the B3LYP and B2PLYP levels of theory. It was shown that the 6-311(3df) basis set gives reasonably vibrational wavenumbers for simulation of perchlorate ion experimental vibrational wavenumbers. Therefore, the B3LYP/6-311G(3df) level was used to calculate the vibrational spectra of pyridine perchlorate salt in CH<sub>3</sub>CN solution. For comparison, the vibrational wavenumbers were also calculated at the B3LYP/aug-cc-pVTZ level. The geometry of PyHClO<sub>4</sub> was calculated in the gas phase as well as in solutions, using SCRF-PCM method. According to these calculations, the structure and hydrogen bonding in PyHClO<sub>4</sub> is highly affected by media. Two hydrogen bonding systems between ClO<sub>4</sub><sup>-</sup> and pyridinium ions were recognized. The nature of these hydrogen bonds is theoretically investigated by using atoms in molecule (AIM) method and natural bond orbital (NBO) analysis. A normal coordinate analysis was performed by using the internal coordinates calculated at the B3LYP/6-311G(3df,p) level for the vibrational normal modes of the titled compound.

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## 1. Introduction

Pyridine (azabenzene), Py, is a heterocyclic aromatic tertiary amine that is characterized by a six-membered ring structure, which replaces one carbon-hydrogen unit in the benzene ring (C<sub>5</sub>H<sub>5</sub>N) with a nitrogen atom. The simplest member of the py family is py itself. Py and its derivatives are very important in industrial field as well as in biochemistry [1–3]. These compounds are very important in many biological processes [4]. They can be the parent compound of many drugs, including the barbiturates. These compounds are used as solvents and starting material for the synthesis of some important compounds such as insecticides, herbicides [5], medicines, vitamins [3], food flavorings, feed additives [6], rubber chemicals [7], explosives [8], disinfectants [9] and adhesives [10]. Py and its derivatives have been of spectroscopic significance as demonstrated by a huge number of studies in the past several decades [11–22].

Pyridinium salts are intermediates for synthesis of biological compounds [23,24] and exhibit antimicrobial and antiviral activity [25]. However, in spite of several works considering the vibrational spectroscopy study of these salts [26–32], to the best of our knowledge, there has been no report on the normal coordinate analysis, theoretical calculations, and the nature of hydrogen bonding of the pyridinium salts.

The aim of present work is the study of vibrational spectra and the nature of hydrogen bonding of pyridinium perchlorate, PyHClO<sub>4</sub>, by means of density functional theory, normal coordinate analysis, natural bond orbital analysis, NBO, and atoms in molecule theory, AIM. The results will be also used to see the effects of salt formation on the structure, vibrational frequencies of normal modes of pyridine ring.

## 2. Experimental

Py was purchased from Aldrich Chemical Company, Inc., and used without further purification. PyHClO<sub>4</sub> was prepared according to literature [26] and dried in an evacuated desiccator over P<sub>2</sub>O<sub>5</sub> for several days.

The IR spectra were recorded on a Bomem B-154 Fourier Transform Spectrophotometer in the 4000–600 cm<sup>-1</sup> region. The spectra were collected at 2 cm<sup>-1</sup> resolution by coadding the results of 15 scans.

The Far-IR spectra in the region 600–300 cm<sup>-1</sup> were obtained using a Thermo Nicolet Nexus 870 FT-IR spectrometer equipped with a DTGS/polyethylene detector and a solid substrate beam splitter. The spectrum was collected with a resolution of 2 cm<sup>-1</sup> 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

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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

Full geometry optimization has been performed for the titled compound, using the density functional three-parameter hybrid model, B3LYP [33,34], using 6-311G(3df,p) and aug-cc-pVTZ basis sets. The same methodology was used to calculate the harmonic vibrational frequencies. The polarizable continuum model (PCM) was chosen for the self-consistent reaction-field (SCRF) [35,36] calculations for solutions. To understand the efficiency of different basis sets in calculating the vibrational frequencies of the perchlorate counterion, the optimization of perchlorate ion,  $\text{ClO}_4^-$ , was performed at the B3LYP and Grimme's B2PLYP [37] levels with several basis sets. Subsequently, harmonic vibrational frequencies of  $\text{ClO}_4^-$  ion were calculated at the same levels of theory.

The vibrational frequencies of  $\text{PyHClO}_4$  were calculated with B3LYP using aug-cc-pVTZ and 6-311G(3df) basis sets.

The Raman activities are calculated at the B3LYP/6-311G(3df,p) level in  $\text{CH}_3\text{CN}$  solution, using PCM method. All computations were carried out with the Gaussian 09 program [38]. The GaussView program [39] was used to illustrate the calculated atomic displacements associated with normal modes.

A normal coordinate analysis was carried out to provide a complete description of the fundamental vibrational wavenumbers for the  $\text{PyHClO}_4$  molecule. The normal coordinates and potential energy distributions (PED) were calculated from appropriate combinations of internal coordinates obtained from Gaussian outputs, as explained elsewhere [40–42]. The full sets of 59 standard internal coordinates containing 14 redundancies are defined as given in Fig. S1 (Supplementary material). From these internal coordinates, a non-redundant set of local symmetry coordinates was constructed by a suitable linear combination of internal coordinates, which is given in Table S1 (Supplementary material).

By combining the results of GaussView 4.1.2 program [39] with the PEDs, the vibrational 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.

Since the perchlorate salts are highly polar with large dipole moments, the calculated vibrational wavenumbers at the gas phase would be far from those obtained in the condensed phases. Therefore, the vibrational wavenumbers of perchlorate salts were calculated in a solution. The polarizable continuum model (PCM) was chosen for the self-consistent reaction-field (SCRF) calculations for  $\text{CH}_3\text{CN}$  solution. The PCM was applied within the B3LYP/6-311G(3df,p) level to predict the vibrational wavenumbers in solution.

To determine the position of overlapped and hidden band frequencies more precisely, Lorentzian function is utilized for deconvolution of the infrared spectrum of the titled molecule.

AIM 2000 software [43] was applied to obtain the electron density at the hydrogen bond critical points, according to Bader's atoms in molecules (AIM) theory [44,45], to estimate the intramolecular hydrogen bond strength.

Orbital population and Wiberg bond orders [46] were calculated using NBO 3.0 program implemented in Gaussian 09 program.

## 4. Results and Discussion

### 4.1. Molecular Geometry

The atom numbering and structure of Py and  $\text{PyHClO}_4$  are depicted in Fig. 1. The selected geometrical parameters of Py and its perchlorate salt in the gas phase and solution, are compared in Table 1. As it is shown in this table, the C—C and C—N bond length are highly changed upon formation of salt. This could be explained by charge redistribution on the pyridine ring atoms due to participating of electron lone pairs of nitrogen atom in the N—H bond, see Section 4.2. On the other hand, according to Table 1, for both molecules, Py and  $\text{PyHClO}_4$ , C1—C2, C3—C4, and C4—C5 bond lengths in solution are considerably longer than the corresponding values in the gas phase, while the C1—N, C2—C3, and C5—N bond lengths are shorter in solution than those in the gas phase. The N—H bond length and  $\text{NH}\cdots\text{O}$  distance in the  $\text{PyHClO}_4$  are highly affected by the media. As Table 1 shows, the  $\text{NH}\cdots\text{O}$  intermolecular hydrogen bond is very strong in the gas phase and by increasing the dielectric constant of solvent, its strength reduces. The N—H6 $\cdots$ O1 angle is about  $174^\circ$  in the gas phase and slightly increases in solution by about  $3^\circ$ , while the C1—H1 $\cdots$ O2 angle is very small, about  $125^\circ$  in the gas phase, which in solution increases to about  $129^\circ$ . Our calculations also indicate the formation of a weak intermolecular hydrogen bond between C1H1 and O2 atom of  $\text{ClO}_4$  group. The strength of this bond is also reducing by increasing the dielectric constant of solvent. The effect of media on the  $\text{O}\cdots\text{N}$  distance is shown in Fig. 2a. The excellent linear correlation between  $\text{CH1}\cdots\text{O2}$  and  $\text{O1}\cdots\text{N}$  distances ( $R^2 = 0.9987$ ) is also shown in Fig. 2b. This figure indicates that the polar solvents try to pull apart the pyridinium and perchlorate ions, which results in weakening of both hydrogen bonds.

### 4.2. Aim Analysis

In the topological theory of atoms in molecule (AIM), upon formation of a chemical bond between two neighboring atoms, a bond critical point, BCP, appears between them, which the nature of the bond is described by total electronic density,  $\rho(r)$ , and its corresponding Laplacian,  $\nabla^2\rho(r)$  at this point [44]. The relation between Laplacian of total

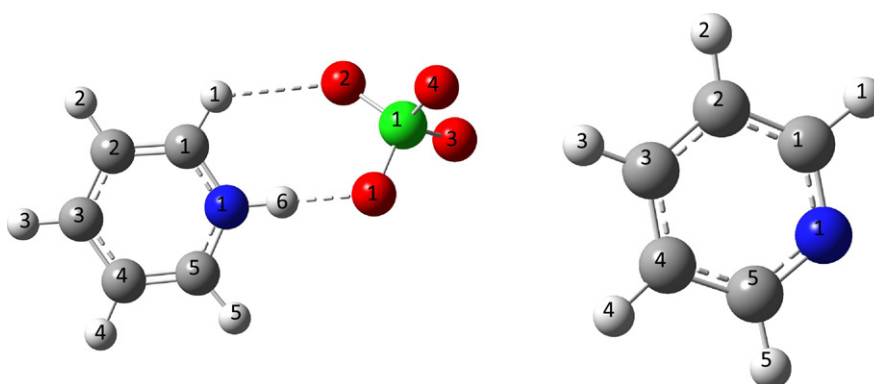


Fig. 1. Geometry and atom numbering of  $\text{PyHClO}_4$ .

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