



# Analysis of vibrational spectra of 2 and 3-methylpiperidine based on density functional theory calculations

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## ABSTRACT

The experimental and theoretical vibrational spectra of 2 and 3-methylpiperidine (abbreviated as 2-MP and 3-MP) were studied. The FT-Infrared spectra of 2-MP and 3-MP molecules were recorded in the liquid phase. The structural and spectroscopic analysis of the title molecules were made by using density functional harmonic calculations. For the title molecules, only one form was found most stable structure by using B3LYP level with the 6-311G (d,p) basis set. Selected experimental bands were assigned and characterized based on the scaled theoretical wave numbers by their total energy distribution (TED).

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## 1. Introduction

Piperidine, hexahydropyridine, is a family of heterocyclic organic compound derived from pyridine through hydrogenation. It has one nitrogen atom in the cycle. It is a clear liquid with pepper-like aroma. It boils at 106 °C, soluble in water, alcohol, and ether. The major application of piperidine is for the production of dipiperidinyl dithium tetra sulfide used as a rubber vulcanization accelerator. In pharmaceutical synthesis industry, it is used as a special solvent and a protecting group for peptide synthesis. Piperidine derivative compounds are used as intermediate to make crystal derivative of aromatic nitrogen compounds containing nuclear halogen atoms. Ring system compounds with nitrogen which have basic property play important roles as cyclic component in industrial field such as raw materials for hardener of epoxy resins, corrosion inhibitors, insecticides, accelerators for rubber, urethane catalysts, antioxidants and as a catalyst for silicone esters. They are used in manufacturing pharmaceuticals [1].

In our previous work [2], we reported the molecular structure and vibrational spectra of piperidine and 4-methylpiperidine by density functional theory calculations. In this work, we report DFT/B3LYP calculation results on 2 and 3-methylpiperidine molecules. The aim of this study is to give optimal molecular geometry, vibrational wave numbers and modes of free and deuterated species of 2 and 3 methylpiperidine and its deuterated species. The isotope effects of D atom were discussed for sensitive band to deuterated substitution.

## 2. Computational details

The molecular structures of 2 and 3-methylpiperidine (in vacuum) in the ground state were optimized by B3LYP with the 6-311G (d,p), 6-311++G (d,p) and cc-pVQZ basis sets. Density functional for all studies reported in this paper has the following form

$$E_{XC} = (1 - a_0)E_X^{LSDA} + a_0E_X^{HF} + a_X \Delta E_X^{B88} + a_c E_C^{LYP} + (1 - a_c)E_C^{VWN}$$

where the energy terms are the Slater exchange, the Hartree–Fock exchange, Becke's exchange functional correction, and the gradient corrected correlation functional of Lee, Yang and Parr and the local correlation functional of Vosko et al. [3]. RB3LYP with several basis sets levels of theory with the optimized geometries have been used to calculate all parameters of the title molecules.

Three sets of vibrational frequencies for these species were calculated with these methods and then scaled by corresponding scaling factors [4]. All the calculations were performed by using Gauss-view molecular visualization program and Gaussian 03 program package on the personal computer [5,6].

## 3. Result and discussion

Piperidine has two possible chair conformations, which differ in the axial (A) or equatorial (E) position of the N–H group. Other conformations that differ from the chair (boat, envelope or twist boat) were not considered because of their high energy [7–10]. The methyl derivatives in positions C<sub>2</sub> and C<sub>3</sub> of the ring can have four chair conformations characterized by the relative orientations of the N–H group (A or E) and of the C–Me group (a or e) [11]. All conformations were optimized by B3LYP/6-311G (d,p) basis set. The

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**Table 1**

The selected molecular properties of conformation of the 2 and 3-methylpiperidine (with the B3LYP/6-311G (d,p)).

		Energy (a.u.)	Energy differences (kcal/mol)	$E_{\text{HOMO}}$ (eV)	$E_{\text{LUMO}}$ (eV)	$\Delta E$ (eV)	$\mu$ (Debye)
3MP (Chair)	Ee	-291.300655553	0.00	-6.025	1.133	7.158	1.070
	Ae	-291.299849551	0.50	-5.842	0.915	6.757	1.078
	Ea	-291.298405852	1.41	-6.021	0.970	6.991	0.915
	Aa	-291.297162924	2.19	-5.854	1.045	6.899	1.132
2MP (Chair)	Ee	-291.303288058	0.00	-6.050	1.087	7.137	0.834
	Ae	-291.302041815	0.78	-5.884	1.119	7.003	1.024
	Ea	-291.298484584	3.01	-5.912	0.919	6.831	0.815
	Aa	-291.298005869	3.31	-5.862	0.909	6.771	1.059

selected molecular properties of all conformation of the 2 and 3-methylpiperidine listed in Table 1. As seen in Table 1, the 2 and 3-methylpiperidine molecules show the double equatorial form as the most stable.

### 3.1. Geometrical structures

The optimized geometric parameters (bond lengths and bond angles) of the title molecules were given in Table 2 by using B3LYP with 6-311G (d,p), 6-311++G (d,p) and cc-pVQZ basis sets. The atomic numbering is given in Fig. 1. The molecular structures of 2 and 3-methylpiperidine have been not studied by any diffraction technique. Therefore, the molecular structure of 2 and 3-methylpiperidine were compared with those of X-ray and electron diffraction data of piperidine [10,12].

Vayner and Ball [9] give only representative bond distance, bond angles and dihedral angles, or where appropriate, ranges for the parameter type (i.e. C–H bonds). In that study the C–N–C bond angles are slightly larger than the C–C–C or N–C–C bond angles while the C–N bond distances are predicted to be slightly shorter than C–C bond distances. Our data is consistent with those observations which can be seen from Table 1.

### 3.2. Assignment of fundamentals

The molecules of 2 and 3-methylpiperidine consist of 20 atoms, so it has 54 normal vibrational modes. The title molecules belong to  $C_1$  symmetry. The detailed vibrational assignments of fundamental modes free 2 and 3-methylpiperidine and its deuterated species along with the calculated IR intensities and normal mode description (characterized by TED) were reported in Table 3. The total energy distribution (TED) was calculated by using the Scaled Quantum Mechanics program (SQM) [13].

Chemicals were purchased from the Aldrich Chemical Company Inc., and used as received. The FT-IR spectra of the title molecules are shown in Fig. 2. The samples of 2 and 3-methylpiperidine are in liquid forms at room temperature. The FT-IR of the title molecules were recorded between  $4000\text{ cm}^{-1}$  and  $400\text{ cm}^{-1}$  region on a Mattson 1000 FT-IR spectrometer which was calibrated using polystyrene bands.

In  $4000\text{--}2000\text{ cm}^{-1}$  region, the vibrational spectra show characteristic bands of normal modes related to the asymmetric and symmetric stretching of the NH, CH bonds of methyl group, as well as the CH stretching modes of ring.

#### 3.2.1. NH vibration

The band recorded in the room temperature FT-IR spectrum at  $3276\text{ cm}^{-1}$  (3MP) and  $3274\text{ cm}^{-1}$  (2MP), are assigned to NH stretching. These bands were calculated  $3456\text{ cm}^{-1}$ ,  $3408\text{ cm}^{-1}$  and  $3417\text{ cm}^{-1}$  for 3-methylpiperidine and  $3442\text{ cm}^{-1}$ ,  $3396\text{ cm}^{-1}$  and  $3405\text{ cm}^{-1}$  for 2-methylpiperidine (respectively 6-311++G (d,p), 6-311G (d,p) and cc-pVQZ basis sets).

The NH stretching fundamental of piperidine was observed to the vapour band at  $3364\text{ cm}^{-1}$  [7]. Güllüoğlu et al. [14,15] was observed to the liquid band at  $3340\text{ cm}^{-1}$  for the NH stretching of the piperidine. The position of the methyl group in the piperidine ring influence the NH stretching wave number, which are decreased in the order 3-methylpiperidine > 2-methylpiperidine in the both experimental and theoretical calculations.

The NH stretching vibration was showed shifts toward a lower wave number ( $\sim 900\text{ cm}^{-1}$ ) in the deuterated derivative of 2 and 3-methylpiperidine. The isotopic ratios ( $\nu_{\text{NH}}/\nu_{\text{ND}}$ ) were (around) 1.36 (for 2 and 3-methylpiperidine). In addition to, some vibrations ( $\nu_{35}$ ,  $\nu_{28}$ ,  $\nu_{21}$ ,  $\nu_{20}$ ,  $\nu_{19}$  and  $\nu_{10}$ , etc.) were showed a small wave number ( $\sim 50\text{ cm}^{-1}$ ) (for 2-MP and 3-MP). These vibrations assigned at NCH bend and CN Str. Other vibrations were slightly different than its deuterated derivative. These shifts to lower values show

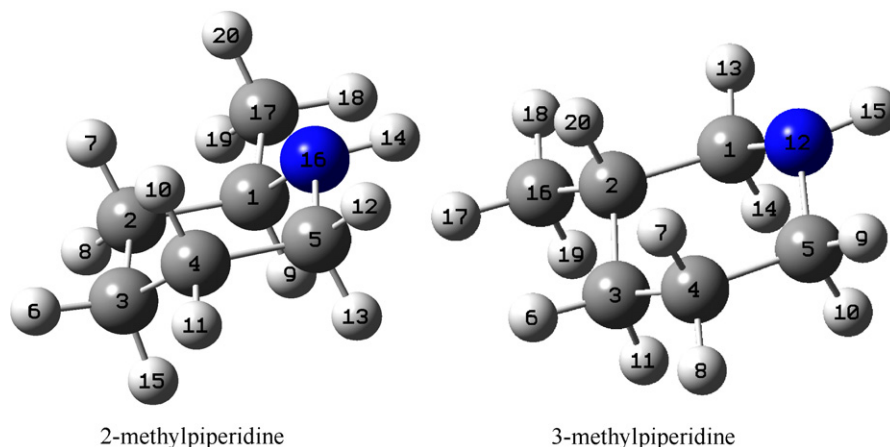


Fig. 1. Atomic numbering for studied molecules (in Ee conformations).

**Table 2**  
Bond lengths and bond angles for 2 and 3-methylpiperidine (in Ee conformation).

Bond angles	2-methylpiperidine					3-methylpiperidine					
	cc-pvqz	6-311G (d,p)	6-311++G (d,p)	X-ray <sup>a</sup>	E.D. <sup>b</sup>	cc-pvqz	6-311G (d,p)	6-311++G (d,p)	X-ray <sup>a</sup>	E.D. <sup>b</sup>	
C <sub>1</sub> –C <sub>2</sub>	1.531	1.535	1.535	1.523	1.530	C <sub>1</sub> –C <sub>2</sub>	1.531	1.535	1.535	1.523	1.530
C <sub>1</sub> –H <sub>9</sub>	1.105	1.108	1.108	0.980	1.098	C <sub>1</sub> –N <sub>12</sub>	1.460	1.463	1.464	1.464	1.461
C <sub>1</sub> –N <sub>16</sub>	1.464	1.468	1.468	1.460	1.469	C <sub>1</sub> –H <sub>13</sub>	1.091	1.094	1.094	0.980	1.098
C <sub>1</sub> –C <sub>17</sub>	1.522	1.526	1.526	–	–	C <sub>1</sub> –H <sub>14</sub>	1.104	1.108	1.107	0.980	1.098
C <sub>2</sub> –C <sub>3</sub>	1.531	1.535	1.535	1.523	1.530	C <sub>2</sub> –C <sub>3</sub>	1.534	1.538	1.538	1.518	1.530
C <sub>2</sub> –H <sub>7</sub>	1.093	1.096	1.096	0.980	1.098	C <sub>2</sub> –C <sub>16</sub>	1.527	1.530	1.530	–	–
C <sub>2</sub> –H <sub>8</sub>	1.092	1.095	1.095	0.980	1.098	C <sub>2</sub> –H <sub>20</sub>	1.094	1.097	1.097	0.980	1.098
C <sub>3</sub> –C <sub>4</sub>	1.530	1.534	1.534	1.518	1.530	C <sub>3</sub> –C <sub>4</sub>	1.531	1.535	1.535	1.520	1.530
C <sub>3</sub> –H <sub>6</sub>	1.091	1.094	1.094	0.980	1.098	C <sub>3</sub> –H <sub>6</sub>	1.092	1.095	1.095	0.980	1.098
C <sub>3</sub> –H <sub>15</sub>	1.094	1.097	1.097	0.980	1.098	C <sub>3</sub> –H <sub>11</sub>	1.095	1.099	1.099	0.980	1.098
C <sub>4</sub> –C <sub>5</sub>	1.526	1.530	1.530	1.520	1.530	C <sub>4</sub> –C <sub>5</sub>	1.526	1.530	1.530	1.518	1.530
C <sub>4</sub> –H <sub>10</sub>	1.092	1.095	1.095	0.980	1.098	C <sub>4</sub> –H <sub>7</sub>	1.092	1.095	1.095	0.980	1.098
C <sub>4</sub> –H <sub>11</sub>	1.091	1.094	1.094	0.980	1.098	C <sub>4</sub> –H <sub>8</sub>	1.091	1.094	1.095	0.980	1.098
C <sub>5</sub> –H <sub>12</sub>	1.090	1.093	1.093	0.980	1.098	C <sub>5</sub> –H <sub>9</sub>	1.090	1.093	1.093	0.980	1.098
C <sub>5</sub> –H <sub>13</sub>	1.103	1.107	1.106	0.980	1.098	C <sub>5</sub> –H <sub>10</sub>	1.103	1.107	1.107	0.980	1.098
C <sub>5</sub> –N <sub>16</sub>	1.460	1.464	1.464	1.461	1.469	C <sub>5</sub> –N <sub>12</sub>	1.460	1.463	1.464	1.464	1.461
H <sub>14</sub> –N <sub>16</sub>	1.011	1.014	1.014	0.849	1.015	N <sub>12</sub> –H <sub>15</sub>	1.010	1.013	1.013	0.849	1.015
C <sub>17</sub> –H <sub>18</sub>	1.091	1.095	1.095	–	–	C <sub>16</sub> –H <sub>17</sub>	1.090	1.093	1.094	–	–
C <sub>17</sub> –H <sub>19</sub>	1.090	1.093	1.093	–	–	C <sub>16</sub> –H <sub>18</sub>	1.091	1.094	1.094	–	–
C <sub>17</sub> –H <sub>20</sub>	1.090	1.093	1.093	–	–	C <sub>16</sub> –H <sub>19</sub>	1.092	1.095	1.095	–	–
<b>Bond lengths</b>											
C <sub>2</sub> –C <sub>1</sub> –H <sub>9</sub>	107.3	107.3	107.3	109.3	–	C <sub>2</sub> –C <sub>1</sub> –N <sub>12</sub>	110.4	110.2	110.4	109.8	110.5
C <sub>2</sub> –C <sub>1</sub> –N <sub>16</sub>	108.6	108.5	108.6	109.3	–	C <sub>2</sub> –C <sub>1</sub> –H <sub>13</sub>	110.0	109.8	110.0	109.2	–
H <sub>9</sub> –C <sub>1</sub> –N <sub>16</sub>	112.2	112.1	112.2	109.3	–	C <sub>2</sub> –C <sub>1</sub> –H <sub>14</sub>	108.3	108.4	108.4	109.3	–
C <sub>2</sub> –C <sub>1</sub> –C <sub>17</sub>	110.6	110.8	110.5	110.7	109.6	N <sub>12</sub> –C <sub>1</sub> –H <sub>13</sub>	108.5	108.5	108.4	109.3	–
H <sub>9</sub> –C <sub>1</sub> –C <sub>17</sub>	108.2	108.3	108.2	–	–	N <sub>12</sub> –C <sub>1</sub> –H <sub>14</sub>	112.1	112.4	112.1	109.3	–
N <sub>16</sub> –C <sub>1</sub> –C <sub>17</sub>	109.7	109.5	109.7	–	–	H <sub>13</sub> –C <sub>1</sub> –H <sub>14</sub>	107.1	107.2	107.2	109.4	–
C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	111.6	111.5	111.5	110.2	109.6	C <sub>1</sub> –C <sub>2</sub> –C <sub>3</sub>	109.5	109.5	109.5	110.7	109.6
C <sub>1</sub> –C <sub>2</sub> –H <sub>7</sub>	108.2	108.2	108.2	109.2	–	C <sub>1</sub> –C <sub>2</sub> –C <sub>16</sub>	111.5	111.6	111.5	–	–
C <sub>1</sub> –C <sub>2</sub> –H <sub>8</sub>	109.4	109.4	109.4	109.2	–	C <sub>1</sub> –C <sub>2</sub> –H <sub>20</sub>	106.8	106.7	106.8	109.1	–
C <sub>3</sub> –C <sub>2</sub> –H <sub>7</sub>	109.6	109.6	109.7	109.2	–	C <sub>3</sub> –C <sub>2</sub> –C <sub>16</sub>	111.9	111.9	111.9	–	–
C <sub>3</sub> –C <sub>2</sub> –H <sub>8</sub>	110.3	110.4	110.3	109.2	–	C <sub>3</sub> –C <sub>2</sub> –H <sub>20</sub>	107.9	107.9	108.0	109.2	–
H <sub>7</sub> –C <sub>2</sub> –H <sub>8</sub>	107.3	107.3	107.3	109.4	110.0	C <sub>16</sub> –C <sub>2</sub> –H <sub>20</sub>	108.6	108.7	108.7	–	–
C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub>	110.9	110.9	110.9	110.3	111.1	C <sub>2</sub> –C <sub>3</sub> –C <sub>4</sub>	111.8	111.8	111.8	110.3	111.1
C <sub>2</sub> –C <sub>3</sub> –H <sub>6</sub>	110.3	110.3	110.3	109.3	–	C <sub>2</sub> –C <sub>3</sub> –H <sub>6</sub>	110.0	110.0	110.0	109.2	–
C <sub>2</sub> –C <sub>3</sub> –H <sub>15</sub>	109.1	109.1	109.2	109.2	–	C <sub>2</sub> –C <sub>3</sub> –H <sub>11</sub>	108.7	108.6	108.7	109.2	–
C <sub>4</sub> –C <sub>3</sub> –H <sub>6</sub>	110.5	110.5	110.5	109.2	–	C <sub>4</sub> –C <sub>3</sub> –H <sub>6</sub>	110.4	110.4	110.3	109.2	–
C <sub>4</sub> –C <sub>3</sub> –H <sub>15</sub>	109.1	109.1	109.1	109.2	–	C <sub>4</sub> –C <sub>3</sub> –H <sub>11</sub>	109.2	109.2	109.2	109.2	–
H <sub>6</sub> –C <sub>3</sub> –H <sub>15</sub>	106.5	106.5	106.5	109.4	110.0	H <sub>6</sub> –C <sub>3</sub> –H <sub>11</sub>	106.4	106.4	106.4	109.4	–
C <sub>3</sub> –C <sub>4</sub> –C <sub>5</sub>	110.5	110.4	110.5	110.7	109.6	C <sub>3</sub> –C <sub>4</sub> –C <sub>5</sub>	110.8	110.7	110.7	110.2	109.6
C <sub>3</sub> –C <sub>4</sub> –H <sub>10</sub>	109.6	109.6	109.7	109.8	–	C <sub>3</sub> –C <sub>4</sub> –H <sub>7</sub>	109.6	109.6	109.6	109.2	–
C <sub>3</sub> –C <sub>4</sub> –H <sub>11</sub>	110.5	110.6	110.5	109.1	–	C <sub>3</sub> –C <sub>4</sub> –H <sub>8</sub>	110.4	110.4	110.4	109.2	–
C <sub>5</sub> –C <sub>4</sub> –H <sub>10</sub>	108.7	108.5	108.7	109.3	–	C <sub>5</sub> –C <sub>4</sub> –H <sub>7</sub>	108.6	108.5	108.7	109.3	–
C <sub>5</sub> –C <sub>4</sub> –H <sub>11</sub>	109.8	109.9	109.7	109.3	–	C <sub>5</sub> –C <sub>4</sub> –H <sub>8</sub>	109.8	109.9	109.7	109.2	–
H <sub>10</sub> –C <sub>4</sub> –H <sub>11</sub>	107.4	107.4	107.4	109.4	110.0	H <sub>7</sub> –C <sub>4</sub> –H <sub>8</sub>	107.3	107.4	107.3	109.4	110.0
C <sub>4</sub> –C <sub>5</sub> –H <sub>12</sub>	110.4	110.3	110.4	109.3	–	C <sub>4</sub> –C <sub>5</sub> –H <sub>9</sub>	110.4	110.3	110.4	109.2	–
C <sub>4</sub> –C <sub>5</sub> –H <sub>13</sub>	108.7	108.8	108.8	109.3	–	C <sub>4</sub> –C <sub>5</sub> –H <sub>10</sub>	108.8	108.8	108.8	109.2	–
C <sub>4</sub> –C <sub>5</sub> –N <sub>16</sub>	109.8	109.6	109.8	109.8	110.5	C <sub>4</sub> –C <sub>5</sub> –N <sub>12</sub>	109.5	109.3	109.5	109.9	110.5
H <sub>12</sub> –C <sub>5</sub> –H <sub>13</sub>	107.1	107.2	107.2	109.4	110.0	H <sub>9</sub> –C <sub>5</sub> –H <sub>10</sub>	107.2	107.3	107.3	109.4	110.0
H <sub>12</sub> –C <sub>5</sub> –N <sub>16</sub>	108.4	108.4	108.4	109.3	–	H <sub>9</sub> –C <sub>5</sub> –N <sub>12</sub>	108.6	108.5	108.5	109.3	–
H <sub>13</sub> –C <sub>5</sub> –N <sub>16</sub>	112.0	112.3	112.0	109.3	–	H <sub>10</sub> –C <sub>5</sub> –N <sub>12</sub>	112.1	112.3	112.0	109.3	–
C <sub>1</sub> –N <sub>16</sub> –C <sub>5</sub>	113.4	113.1	113.3	111.0	110.7	C <sub>1</sub> –N <sub>12</sub> –C <sub>5</sub>	112.5	112.2	112.5	111.0	110.7
C <sub>1</sub> –N <sub>16</sub> –H <sub>14</sub>	110.0	109.5	110.0	108.2	108.4	C <sub>1</sub> –N <sub>12</sub> –H <sub>15</sub>	110.4	109.9	110.4	108.2	108.4
C <sub>5</sub> –N <sub>16</sub> –H <sub>14</sub>	110.3	109.8	110.3	108.5	108.4	C <sub>5</sub> –N <sub>12</sub> –H <sub>15</sub>	110.5	110.0	110.5	108.5	108.4
C <sub>1</sub> –C <sub>17</sub> –H <sub>18</sub>	111.1	111.1	111.1	–	–	C <sub>2</sub> –C <sub>16</sub> –H <sub>17</sub>	111.0	111.0	111.0	–	–
C <sub>1</sub> –C <sub>17</sub> –H <sub>19</sub>	110.8	110.9	110.7	–	–	C <sub>2</sub> –C <sub>16</sub> –H <sub>18</sub>	111.4	111.4	111.4	–	–
C <sub>1</sub> –C <sub>17</sub> –H <sub>20</sub>	110.4	110.2	110.4	–	–	C <sub>2</sub> –C <sub>16</sub> –H <sub>19</sub>	111.1	111.2	111.2	–	–
H <sub>18</sub> –C <sub>17</sub> –H <sub>19</sub>	107.6	107.6	107.6	–	–	H <sub>17</sub> –C <sub>16</sub> –H <sub>18</sub>	107.6	107.6	107.6	–	–
H <sub>18</sub> –C <sub>17</sub> –H <sub>20</sub>	108.0	108.0	108.0	–	–	H <sub>17</sub> –C <sub>16</sub> –H <sub>19</sub>	107.5	107.5	107.5	–	–
H <sub>19</sub> –C <sub>17</sub> –H <sub>20</sub>	108.6	108.7	108.6	–	–	H <sub>18</sub> –C <sub>16</sub> –H <sub>19</sub>	107.7	107.7	107.7	–	–

<sup>a</sup> X-ray data taken from [12].

<sup>b</sup> Electron diffraction data taken from [10].

that these NH stretching, NCH bending and NC stretching modes were sensitive to deuterated substitution.

### 3.2.2. CH stretching vibrations

The CH stretching modes of the ring and methyl group were experimentally observed at 2730 cm<sup>-1</sup>, 2796 cm<sup>-1</sup>, 2854 cm<sup>-1</sup>, 2919 cm<sup>-1</sup> and 2933 cm<sup>-1</sup> for 2-methylpiperidine, 2730 cm<sup>-1</sup>, 2800 cm<sup>-1</sup>, 2868 cm<sup>-1</sup> and 2920 cm<sup>-1</sup> for 3-methylpiperidine.

Eleven C–H stretching modes ( $\nu_{42}$ – $\nu_{53}$ ) were predicted in the range from 2770 cm<sup>-1</sup> to 3000 cm<sup>-1</sup> for both molecules. The C–H stretching modes of the 3-methylpiperidine were experimentally slightly larger than those of 2-methylpiperidine.

### 3.2.3. CC–CN vibrations

The CC and CN stretching vibrations were observed at 1317 cm<sup>-1</sup>(CN Str), 1051 cm<sup>-1</sup>(CC Str) for piperidine [16].

**Table 3**  
Comparison of the observed and calculated vibrational spectra of 2 and 3-methylpiperidine (for B3LYP calculations).

2-Methylpiperidine						3-Methylpiperidine							
6-311++G (d,p)		6-311G (d,p)		cc-pVQZ	Exp. IR	TED <sup>b</sup> (%)	6-311++G (d,p)		6-311 G (d,p)		cc-pVQZ	Exp. IR	TED <sup>b</sup> (%)
NH		ND		NH			NH		ND		NH		
Freq <sup>c</sup>	IR <sup>a</sup>	Freq <sup>c</sup>	Freq <sup>d</sup>	Freq <sup>e</sup>			Freq <sup>c</sup>	IR <sup>a</sup>	Freq <sup>c</sup>	Freq <sup>d</sup>	Freq <sup>e</sup>		
$\nu_1$	156	0.330	154	153	155	$\Gamma_{\text{CNCC}}(38) \Gamma_{\text{CCCH}}(26)$	155	0.261	155	152	154		$\Gamma_{\text{CCCH}}(23) \Gamma_{\text{CCCC}}(14) \text{(R-M)} \Gamma_{\text{HCCC}}(12)$
$\nu_2$	218	0.270	218	216	215	$\Gamma_{\text{HCCC}}(26) \Gamma_{\text{HCCN}}(26) \Gamma_{\text{HCCH}}(11)$	208	0.081	207	206	205		$\Gamma_{\text{HCCC}}(69) \Gamma_{\text{HCH}}(19) \text{R-M}$
$\nu_3$	244	1.241	239	242	241	$\Gamma_{\text{CCCH}}(15) \Gamma_{\text{CNCH}}(12) \Gamma_{\text{HCCH}}(15) \text{(R-M)}$	241	0.910	237	239	238		$\Gamma_{\text{HCCC}}(10) \Gamma_{\text{CHCH}}(10)$
$\nu_4$	304	0.617	302	301	302	$\delta_{\text{CCH}_3}(22) \delta_{\text{NCH}_3}(16) \text{(R)} \Gamma_{\text{HNCC}}(12) \text{(R-M)}$	299	0.140	297	296	297		$\delta_{\text{CCC}}(40) \Gamma_{\text{HCCC}}(30) \text{R-M}$
$\nu_5$	329	1.119	329	326	326	$\Gamma_{\text{CCCH}}(20) \Gamma_{\text{NCCH}}(12) \Gamma_{\text{NCCC}}(11)$	341	1.370	331	338	338		$\Gamma_{\text{HCCC}}(18) \Gamma_{\text{CHCC}}(11) \Gamma_{\text{CHCH}}(13) \Gamma_{\text{HCCH}}(12)$
$\nu_6$	413	0.808	410	409	411	$\delta_{\text{NCC}}(14) \nu_{\text{CC}}(13)$	412	2.831	404	408	409		$\delta_{\text{CCC}}(19) \Gamma_{\text{CCCH}}(12) \Gamma_{\text{CNCH}}(10)$
$\nu_7$	449	2.769	432	444	446	$\delta_{\text{CCC}}(18)$	427	2.081	425	423	423	425 vw	$\Gamma_{\text{CCCH}}(39)$
$\nu_8$	474	9.206	456	470	471	$\Gamma_{\text{HCCN}}(15) \Gamma_{\text{HNCC}}(13) \Gamma_{\text{CNCC}}(11)$	445	4.123	439	440	442	456 vw	$\delta_{\text{CCC}}(21) \Gamma_{\text{CCCH}}(14) \Gamma_{\text{CHCH}}(11)$
$\nu_9$	548	8.921	528	542	545	$\delta_{\text{NCC}}(10) \Gamma_{\text{HCCC}}(10)$	547	21.49	506	542	543	564 s	$\Gamma_{\text{CNCH}}(17) \delta_{\text{NCC}}(12)$
$\nu_{10}$	729	64.01	635	731	723	$\nu_{\text{CN}}(19) \Gamma_{\text{HNCH}}(18) \Gamma_{\text{HNCC}}(16)$	735	52.42	642	738	731	747 vs	$\Gamma_{\text{HNCH}}(26) \nu_{\text{CC}}(22) \Gamma_{\text{HNCC}}(15) \delta_{\text{HNC}}(10)$
$\nu_{11}$	773	1.050	766	766	767	$\nu_{\text{CC}}(45) \nu_{\text{CN}}(12)$	770	3.862	766	762	764		$\nu_{\text{CC}}(37) + \nu_{\text{NC}}(8)$
$\nu_{12}$	820	2.492	813	812	814	$\Gamma_{\text{HCCH}}(13) \nu_{\text{CC}}(10)$	844	3.296	819	836	837	790 vw	$\nu_{\text{CC}}(41) + \nu_{\text{CN}}(18)$
$\nu_{13}$	838	0.149	825	829	831	$\nu_{\text{CC}}(58)$	857	5.812	850	848	850	855 s	$\nu_{\text{CC}}(29)$
$\nu_{14}$	875	0.867	858	867	868	$\nu_{\text{CC}}(41) \delta_{\text{CCH}_3}(15) \nu_{\text{CN}}(16)$	882	1.739	872	874	876	872 w	$\nu_{\text{NC}}(24) \nu_{\text{CC}}(13) \text{R} \delta_{\text{CCH}}(16) \text{R-M}$
$\nu_{15}$	893	5.410	882	886	887	$\Gamma_{\text{HCCH}}(26) \delta_{\text{CCH}}(11) \Gamma_{\text{HNCH}}(10)$	894	5.481	888	887	888	912 m	$\delta_{\text{CCH}}(17) \text{R-M} \Gamma_{\text{HNCH}}(12) \text{R}$
$\nu_{16}$	958	1.582	932	948	950	$\nu_{\text{CCH}_3}(23) \nu_{\text{CC}}(18) \delta_{\text{CCH}}(10)$	963	3.841	945	953	956		$\nu_{\text{C-CH}_3}(16) \nu_{\text{NC}}(10) \nu_{\text{CC}}(9) \text{R-M}$
$\nu_{17}$	968	1.562	953	960	961	$\delta_{\text{CCH}_3}(25) \nu_{\text{CC}}(29) \nu_{\text{CN}}(10)$	969	1.915	963	959	961	960 w	$\nu_{\text{CC}}(24) + \nu_{\text{C-CH}_3}(18) + \delta_{\text{CCH}}(19) \text{R-M}$
$\nu_{18}$	996	1.746	990	986	988	$\delta_{\text{CCH}_3}(16) \delta_{\text{CCH}}(12)$	986	1.517	974	976	978	978 m	$\delta_{\text{CCH}}(12) \nu_{\text{CC}}(10) \text{R-M}$
$\nu_{19}$	1040	4.114	995	1029	1031	$\nu_{\text{CC}}(45)$	1037	0.756	992	1027	1028	998 w	$\nu_{\text{CC}}(55)$
$\nu_{20}$	1071	8.456	1056	1059	1062	$\nu_{\text{CCH}_3}(18) \nu_{\text{CN}}(18) \nu_{\text{CC}}(10)$	1088	3.198	1041	1077	1080	1055 w	$\nu_{\text{CCH}_3}(37) \nu_{\text{CC}}(26)$
$\nu_{21}$	1107	11.99	1071	1096	1098	$\nu_{\text{CN}}(22) \nu_{\text{CCH}_3}(15) \delta_{\text{ring}}(11)$	1111	14.67	1085	1099	1100		$\nu_{\text{CN}}(37) \nu_{\text{CC}}(26)$
$\nu_{22}$	1113	15.79	1113	1101	1102	$\nu_{\text{CN}}(25) \nu_{\text{CC}}(22)$	1123	0.623	1111	1111	1114		$\nu_{\text{CN}}(20) \nu_{\text{CC}}(14) \text{R} \delta_{\text{HCC}}(12) \text{RM}$
$\nu_{23}$	1144	2.231	1122	1132	1137	$\delta_{\text{HCH}}(12)$	1146	3.118	1144	1134	1140	1121 s	$\delta_{\text{CCH}}(12)$
$\nu_{24}$	1153	0.786	1145	1141	1145	$\delta_{\text{CCH}}(17) \delta_{\text{NCH}}(10)$	1155	7.014	1147	1142	1146	1160 s	$\delta_{\text{NCH}}(19) \nu_{\text{NC}}(14) \text{R} \Gamma_{\text{CCCH}}(9) \text{R-M}$
$\nu_{25}$	1218	3.129	1198	1206	1209	$\delta_{\text{CCH}}(17) \nu_{\text{NC}}(11)$	1216	0.957	1194	1203	1206	1222 m	$\delta_{\text{CCH}}(28)$
$\nu_{26}$	1259	2.358	1240	1246	1249	$\delta_{\text{CCH}}(35) \delta_{\text{NCH}}(12) \Gamma_{\text{CCCH}}(10)$	1264	0.720	1241	1249	1253		$\delta_{\text{CCH}}(42) \delta_{\text{NCH}}(10)$
$\nu_{27}$	1265	2.412	1260	1252	1255	$\delta_{\text{CCH}}(31)$	1274	3.125	1270	1261	1264	1282 m	$\delta_{\text{HCH}}(25) \delta_{\text{CCH}}(17)$
$\nu_{28}$	1309	9.310	1272	1295	1300	$\delta_{\text{CCH}}(30) \Gamma_{\text{CNCH}}(11) \Gamma_{\text{HCCH}}(10)$	1287	8.839	1275	1272	1277		$\delta_{\text{HCH}}(21) \Gamma_{\text{HCCH}}(17) \delta_{\text{CCH}}(11)$
$\nu_{29}$	1325	22.01	1312	1311	1315	$\Gamma_{\text{HCCH}}(24) \delta_{\text{CCH}}(14)$	1310	1.913	1301	1297	1301	1309 vw	$\delta_{\text{CCH}}(35) \Gamma_{\text{HCCH}}(13)$
$\nu_{30}$	1335	1.422	1331	1322	1328	$\delta_{\text{CCH}}(35) \Gamma_{\text{HCCH}}(16)$	1336	8.063	1312	1323	1325		$\Gamma_{\text{HCCH}}(13) \delta_{\text{CCH}}(18) \text{R} \Gamma_{\text{HCCH}}(14) \text{R-M}$
$\nu_{31}$	1347	0.904	1342	1334	1336	$\delta_{\text{CCH}}(30) \Gamma_{\text{HCCH}}(17)$	1344	0.076	1344	1330	1335	1336 w	$\delta_{\text{CCH}}(40) \Gamma_{\text{HCCH}}(14)$
$\nu_{32}$	1353	0.376	1347	1339	1344	$\delta_{\text{CCH}}(13) \Gamma_{\text{HCCH}}(12)$	1357	0.606	1347	1344	1346		$\Gamma_{\text{HCCH}}(28) \text{R-M} \delta_{\text{CCH}}(21)$
$\nu_{33}$	1378	3.008	1368	1363	1367	$\delta_{\text{CCH}}(16) \text{R} \Gamma_{\text{CNCH}}(14) \Gamma_{\text{HCCH}}(10) \text{M}$	1378	3.237	1366	1364	1368	1376 m	$\delta_{\text{HCH}}(44) \text{M} \delta_{\text{HCC}}(39) \text{R-M}$
$\nu_{34}$	1378	12.83	1377	1367	1368	$\delta_{\text{HCH}}(42) \text{M} \delta_{\text{CCH}}(38) \text{R-M}$	1388	2.347	1378	1376	1379		$\delta_{\text{HCC}}(20) \Gamma_{\text{CNCH}}(11)$
$\nu_{35}$	1439	6.996	1378	1424	1428	$\delta_{\text{HCH}}(13) \text{R} \delta_{\text{CNH}}(12) \delta_{\text{HCH}}(11) \text{M}$	1447	3.987	1386	1431	1437		$\Gamma_{\text{HCCH}}(22) \delta_{\text{HNC}}(20) \delta_{\text{HCH}}(11)$
$\nu_{36}$	1449	0.680	1444	1433	1437	$\delta_{\text{HCH}}(14) \text{R} \delta_{\text{HCH}}(13) \text{M} \delta_{\text{CNH}}(11) \text{R}$	1450	2.560	1449	1435	1439		$\delta_{\text{HNC}}(14) \Gamma_{\text{HCCH}}(12) \delta_{\text{HCH}}(12)$
$\nu_{37}$	1452	8.164	1451	1436	1441	$\Gamma_{\text{HCCH}}(32) \delta_{\text{HCH}}(26)$	1456	3.379	1455	1440	1444	1443 vw	$\Gamma_{\text{HCCH}}(35) \delta_{\text{HCH}}(24)$
$\nu_{38}$	1460	6.344	1459	1444	1448	$\Gamma_{\text{HCCH}}(28) \delta_{\text{HCH}}(19)$	1462	0.038	1460	1446	1451	1458 s	$\delta_{\text{HCH}}(23) \Gamma_{\text{HNCH}}(14) \Gamma_{\text{CNCH}}(10)$
$\nu_{39}$	1466	2.211	1460	1452	1454	$\delta_{\text{CCH}}(33) \text{R-M} \Gamma_{\text{HCCC}}(10) \text{M}$	1465	5.161	1465	1450	1453		$\delta_{\text{HCH}}(43) \Gamma_{\text{HCCC}}(19) \delta_{\text{HCC}}(12) \Gamma_{\text{HCCH}}(10)$
$\nu_{40}$	1470	7.463	1466	1455	1458	$\delta_{\text{HCH}}(28) \delta_{\text{CHH}}(16) \Gamma_{\text{HCCH}}(10) \text{M}$	1468	4.304	1467	1453	1455		$\delta_{\text{HCH}}(43) \Gamma_{\text{HCCC}}(12) \text{M} \delta_{\text{HCC}}(12) \text{R-M}$
$\nu_{41}$	1472	1.292	1472	1457	1461	$\delta_{\text{HCH}}(21) \Gamma_{\text{HCCH}}(11) \Gamma_{\text{CNCH}}(10)$	1475	5.028	1475	1460	1464		$\delta_{\text{HCH}}(26) \Gamma_{\text{HCCH}}(10)$
$\nu_{42}$	2810	55.93	2810	2776	2782	$\nu_{\text{CH}}(98)$	2821	41.06	2821	2784	2794	2730 m	$\nu_{\text{CH}}(99)$
$\nu_{43}$	2833	100	2833	2798	2807	$\nu_{\text{CH}}(98)$	2829	100	2829	2793	2803	2800 s	$\nu_{\text{CH}}(99)$
$\nu_{44}$	2935	24.28	2935	2904	2909	$\nu_{\text{CH}}(85)$	2923	14.16	2923	2892	2897	2868 w	$\nu_{\text{CH}}(90)$
$\nu_{45}$	2946	18.02	2946	2914	2919	$\nu_{\text{CH}_2}(88)$	2942	12.26	2942	2910	2914		$\nu_{\text{CH}_2}(84)$
$\nu_{46}$	2953	48.69	2953	2921	2927	$\nu_{\text{CH}_3}(61) \nu_{\text{CH}_2}(32) \text{M}$	2948	40.09	2948	2916	2923	2920 s	$\nu_{\text{CH}_3}(90) \text{M}$
$\nu_{47}$	2953	7.084	2953	2921	2928	$\nu_{\text{CH}_2}(60) \nu_{\text{CH}_3}(31) \text{M}$	2953	14.53	2953	2921	2926		$\nu_{\text{CH}_2}(90) \text{M}$

$\nu_{48}$	2982	52.27	2982	2950	2955	2976	46.29	2976	2944	2949	$\nu_{\text{CH}_2}$ (81)	$\nu_{\text{CH}}$ (14)
$\nu_{49}$	2988	34.40	2988	2954	2960	2984	24.22	2984	2948	2954	$\nu_{\text{CH}}$ (91)	
$\nu_{50}$	2989	31.92	2989	2956	2960	2990	37.11	2990	2955	2961	$\nu_{\text{CH}}$ (98)	
$\nu_{51}$	2996	56.82	2996	2964	2968	2994	31.30	2994	2962	2966	$\nu_{\text{CH}_2}$ (84)	
$\nu_{52}$	3011	30.75	3011	2978	2983	3006	49.19	3006	2974	2979	$\nu_{\text{CH}_2}$ (94)M	
$\nu_{53}$	3028	28.99	3028	2996	2999	3012	29.09	3012	2980	2985	$\nu_{\text{CH}_2}$ (99)M	
$\nu_{54}$	3442	0.086	2518	3396	3405	3456	0.068	2528	3408	3417	$\nu_{\text{NH}}$ (100)	

R: The ring of piperidine, M: Methyl group,  $\nu$ : Stretching,  $\delta$ : Bending,  $\Gamma$ : Torsion, vw: Very weak, w: Weak, m: Medium, s: Strong, vs: Very strong.

<sup>a</sup> Relative absorption intensities normalized with highest peak absorption equal to 100.

<sup>b</sup> Total energy distribution calculated B3LYP/6-311++G (d,p).

<sup>c</sup> Scaling factor: 0.978.

<sup>d</sup> Scaling factor: 0.967.

<sup>e</sup> Scaling factor: 0.969.

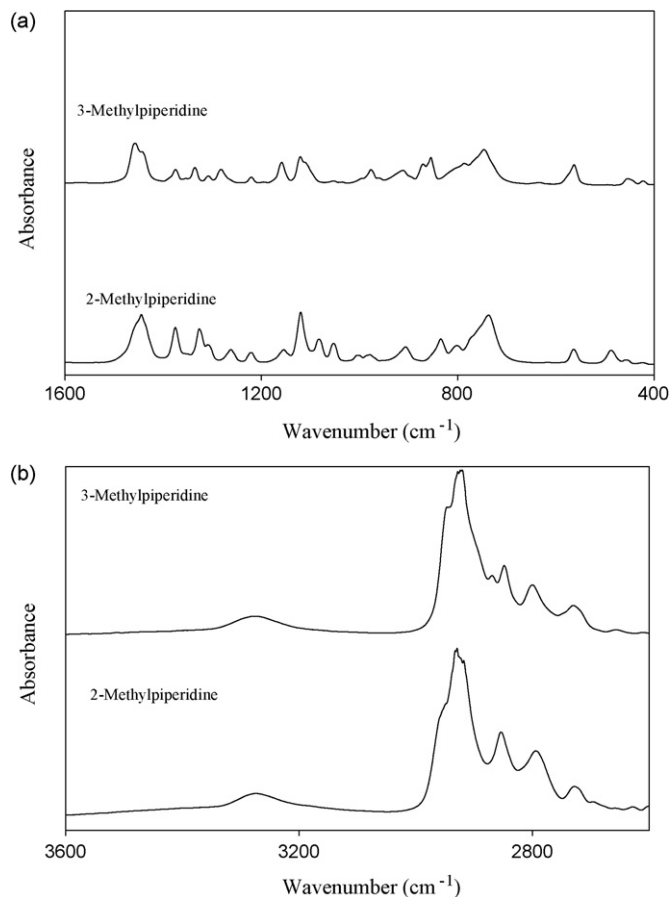
These vibrations were observed  $1045\text{ cm}^{-1}$  (Ring Str) for 4-methylpiperidine [2]. As seen in Table 3, seven peaks were observed in the  $740\text{--}1085\text{ cm}^{-1}$  range, which were at  $740\text{ cm}^{-1}$ ,  $804\text{ cm}^{-1}$ ,  $908\text{ cm}^{-1}$ ,  $982\text{ cm}^{-1}$ ,  $1006\text{ cm}^{-1}$ ,  $1055\text{ cm}^{-1}$  and  $1085\text{ cm}^{-1}$  for 2-methylpiperidine. The six peaks were observed in the  $747\text{--}1055\text{ cm}^{-1}$  range, which were at  $747\text{ cm}^{-1}$ ,  $790\text{ cm}^{-1}$ ,  $912\text{ cm}^{-1}$ ,  $978\text{ cm}^{-1}$ ,  $998\text{ cm}^{-1}$  and  $1055\text{ cm}^{-1}$  for 3-methylpiperidine. These vibrations revealed to be mixed with C–C, C–N stretching and some bending vibrations. The position of the methyl group in the piperidine ring influence the CC and CN stretching wave number, which are decreased in the order 2-methylpiperidine > 3-methylpiperidine in the both experimental and theoretical calculations.

### 3.2.4. Methylene group vibrations

For the assignments of  $\text{CH}_2$  group frequencies, basically six fundamentals can be associated to each  $\text{CH}_2$  group namely;  $\text{CH}_2$  sy-symmetric stretch;  $\text{CH}_2$  asy-asymmetric stretch;  $\text{CH}_2$  sciss-scissoring;  $\text{CH}_2$  rock-rocking,  $\text{CH}_2$  wag-wagging and  $\text{CH}_2$  twist-twisting modes of  $\text{CH}_2$  group would be expected. The fundamental  $\text{CH}_2$  vibrations are able to scissoring, wagging, twisting and rocking appear in the expected frequency regions  $1500\text{--}800\text{ cm}^{-1}$ . We determined the scissoring vibrations of the  $\text{CH}_2$  ( $\nu_{41}\text{--}\nu_{35}$ ), the wagging vibrations of the  $\text{CH}_2$  ( $\nu_{34}\text{--}\nu_{29}$ ), the twisting vibrations of the  $\text{CH}_2$  ( $\nu_{28}\text{--}\nu_{23}$ ) and the rocking vibrations of the  $\text{CH}_2$  ( $\nu_{18}\text{--}\nu_{13}$ ) every one molecules.

### 3.2.5. Methyl group vibrations

Vibrations of the methyl group in the 2 and 3-MP should be described by 12 normal modes. The  $\text{CH}_3$  fundamental modes are



**Fig. 2.** (a) The infrared spectra of 2 and 3-methylpiperidine for under  $1600\text{ cm}^{-1}$  wave numbers and (b) The infrared spectra of 2 and 3-methylpiperidine for over  $2600\text{ cm}^{-1}$  wave numbers.



two asymmetric CH<sub>3</sub> stretching, one symmetric CH<sub>3</sub> stretching, two asymmetric CH<sub>3</sub> bending, one symmetric CH<sub>3</sub> bending, two CH<sub>3</sub> rocking and one CH<sub>3</sub> torsional vibrations. The C–CH<sub>3</sub> fundamental modes are one C–CH<sub>3</sub> stretch and two C–CH<sub>3</sub> bending vibrations.

For the CH<sub>3</sub> stretching vibrations, we expect to observe three bands at about 3020–2920 cm<sup>-1</sup> region. Three CH<sub>3</sub> stretching modes ( $\nu_{53}$ ,  $\nu_{52}$ ,  $\nu_{47}$ ) were predicted in this region. The Symmetric CH<sub>3</sub> stretching vibrations were observed at 2919 cm<sup>-1</sup> (2-MP) and 2920 cm<sup>-1</sup> (3-MP) in the FT-IR spectrum for free 2-MP and 3-MP molecules.

The asymmetric CH<sub>3</sub> bending bands usually occur between at 1430 cm<sup>-1</sup> and 1470 cm<sup>-1</sup> region. The asymmetric CH<sub>3</sub> bending modes ( $\nu_{40}$ ,  $\nu_{39}$ ) were predicted in the region. The asymmetric CH<sub>3</sub> bending vibrations ( $\nu_{35}$ ) were observed at 1445 cm<sup>-1</sup> (for 2MP) and 1433 cm<sup>-1</sup> (for 3MP) in the FT-IR spectra. On the other hand, the symmetric CH<sub>3</sub> bending vibration appears in the 1360–1400 cm<sup>-1</sup> region. The symmetric CH<sub>3</sub> bending vibrations ( $\nu_{34}$ ) were observed 1376 cm<sup>-1</sup> for title molecules in the FT-IR spectra [17].

The C–CH<sub>3</sub> stretching vibration was observed at 1055 cm<sup>-1</sup> for both molecules in the FT-IR spectra. This peak ( $\nu_{20}$ ) were predicted at 1071 cm<sup>-1</sup> (6-311++G (d,p)), 1059 cm<sup>-1</sup> (6-311G (d,p)) and 1062 cm<sup>-1</sup> (cc-PVQZ) for 2-methylpiperidine. In-plane C–CH<sub>3</sub> bending vibration were predicted ( $\nu_4$ ) at 304 cm<sup>-1</sup> (6-311++G (d,p)), 302 cm<sup>-1</sup> (6-311G (d,p)) and 302 cm<sup>-1</sup> (cc-PVQZ) for 2-MP. This peak were theoretical predicted at 299 cm<sup>-1</sup> (6-311++G (d,p)), 296 cm<sup>-1</sup> (6-311G (d,p)) and 297 cm<sup>-1</sup> (cc-PVQZ) for 3-MP. In-plane and out-of-plane vibrations of C–CH<sub>3</sub> were not observed in the FT-infrared spectra.

#### 4. Conclusion

The IR spectra of the title molecules were computed by the B3LYP methods in conjunction with the 6-311++G (d,p), 6-311G (d,p) and cc-pVQZ basis sets. Results were in good agreement with its observed FT-IR spectrum. The vibrational spectra provided by B3LYP functional with 6-311G (d,p) and cc-pVQZ basis sets were the closest to the experimental values. The RMS values were about 31.62 cm<sup>-1</sup> for the first basis set and 34.10 cm<sup>-1</sup> for the second one. The scale factors were used in order to compare how the calculated wave numbers are consistent with those of the experimental ones. By taking into account small variations of the scaling factors for the derivatives of the title molecules, for future IR spectral predictions for unknown molecules of this class, one can recommend same scaling factors for the methods mentioned above.

The isotope effects of D atom were discussed for sensitive band to deuterated substitution. The NH, CN stretching and NCH bending modes were showed shifts toward a lower wave number in the deuterated derivative of selected molecules. This means that NH,

CN stretching and NCH bending modes were sensitive to deuterated coordination.

The experimental geometric parameters were in better agreement with the optimized geometric parameters. Optimized bond lengths of studied molecules were found to have a good correlation for cc-pVQZ basis set than 6-311G (d,p) and 6-311G++ (d,p) basis sets. The RMS values were 0.095 Å (for cc-pVQZ basis set), 0.097 (for 6-311G (d,p) and 6-311G++ (d,p) basis sets). However, the results showed that experimental and theoretical bond angles were in good agreement for B3LYP/6-311G (d,p) level of theory.

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