

## Vibrational spectroscopic studies and ab initio calculations of 3-Nitroacetanilide

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### ABSTRACT

A complete vibrational spectrum analysis of 3-Nitroacetanilide is performed. The wavenumbers are calculated on the basis of ab initio theory using Hartree-Fock/6-31G\* basis set. The predicted infrared intensities and Raman activities are reported. The red shift of the NH stretching wavenumber indicates the weakening of the N-H bond resulting in proton transfer to the neighbouring oxygen atom. The calculated first hyperpolarizability is comparable with the reported values of similar derivatives and is an attractive object for future studies of non linear optics.

**Key words:** Hartree-Fock ab initio calculations, Acetanilide, Acetylamino.

### INTRODUCTION

Acetanilide derivatives exhibit various types of biological properties such as anthelmintic, antihistaminic, antifungal, and antibacterial<sup>1</sup>. Raju *et al.*<sup>2</sup> reported the vibrational spectroscopic studies and DFT calculations of 4-hydroxyacetanilide. Computational method is at present widely used for simulating IR spectrum. Such simulations are indispensable tools to perform normal coordinate analysis so that modern vibrational spectroscopy is unimaginable without involving them. In the present study, the IR and theoretical calculations of the wavenumbers of the title compound are reported.

#### Computational details

Calculations of the title compound were carried out with Gaussian03 program<sup>3</sup> using the HF/6-31G\* basis set to predict the molecular structure

and wavenumbers. Molecular geometry was fully optimized by Bery's optimization algorithm using redundant internal coordinates. Harmonic vibrational wavenumbers were calculated using the analytic second derivatives to confirm the convergence to minimum on the potential surface. The wavenumber values computed at the Hartree-Fock level contain known systematic errors due to the negligence of electron correlation<sup>4</sup>. We therefore, have used the scaling factor value of 0.8929 for HF/6-31G\* basis set. The absence of imaginary wavenumber on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

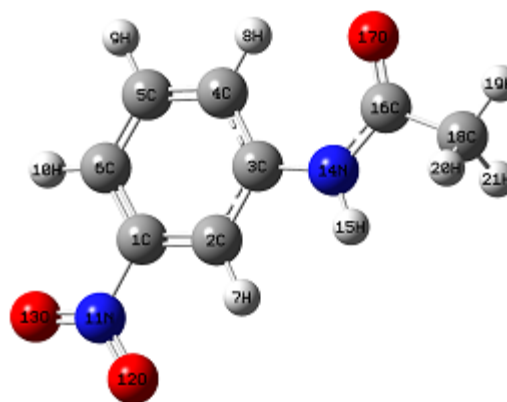
### RESULTS AND DISCUSSION

The IR spectrum of the title compound is downloaded from the website [www.aist.go.jp](http://www.aist.go.jp). The calculated wavenumbers and observed IR bands and band assignments are given in Table 1.

### Acetylamino group-NHC(=O)Me vibrations

The NH stretching vibration<sup>5</sup> in N-substituted acetamides appears strongly and broadly in the region  $3280 \pm 60 \text{ cm}^{-1}$ . For the title compound, the strong band at  $3304 \text{ cm}^{-1}$  in the IR spectrum is assigned as  $\nu_{\text{NH}}$  mode. The calculated value for this mode is  $3456 \text{ cm}^{-1}$ . The NH stretching wavenumber is redshifted by  $152 \text{ cm}^{-1}$ , in IR with a strong intensity from the computed wavenumber, which indicates the weakening of the N-H bond resulting in proton transfer to the neighbouring oxygen atom<sup>6</sup>. In the spectra of methyl esters, the overlap of the regions in which both asymmetric stretching<sup>5</sup>  $\nu_{\text{as}}\text{CH}_3$  absorb with weak intensity ( $2990 \pm 20$  and  $2965 \pm 35 \text{ cm}^{-1}$ ) is not large. The computed wavenumbers of modes corresponding to  $\nu_{\text{as}}\text{CH}_3$  group are  $2985$  and  $2925 \text{ cm}^{-1}$ . In this mode two C-H bonds of the methyl group are extending while the third one is contracting. The symmetrical stretching mode  $\nu_{\text{s}}\text{CH}_3$  is expected in the range  $2900 \pm 45 \text{ cm}^{-1}$  in which all the three C-H bonds extend and contract in phase<sup>5</sup>. The HF calculations give this mode at  $2872 \text{ cm}^{-1}$ . Two bending vibrations can occur within a methyl group, the first of these, the symmetrical bending vibration  $\nu_{\text{s}}\text{CH}_3$  involves the in-phase bending of C-H bonds. The second, the asymmetric bending mode  $\nu_{\text{as}}\text{CH}_3$  involves out-of-phase bending of the C-H bonds<sup>7</sup>. The methyl asymmetric deformations<sup>5</sup> provide a weak to moderate band in the regions  $1450 \pm 30 \text{ cm}^{-1}$  and  $1420 \pm 20 \text{ cm}^{-1}$ . As contrasted with the very weak stretching, the methyl symmetric deformation<sup>5</sup> appears more strongly in the region  $1365 \pm 10 \text{ cm}^{-1}$ . The HF calculations give  $1453$ ,  $1443$  and  $1387 \text{ cm}^{-1}$  as asymmetric and symmetric methyl deformations, respectively, for the title compound. The bands at  $1433$  and  $1371$  in the IR spectrum are assigned as these deformation modes. El-Shahawy *et al.*<sup>8</sup> reported  $1440$  and  $1370 \text{ cm}^{-1}$  as  $\delta_{\text{as}}\text{CH}_3$  and  $\delta_{\text{s}}\text{CH}_3$  modes. The carbonyl stretching C=O vibration<sup>5,6</sup> is expected in the region  $1715$ - $1680 \text{ cm}^{-1}$  and in the present study this mode appears at  $1676 \text{ cm}^{-1}$  in the IR spectrum. The HF calculations give this mode at  $1774 \text{ cm}^{-1}$ . El-Shahawy *et al.*<sup>8</sup> reported a value of  $1640 \text{ cm}^{-1}$  in the IR spectrum as  $\nu_{\text{C=O}}$  for paracetamol. The deviation of the calculated wavenumber for this mode can be attributed to the under estimation of the large degree of  $\pi$ -electron delocalization due to conjugation of the molecule<sup>9</sup>.

The CNH vibration in which N and H atoms move in opposite direction of carbon atom in the amide moiety appears at  $1541 \text{ cm}^{-1}$  in the IR spectrum and at  $1544 \text{ cm}^{-1}$  theoretically and the CNH vibration in which N and H atoms move in the same direction of carbon atom in the amide group appear at  $1276 \text{ cm}^{-1}$  in IR and  $1260 \text{ cm}^{-1}$  theoretically<sup>8,10,11</sup>. The NH rock in the plane is assigned at  $1189 \text{ cm}^{-1}$  theoretically<sup>8</sup>. The out-of-plane wagging<sup>5</sup> of NH is moderately active with a broad band in the region  $790 \pm 70 \text{ cm}^{-1}$  and the band at  $826 \text{ cm}^{-1}$  in IR and  $821$  (HF) is assigned as this mode. The C-N stretching vibration<sup>5</sup> coupled with  $\delta_{\text{NH}}$ , is moderately to strongly active in the region  $1275 \pm 55 \text{ cm}^{-1}$ . In the present case the HF calculation give this mode at  $1217 \text{ cm}^{-1}$ . The methyl rocks<sup>5</sup> are observed as weak to medium bands in the region  $1090 \pm 40$  and  $1015 \pm 35 \text{ cm}^{-1}$ . The bands calculated at  $1098$  and  $1015 \text{ cm}^{-1}$  are assigned as  $\rho\text{CH}_3$  modes. The  $\nu_{\text{CC}}$  absorbs<sup>5</sup> weakly to moderately in the region  $915 \pm 65 \text{ cm}^{-1}$ . N-phenyl substituted acetamides<sup>5</sup> give this C-C stretching vibration near  $965 \text{ cm}^{-1}$ . For the title compound the band at  $957 \text{ cm}^{-1}$  (HF) is assigned as this mode. The  $\delta_{\text{C=O}}$  in-plane deformation has been found in the region  $625 \pm 70 \text{ cm}^{-1}$  and the band at  $637 \text{ cm}^{-1}$  (HF) is assigned as this mode. The C=O out-of-plane deformation<sup>5</sup> is in the range  $540 \pm 80 \text{ cm}^{-1}$  and the HF calculation give this mode at  $539 \text{ cm}^{-1}$ , while the IR spectrum give it at  $522 \text{ cm}^{-1}$ . Acetylamino compounds<sup>5</sup> display the in-plane skeletal N-C-C deformation in the region  $420 \pm 55 \text{ cm}^{-1}$  and the external -N-C deformation in the region  $310 \pm 65 \text{ cm}^{-1}$ . The NHC(=O)Me torsion<sup>5</sup> is expected in the region  $225 \pm 65 \text{ cm}^{-1}$ . Usually the methyl



**Table 1 : Calculated vibrational waveumbers aud baud assigumeuts**

$\nu_{(\text{HF})}$ $\text{cm}^{-1}$	$\nu_{(\text{IR})}$ $\text{cm}^{-1}$	IR luteusity (KM/Mole)	Ramau activity ( $\text{A}^{**4}/\text{AMU}$ )	Assigumeuts
3456	3304	35.30	44.27	$\nu_{\text{NH}}$
3098	3194	5.58	53.84	$\nu_{\text{CH}}$
3075	3132	1.81	74.06	$\nu_{\text{CH}}$
3053	3099	2.84	43.72	$\nu_{\text{CH}}$
3024	3079	11.81	96.47	$\nu_{\text{CH}}$
2985		7.47	84.13	$\nu_{\text{as}} \text{Me}$
2925		14.92	61.17	$\nu_{\text{as}} \text{Me}$
2872		6.31	111.76	$\nu_{\text{s}} \text{Me}$
1774	1676	267.73	9.91	$\nu_{\text{C=O}}$
1669	1646	284.50	3.98	$\nu_{\text{as}} \text{NO}_2$
1610		275.46	49.33	$\nu_{\text{Ph}}$
1601	1601	64.53	24.35	$\nu_{\text{Ph}}$
1544	1541	390.10	11.33	$\delta_{\text{UH}}$
1488	1479	57.31	8.25	$\nu_{\text{Ph}}$
1466		344.15	95.22	$\nu_{\text{Ph}}$
1453		8.47	20.05	$\delta_{\text{as}} \text{Me}$
1443	1433	2.61	14.60	$\delta_{\text{as}} \text{Me}$
1413	1426	152.75	2.22	$\nu_{\text{s}} \text{NO}_2$
1387	1371	15.17	1.80	$\delta_{\text{s}} \text{Me}$
1299	1296	72.04	2.51	$\nu_{\text{Ph}}$
1260	1276	235.06	21.69	$\delta_{\text{NH}}, \delta_{\text{CH}}$
1217		29.73	19.51	$\nu_{\text{CN}}$
1189		25.31	1.89	$\rho_{\text{NH}}, \delta_{\text{CH}}$
1119		13.27	3.29	$\delta_{\text{CH}}$
1098		29.91	8.66	$\rho_{\text{CH}_3}$
1073	1079	2.22	2.96	$\delta_{\text{CH}}$
1042		7.97	1.06	$\delta_{\text{CH}}$
1015	1019	1.99	0.54	$\rho_{\text{CH}_3}$
1001	1000	24.96	0.84	$\nu_{\text{Ph}}$
972	988	0.54	38.80	$\gamma_{\text{CH}}$
957		11.50	3.46	$\nu_{\text{CC}}$
955		0.01	1.17	$\gamma_{\text{CH}}$
911		30.15	1.37	$\gamma_{\text{CH}}$
887		22.19	1.59	$\gamma_{\text{CH}}$
821	826	12.70	0.87	$\omega_{\text{UH}}$
811	806	41.04	5.20	$\nu_{\text{CX(X)}}$
761	762	72.82	3.16	$\gamma_{\text{CH}}, \delta_{\text{NO}_2}$
698		6.49	2.42	$\gamma_{\text{Ph}}$
665	672	11.93	0.47	$\omega_{\text{NO}_2}$
637		5.73	5.83	$\delta_{\text{C=O}}$
595		0.52	0.98	$\gamma_{\text{Ph(X)}}$
540	535	9.35	1.81	$\rho_{\text{NO}_2}$
539	522	0.82	0.48	$\gamma_{\text{C=O}}$
509		22.57	2.24	$\gamma_{\text{Ph(X)}}$
497		107.38	1.39	$\nu_{\text{NC-C}}$
427		0.45	0.17	$\gamma_{\text{Ph}}$

404	5.15	1.05	$\delta\text{Ph(X)}$
347	0.21	1.27	$\delta\text{U-C}$
302	2.15	4.64	$\tau\text{UHC(=O)Me}$
248	0.07	2.15	$\tau\text{Me}$
220	2.02	1.35	$\gamma\text{CX(X)}$
167	2.24	2.18	$\delta\text{CX(X)}$
128	9.31	0.09	$\tau\text{NO}_2$
84	3.84	1.03	$\tau\text{C(=O)Me}$
44	0.69	0.58	$\tau\text{C(=O)Me}$
24	11.70	0.20	tPh
23	0.08	0.41	tPh

$\nu$ -stretching;  $\delta$ -in-plane deformation;  $\gamma$ -out-of-plane deformation;  $\tau$ -torsion; rocking;  $\omega$ -wagging;  
X-substituent sensitive; Ph-Phenyl; subscripts: as – asymmetric, s- symmetric.

torsion absorbs at  $200 \pm 65 \text{ cm}^{-1}$  and the C(=O)Me torsion at lower wavenumbers<sup>5</sup>,  $100 \pm 40 \text{ cm}^{-1}$ . For the title compound, these skeletal deformations and torsions are found below  $400 \text{ cm}^{-1}$ .

#### Nitro group vibrations

The most characteristic bands in the spectra of nitro compounds are due to  $\text{NO}_2$  stretching vibrations, which are the two most useful group wavenumbers, not only because of their spectral position but also for their strong intensity<sup>5</sup>. The symmetric and antisymmetric  $\text{NO}_2$  stretching vibrations of nitro compounds are expected respectively in the ranges 1360-1400 and 1500-1660  $\text{cm}^{-1}$ . In substituted nitrobenzenes,  $\nu_s\text{NO}_2$  appears strongly in the range  $1345 \pm 30 \text{ cm}^{-1}$ , in 3-nitropyridine<sup>12</sup> in the range  $1350 \pm 20 \text{ cm}^{-1}$  and in conjugated nitroalkenes<sup>13</sup> at  $1345 \pm 15 \text{ cm}^{-1}$ . In the present case the bands at 1669 (HF), 1646 (IR) and 1413 (HF), 1426 (IR), are assigned as asymmetric and symmetric  $\text{NO}_2$  stretching modes, respectively. The  $\text{NO}_2$  scissoring<sup>5,14-16</sup> occur in the region  $850 \pm 60 \text{ cm}^{-1}$  when conjugated to C=C or aromatic molecules, with a contribution of the  $\nu\text{CN}$ , which is expected to be near  $1120 \text{ cm}^{-1}$ . The  $\delta\text{NO}_2$  vibration is reported to be at  $852 \text{ cm}^{-1}$  for nitrobenzene, at  $890 \text{ cm}^{-1}$  for  $\text{H}_2\text{C}=\text{CHNO}_2$ , and at 904 and  $834 \text{ cm}^{-1}$  for 1,3-dinitrobenzene. In aromatic compounds, the wagging mode,  $\omega\text{NO}_2$  is assigned at  $740 \pm 50 \text{ cm}^{-1}$  with a moderate to strong intensity, a region in which  $\rho\text{CH}$  is also active<sup>5</sup>. The  $\delta\text{NO}_2$  is reported at 701 and  $728 \text{ cm}^{-1}$  for 1,2-dinitrobenzene and at 710 and  $772 \text{ cm}^{-1}$  for 1,4-dinitrobenzene<sup>5</sup>. In aromatic compounds, the rocking mode  $\rho\text{NO}_2$  is

active in the region  $545 \pm 45 \text{ cm}^{-1}$ . Nitrobenzene<sup>5</sup> shows this rocking mode at  $531 \text{ cm}^{-1}$ . Sundaraganesan *et al.*<sup>17</sup> reported the  $\text{NO}_2$  deformation bands at 839, 744 and  $398 \text{ cm}^{-1}$  (experimental), and at 812, 716, 703 and  $327 \text{ cm}^{-1}$  theoretically. For the title compound the deformation bands are assigned at 761, 665, 540 (HF), 762, 672,  $535 \text{ cm}^{-1}$  (IR).

#### Phenyl ring vibrations

The benzene ring possesses six ring stretching vibrations of which the four with the highest wavenumbers occurring near 1600, 1580, 1490 and  $1440 \text{ cm}^{-1}$  are good group vibrations<sup>5</sup>. With heavy substituents, the bands tend to shift to somewhat lower wavenumbers and the greater the number of substituents on the ring, the broader the absorption regions<sup>5</sup>. In the case of C=O substitution, the band near  $1490 \text{ cm}^{-1}$  can be very weak<sup>5</sup>. The fifth ring stretching vibration is active near  $1315 \pm 65 \text{ cm}^{-1}$ , a region that overlaps strongly with that of the CH in-plane deformation<sup>5</sup>. The sixth ring stretching vibration, the ring breathing mode appears as a weak band near  $1000 \text{ cm}^{-1}$  in mono-, 1,3-di and 1,3,5-trisubstituted benzenes. In the otherwise substituted benzenes, however, this vibration is substituent sensitive and difficult to distinguish from other modes. For the title compound, the ring breathing mode appears at  $1000 \text{ cm}^{-1}$  in the IR spectrum and at  $1001 \text{ cm}^{-1}$  theoretically. The in-plane and out-of-plane CH deformations of the phenyl ring are expected in the regions  $1320\text{-}1040 \text{ cm}^{-1}$  and  $990\text{-}730 \text{ cm}^{-1}$ , respectively<sup>5</sup>.

Analysis of organic molecules having conjugated  $\pi$ -electron systems and large hyperpolarizability using infrared and Raman spectroscopy has evolved as a subject of research<sup>18</sup>. The potential application of the title compound in the field of non linear optics demands the investigation of its structural and bonding features contributing to the hyperpolarizability enhancement,

by analyzing the vibrational modes using the IR and Raman spectrum. The calculated first hyperpolarizability of the title compound is  $1.03 \times 10^{-30}$  esu, which is comparable with the reported values of similar derivatives<sup>19</sup>. We conclude that the title compound is an attractive object for future studies of non linear optical properties.

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