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# Vibrational analysis of nicotinic acid species based on ab initio molecular orbital calculations

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## Abstract

In this work a vibrational investigation of the equilibrium species in aqueous solution of nicotinic acid was performed, by both experimental as well as theoretical methods. The Raman spectra of its aqueous solutions at some pH values were obtained and analyzed considering the equilibrium of three main species: a totally protonated one, a zwitterionic form, and the nicotinate anion. These species were also studied by ab initio (Hartree–Fock and second-order Møller–Plesset perturbation) and hybrid density functional theory calculations. The structures of these species were optimized and the vibrational frequencies calculated. These methods provided a good correlation between the calculated and the experimental vibrational frequencies. A great mixing of the ring vibrational modes, as well as between the ring and the substituent modes, was observed. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Nicotinic acid; Ab initio; Raman spectroscopy; Vibrational analysis; Hartree–Fock; Density functional theory; Second-order Møller–Plesset

## 1. Introduction

Many articles have been published on pyridine carboxylic acids concerning their vibrational spectra [1], the surface enhanced Raman spectroscopy (SERS) effect [2] and as ligands in several coordination compounds with biological properties [3]. Vibrational assignments based on ab initio calculations [4,5] and normal coordinate analysis [6] have been reported for methyl-pyridines but for pyridine carboxylic acids such calculations have not been performed yet. The main nicotinic acid species

present in aqueous solution with pK values from the literature [7] are shown below in Fig. 1.

There are characteristic vibrational frequencies for each species that can be due to the pyridine ring modes or to the substituent modes. In a previous work on the vibrational spectra of picolinic acid in aqueous solution [8] an assignment based on ab initio and DFT calculations was performed. In the present work, the calculations have been extended to the nicotinic acid species.

## 2. Experimental

### 2.1. Solutions

Solutions of nicotinic acid (Aldrich), 0.30 mol l<sup>-1</sup>,

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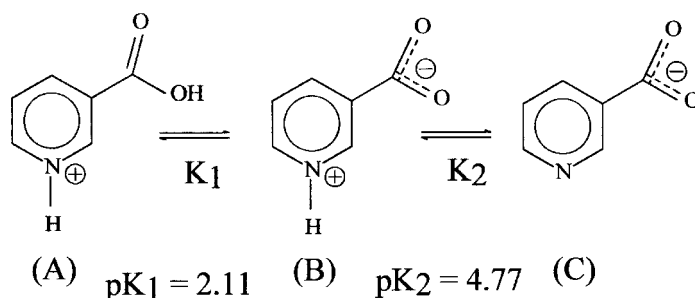


Fig. 1. Nicotinic acid species in aqueous solution.

in several pH values were prepared by adjusting the pH with sodium hydroxide or HCl solutions. The ionic strength was adjusted with sodium chloride.

## 2.2. Spectroscopic methods

The Raman spectra of the nicotinic acid species in aqueous solution were obtained in a Jobin–Yvon U-1000 spectrometer, with the solutions placed in a glass capillary cell. Spectral resolution was set to  $5\text{ cm}^{-1}$ . The 514.5 nm line of an argon ion laser (Coherent Innova 90) was used as the exciting radiation, with a power level of 500 mW.

## 2.3. Computational methods

The optimized structure and vibrational band frequencies of the three species derived from nicotinic acid were calculated at the Hartree–Fock (HF) and the second-order Møller–Plesset (MP2) perturbation levels and by the hybrid DFT/HF method, utilizing Becke's three-parameter exchange functional with the Lee–Yang–Parr non-local correlation functional (B3-LYP). The 6-31G\*\* basis set was used throughout. All the calculations were carried out using the GAUSSIAN 94 and GAUSSIAN 98 programs (Gaussian, Inc.) on IBM/SP2 9076 at NPD-UFSC and on DEC-ALPHA 4100 at LCCA-USP. The normal mode animations were visualized using the Hyperchem 4.5 program (Hypercube, Inc.). Normal coordinate analysis was performed to get a detailed assignment of the normal vibrational modes. Although the potential energy distribution (PED) is not quantitatively described here, it will be reported in a future article. The normal coordinates and PED were calculated by the programs available in the NCTP6 package [9].

## 3. Results and discussion

For all three species a planar geometry with  $C_s$  symmetry was found from all the methods. Fig. 2 shows the Raman spectra of nicotinic acid in aqueous solution at pH values 0.5, 3.0 and 9.0; in these values, the prevalent species are A, B and C, respectively. The total number of normal vibrational modes is 39, 36 and 33 for A, B and C species, respectively, which can be divided into in plane (27, 25 and 23, respectively) and out of plane modes. In the present work only the in plane modes are considered.

The calculated in plane HF, DFT/B3-LYP and MP2 vibrational frequencies and the experimental ones (from the Raman spectra) together with the scaled frequencies and the assignment for the three species are shown in Tables 1–3. The high-frequency region was not measured due to overlapping with the broad and intense water bands. The assignment is based solely on the HF ab initio calculations. The PED was used to help in the assignment; the first mode in each assignment is the major component. A comparative assignment among the three methods with the detailed PED will be published in another work.

A good agreement among the calculated in plane frequencies and the experimental ones was observed for the three methods, even considering the molecule in the vacuum. From the plot of the calculated versus experimental frequencies for each species and each calculation method, the curve fittings gave straight lines, whose equations were used to correct the calculated frequencies ( $\nu_{\text{calc.}}$ ). The scaled frequencies ( $\nu_{\text{scal.}}$ ) were obtained from the expression:  $\nu_{\text{scal.}} = [(\nu_{\text{calc.}}) - (\text{linear coefficient})]/(\text{slope})$ .

The standard deviations of  $\Delta\nu$  ( $\Delta\nu = \nu_{\text{scal.}} - \nu_{\text{exp}}$ ) for the three methods (HF, B3-LYP and MP2) are

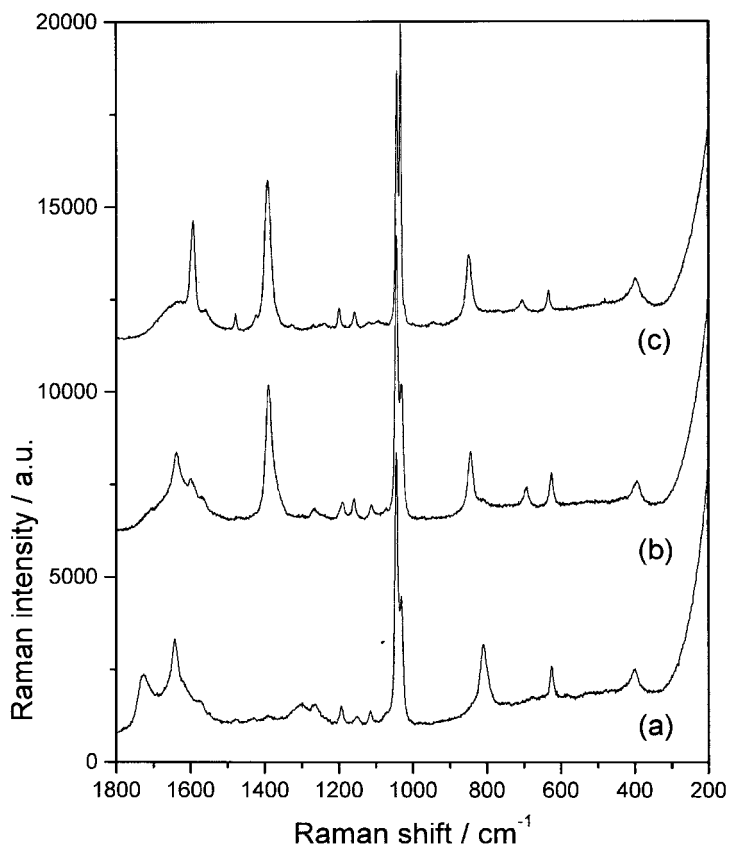


Fig. 2. Raman spectra of nicotinic acid  $0.3 \text{ mol l}^{-1}$  in aqueous solution at the pH values: (a) 0.5; (b) 3.0; and (c) 9.0.

$36$ ,  $26$  and  $23 \text{ cm}^{-1}$  for species A,  $33$ ,  $40$  and  $44 \text{ cm}^{-1}$  for species B and  $18$ ,  $19$  and  $17 \text{ cm}^{-1}$  for species C, respectively.

The HF scaled frequencies showed a better fitting than the other two methods for species B, while for species A the B3-LYP and MP2 methods were better than HF and for species C the three methods gave similar fittings. It seems that the DFT and MP2 methods are overestimating the mixing of  $\nu_s(\text{COO})$  with  $\beta(\text{CH})$  and  $\beta(\text{NH})$  modes for species B, as the  $\nu_s(\text{COO})$  found from these two methods is underestimated. For species A the HF method gave a higher  $\nu(\text{C=O})$  than the DFT and MP2.

It is worth mentioning the considerable mixing of the ring modes, for instance the trigonal ring breathing ( $\nu_{12}$ ) is mixed with ring breathing ( $\nu_1$ ) and  $\beta(\text{CH})$ . A mixing is also observed between some ring and substituent vibrations, e.g. the ring deformation (6a and b) and  $\nu(\text{C-X})$  modes are mixed with  $\delta(\text{COO})$ . The

ring  $\beta(\text{CH})$  deformation modes in the  $1100$ – $1400 \text{ cm}^{-1}$  region are the most difficult to be assigned because of the great number of close frequencies and also because of the mixing of these modes with  $\nu(\text{C-X})$  and substituent vibrations. Their low Raman intensity also makes difficult their observation in the Raman spectra.

There are some vibrational patterns that could be useful to distinguish the different species, for instance,  $\nu_s(\text{COO})$  and  $\nu(\text{C=O})$  modes. Species B and C show two bands ( $626$ ,  $694$  and  $634$ ,  $705 \text{ cm}^{-1}$ , respectively) in the  $600$ – $700 \text{ cm}^{-1}$  region while species A shows only one band at  $623 \text{ cm}^{-1}$ , although the calculation predicts two bands. The band in the region  $800$ – $850 \text{ cm}^{-1}$  provides another example. For the species B and C, this band ( $845$  and  $849 \text{ cm}^{-1}$ , respectively) lies at higher frequency than for species A ( $809 \text{ cm}^{-1}$ ), which can be explained by the distinct mode composition; for the former, the  $\delta(\text{COO})$  has

Table 1

Experimental (Raman), calculated and scaled vibrational frequencies ( $\text{cm}^{-1}$ ) for the totally protonated nicotinic acid species A, with assignment (abbreviations:  $\nu$  = stretching,  $\nu_s$  = symmetric stretching,  $\beta$  = in plane deformation,  $\delta$  = scissoring, X = ring substituent)

Exper.	B3-LYP	B3-LYP scal.	MP2	MP2 scal.	HF	HF scal.	Assignment <sup>a</sup>
–	200	245	207	251	218	268	$\beta(\text{C-X})$
398	376	409	380	410	405	425	$\nu(\text{C-X}) + \delta\text{ring (6a)} + \delta(\text{COO})$
–	493	518	495	515	536	534	$\rho(\text{COO}) + \beta(\text{C-X})$
623	630	645	630	639	676	652	$\delta\text{ring (6b)} + \delta(\text{COO})$
–	647	661	644	652	703	674	$\delta(\text{COO}) + \delta\text{ring (6a)} + \beta(\text{OH})$
809	786	790	791	787	848	796	$\delta\text{ring (6a)} + \nu(\text{C-X}) + \delta(\text{COO})$
1030	1046	1032	1049	1024	1124	1027	$\delta\text{ring (12)} + \nu\text{ring (1)}$
1043	1059	1045	1074	1047	1132	1034	$\delta\text{ring (12)} + \beta\text{CH (18a)}$
1112	1119	1100	1139	1107	1192	1084	$\beta\text{CH (18b)} + \nu(\text{CC}) + \nu(\text{CN})$
1153	1148	1127	1158	1124	1245	1129	$\nu(\text{C-O}) + \beta\text{CH (18a)} + \nu(\text{CX}) + \nu(\text{COOH}) + \delta\text{ring (12)}$
1191	1208	1183	1228	1189	1275	1154	$\beta\text{CH} + \nu\text{ring (14)} ?$
–	1212	1187	1234	1194	1322	1193	$\beta\text{CH} + \beta\text{OH}$
–	1297	1266	1325	1278	1340	1209	$\beta\text{OH} + \beta\text{CH (9a)} + \nu(\text{C-O})$
–	–	–	–	–	1435	1288	$\beta\text{CH}$
1301	1351	1316	1380	1328	1478	1324	$\beta\text{CH (3)}$
–	1392	1355	1425	1370	–	–	–
–	1402	1364	1486	–	1532	1369	$\nu(\text{C-O}) + \nu(\text{C-X}) + \delta(\text{COO}) + \beta\text{OH} + \beta\text{CH (19b)}$
–	1500	1455	1528	1464	1621	1444	$(\nu + \delta)\text{ ring (19b)}$
1571	1588	1537	1607	1537	1732	1537	$(\nu + \delta)\text{ ring (19a)}$
–	1652	1597	1686	1609	1801	1595	$\nu\text{ring (8b)}$
1640	1675	1618	1706	1628	1831	1620	$\nu\text{ring (8a)}$
1725	1858	1788	1861	1770	2061	1813	$\nu(\text{C=O})$

<sup>a</sup> The Wilson numbering is used for ring modes.

a major contribution while for the latter, the  $\delta\text{ring (6a)}$  is preponderant. As mentioned earlier,  $\nu(\text{OH})$  and  $\nu(\text{NH})$  modes, which could be useful in the characterization of the protonated species, could not be observed in the Raman spectra.

#### 4. Conclusions

The calculated in plane vibrational frequencies from the three methods showed a good agreement with the experimental values for the three species of nicotinic acid. For species B the HF method showed a better fitting, especially for the modes involving COO vibrations, while for species A the B3-LYP and MP2 methods are better.

There is a great mixing of the ring vibrational modes and also between the ring and substituent modes. The descriptions of the modes are very complex because of the low symmetry of the

molecules. The modes involving  $\beta\text{CH}$  are the most difficult to be assigned due to the mixing with the other ring modes and also with the substituent modes.

There are some frequencies useful to characterize the three species of nicotinic acid in aqueous solution, for instance, the carboxylate  $\nu_s\text{COO}$  and  $\nu(\text{C=O})$  frequencies and modes in the 600–700, 800–850 and 1500–1650  $\text{cm}^{-1}$  regions.

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Table 2

Experimental (Raman), calculated and scaled vibrational frequencies ( $\text{cm}^{-1}$ ) for the zwitterionic nicotinic acid species B, with assignment

Exper.	B3-LYP	B3-LYP scal.	MP2	MP2 scal.	HF	HF scal.	Assignment
–	189	231	201	252	211	246	$\beta(\text{C-X}) + \rho(\text{COO})$
395	345	381	351	392	379	392	$\nu(\text{C-X}) + \delta\text{ring (6a)}$
–	497	528	498	529	544	535	$\rho(\text{COO}) + \beta(\text{C-X})$
626	630	656	630	653	678	651	$\delta\text{ring (6b)} + \delta\text{ring (12)}$
694	691	714	691	710	751	714	$\delta\text{ring (6a)} + \delta(\text{COO})$
845	801	820	806	817	890	834	$\delta(\text{COO}) + \nu(\text{C-X}) + \delta\text{ring (6a)}$
1030	1041	1051	1045	1041	1113	1027	$\nu\text{ring (1)} + \beta\text{CH (18a)} + \delta\text{ring (12)}$
1044	1042	1052	1062	1056	1124	1037	$\delta\text{ring (12)} + \beta\text{CH (18a)}$
1073	1083	1092	1108	1099	1174	1080	$\beta\text{CH (18b)}$
1111	1124	1131	1145	1134	1241	1138	$\delta\text{ring (12)} + \nu(\text{C-X}) + \beta\text{CH} + \nu\text{ring (1)}$
1189	1183	1188	1209	1194	1276	1168	$\beta\text{CH} + \nu\text{ring}$
1268	1260	1262	1284	1264	1319	1206	$\nu\text{ring (14)} + \beta\text{CH (9a)}$
1370	1310	1310	1319	1297	1454	1322	$\beta\text{CH (3) ?}$
–	–	–	–	–	1400	1276	$\beta\text{CH (15) ?}$
1390	1315	1315	1342	1318	1486	1350	$\nu_s(\text{COO}) + \nu(\text{C-X})$
–	1404	1400	1508	1473	–	–	–
–	1485	1478	1525	1489	1609	1457	$(\nu + \delta)\text{ ring (19b)}$
1567	1550	1541	1570	1531	1703	1538	$(\nu + \delta)\text{ ring (19a)}$
1599	1632	1620	1665	1620	1797	1619	$\nu\text{ring (8a)}$
1638	1657	1644	1692	1645	1804	1625	$\nu\text{ring (8b)}$
1703	1797	1779	1852	1795	1988	1785	$\nu_{\text{as}}(\text{COO}) + \rho(\text{COO})$

Table 3

Experimental (Raman), calculated and scaled vibrational frequencies ( $\text{cm}^{-1}$ ) for the nicotinate anion species C, with assignment

Exper.	B3-LYP	B3-LYP scal.	MP2	MP2 scal.	HF	HF scal.	Assignment
–	210	241	217	252	231	256	$\beta(\text{C-X})$
398	365	390	372	399	399	402	$\nu(\text{C-X}) + \delta\text{ring (6a)}$
–	501	521	503	522	544	528	$\beta(\text{C-X}) + \rho(\text{COO})$
634	632	647	629	641	680	646	$\delta\text{ring (6b)}$
705	710	722	707	715	771	725	$\delta\text{ring (6a)} + \delta(\text{COO}) + \nu(\text{C-X})$
849	824	832	827	828	906	842	$\delta(\text{COO}) + \nu(\text{C-X}) + \delta\text{ring (6a)}$
1033	1042	1041	1048	1036	1120	1027	$\delta\text{ring (12)} + \nu\text{ring (1)} + \beta\text{CH}$
1043	1053	1052	1062	1050	1139	1044	$\beta\text{CH} + \nu\text{ring (1)}$
1094	1097	1094	1116	1100	1179	1079	$\beta\text{CH (18b)} + \nu\text{ring}$
1157	1148	1143	1169	1150	1234	1126	$\beta\text{CH (18a) ?} + \nu(\text{C-X})$
1199	1206	1199	1223	1201	1269	1157	$\beta\text{CH} + \nu(\text{C-X})$
1241	1305	1294	1339	1311	1314	1196	$\beta\text{CH (9b)}$
1326	1324	1313	1406	1374	1443	1307	$\beta\text{CH (3)}$
1392	1356	1344	1375	1345	1526	1379	$\nu_s(\text{COO}) + \beta\text{CH} + \delta(\text{COO}) + \nu(\text{C-X})$
1424	1440	1424	1467	1432	1561	1410	$(\nu + \delta)\text{ ring (19a)}$
1479	1499	1481	1516	1478	1633	1472	$(\nu + \delta)\text{ ring (19b)}$
1559	1618	1596	1637	1592	1779	1599	$\nu\text{ring (8b)}$
1600	1624	1601	1645	1599	1799	1616	$\nu\text{ring (8a)}$
–	1755	1727	1792	1738	1920	1721	$\nu_{\text{as}}(\text{COO})$

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