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Spectroscopic Study of Polyaniline Emeraldine Base: Modelling Approach

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Abstract

The polymerization of aniline by Cu(II) montmorillonite was studied using attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy. Experimental spectra were compared with that calculated by AM1, PM3, PM5, MINDO, Hartree-Fock, HF/6-31g(d), as well as Density Functional Theory, BLYP/DZVP and B3LYP/6-31g(d,p). Furthermore, the final heat of formation is studied as a function of temperature. Results indicate that, for aniline B3LYP/6-31G(d,p) calculated frequencies are in a good agreement with experimental data, while HF/6-31G(d) is the optimal in case of polyaniline. The vibrational calculations of a four-ring unit (emeraldine base: EB) are believed to be a good representation of the polyaniline at Cu(II)-montmorillonite. The final heat of formation is a function of polymerization and changed from aniline monomer to five ring repeat unit of polyaniline structure.

Key words: aniline, polyaniline, vibrational spectroscopy, Ab initio calculation, heat of formation

Introduction

Conducting polymers continue to be the focus of active research in many areas and fields.[1] Polyaniline is unique among conducting polymers in its wide range of electrical, electrochemical, electroluminescence, optical and anticorrosion applications as well as good stability.[2–4] It is typically synthesized by oxidizing aniline monomer either electrochemically.[5–6] or chemically.[7–9] Aniline form complexes with transition metal ions in the montmorillonite interlayer by coordination of the free electron pair of the amino group to the metal ions.[10–12] A reduction in the resistivity from 10^{13} to 10^{3} Ω in the polyaniline polymethylmethacrylate film is noticed as a result of $FeCl_3$ oxidation.[13] Vibrational spectroscopy was used to investigate the infrared optics application of polyaniline emeraldine base films.[14] Furthermore vibrational spectroscopy can be used to study the aggregation and interachain doping in emeraldin base.[15] In addition, vibrational spectroscopy was used to study the interaction of polyaniline with the platinum (IV) ions.[16] and polypyrrole.[17] 4-(3-(4-((4-Nitrophenyl)azo)phenyloxy)propyl) aminobenzene sulfonic acid (C3-ABSA) was designed and synthesized as a novel dopant of polyaniline. The molecular structures were characterized by FTIR, UV-Vis absorption and X-ray diffraction, showing that, the main chain and electronic structure are identical to the doped polyaniline, but exhibit partial crystallinity.[18] Ab initio calculations give an accurate description for the structure and vibrational spectra for huge number of molecules.[19] Car-Parrinello ab initio molecular dynamics MD, was used to investigate polyaniline equilibrium geometries.[20] In addition, the polaron lattice and the mechanism of conduction for doped polyaniline were studied by ab initio MO calculations.[21] A scaled quantum mechanical oligomer force field for oligomers of leucoemeraldine base and for one oligomer of the imine form of polyaniline was established.[22] Semiemperical method AM1 was used to investigate the proton effect on the electropolymerization of aniline.[23] The corrosion inhibition by aniline oligomers through charge transfer was studied using Density Functional Theory DFT.[24] Both vibrational spectroscopy and ab initio calculations were used to study the adsorption and polymerization of aniline on Cu(II) montmorillonite.[25]

The present work is conducted to study the polymerization of aniline by Cu(II) montmorillonite, using attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy. The experimental spectra are compared with AM1, PM3, PM5, MINDO, HF as well as DFT calculated spectra. Furthermore, the final heat of formation is studied as a function of temperature at semiemperical PM3 level.

Experimental

Adsorption experiment: Batch adsorption experiments in the presence of oxygen were performed to study the interlayer reactions of aniline on Cu(II)-montmorillonite in aqueous solutions. At concentrations below a critical value of C_C = 2.6 mmol dm^{-3} only a coloured Cu(II)-aniline complex is formed, characterized by a stability constant of log (K_{ass} /dm^3mol^{-1}) = 1.5. At concentrations beyond C_C aniline polymerizes yielding a dark brown product.[25]

ATR-FTIR spectroscopy: Spectra were recorded interferometrically with a BRUKER EQUINOX-55 spectrometer equipped with a DLATGS detector. Single-beam IR spectra were the result of about 1000 co-added interferograms and ranged from 400 to 2000 cm^{-1} with a spectral resolution of 0.5 cm^{-1}. A ZnSe ATR optical accessory set at 45° was used as a reflectance medium.

Calculations details: Both Hartree-Fock and Density Functional Theory calculations were performed with the Gaussian 98.[26] suite of programs on the CRAY supercomputer at Juelich Research Center, Germany. The geometries were fully optimized without imposing external symmetry constraints. The geometry of aniline was optimized using both DZVP and 6-31G(d,p) basis set, while polyaniline is optimized using DZVP and 6-31G(d). Semiempirical AM1,[27] PM3,[28] PM5 and MINDO[29] calculations were carried out on a personal computer, performed using quantum mechanics package, MOPAC 2002 as implemented with the version 1.33 CAChe Program (by Fujitsu), at Spectroscopy Department, National Research Center, Egypt. A force constant calculation was then performed to obtain the vibrational frequencies. Furthermore, vibrational spectra were performed for each level of theory in the harmonic approximation. The errors within this type of calculations including a significant part of anharmonicity corrections, it can be avoided using empirical scale factor.[30–31]

Results and discussion

For utilizing ATR-FTIR to study the IR spectra of both aniline and polyaniline, we need precise assignements of vibrational wavenumbers. This is achieved by a comparison of the band positions and intensities observed in IR spectra with wavenumbers and intensities from molecular modelling calculations of both aniline and polyaniline. Aniline is optimized at semiemperical AM1, PM3, PM5 and MINDO in addition to Density Functional Theory methods, BLYP/DZVP and B3LYP/6-31G(d,p) respectively.

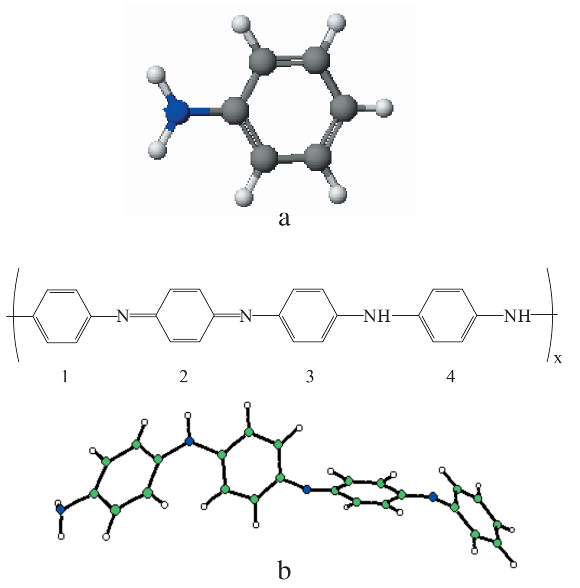

Figure 1. General formula for both aniline and the base form of polyaniline emeraldin base and their calculated structures.

Frequencies were calculated at the same level of theory and no negative frequencies are obtained which indicate that the calculations were done upon the optimized structure. Both experimental and calculated frequencies of aniline are tabulated in Table 1. There are 36 calculated genuine vibrations corresponding to this molecule. The general formual for aniline beside its calculated structure is mentioned in Figure 1a. Aniline has an empirical formula $C_6H_7N_4$ and its molecular point group C_s is equal to 1.

Table 1 presents the experimental vibrational spectrum of aniline in liquid phase. The spectrum of aniline can be assigned as: NH_2 bending or scissors mode which is attributed to 1626 cm^{-1}, a ring stretching with a contribution of the NH_2 scissoring band is appeared at 1604 cm^{-1}. A band at 1498 cm^{-1} is characterized as typical ring stretching. The mode at 1265 cm^{-1} is assigned as partly to C-N stretching and partly to the ring stretching vibration. Comparing between both calculated and experimental frequencies indicate that DFT methods give a good agreement with experimental results, specially B3LYP/6-31G(d,p).

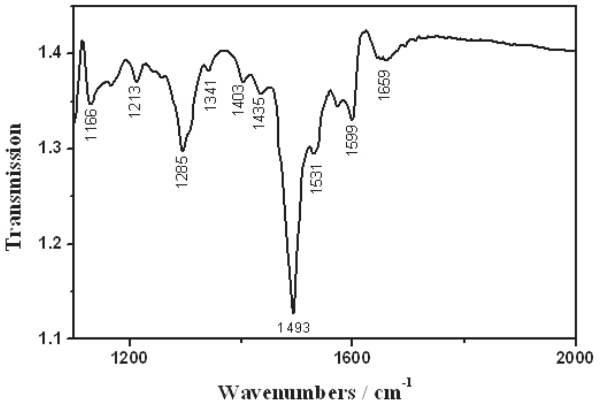

Figure 2. ATR-FTIR spectrum of adsorbed aniline (2.0 mmol g^{-1}) on Cu(II) montmorillonite.

The polymerization of aniline in aqueous solution was already studied.[32] Tochima et al found that, aniline is oxidized by oxygen and subsequently polym-

Table 1. Comparison between calculated and experimental vibrational frequencies (cm^{-1}) of aniline in liquid phase.

AM1	PM3	PM5	MINDO	DFT1	DFT2	Exp.	Assignment[25]
1733	1776	1631	1832	1652	1627	1626	NH_2 sciss, ring str
1665	1678	1538	1632	1637	1608	1604	ring str., NH_2 sciss
1588	1580	1490	1560	1515	1503	1497	C–H bend, ring str
1334	1369	1341	1294	1313	1271	1264	C–N str., ring str
1252	1239	1244	1270	1160	1176	1175	C–H bend, ip
1198	1170	1168	1204	1139	1156	1153	C–H bend
1109	1049	1108	1067	1028	1020	1030	ring def, ip
943	971	902	963	901	994		Ring breathing
670	643	617	823	813	800	792	C–N str., ring str.

DFT1: BLYP/DZVP, DFT2: B3LYP/6-31G(d,p), Exp: Experimental frequencies.

Table 2. Comparison between calculated and experimental vibrational frequencies (cm^{-1}) of the polyaniline emeraldine base.

AM1	PM3	PM5	MINDO	HF	DFT	Exp.	Assignment[25]
1931	1857	1770	1943	1667	1680		Ring 2; C=N
1914	1827	1762	1939	1647	1643	1659	Ring 2; C=N
1733	1679	1543	1829	1624	1628		NH_2
1695	1616	1514	1671	1602	1622		Ring 2; C=N
1637	1465	1491	1647	1599	1586	1599	Ring 2; C=N
1564	1441	1440	1605	1576	1573	1573	Ring 1, 3, 4
1560	1418	1402	1540	1500	1528	1531	Ring 4; C–N
1470	1387	1336	1505	1490	1515	1493	Ring 3; C–N
1245	1204	1258	1488	1373	1365	1341	Ring 4
1093	1091	1176	1387	1246	1327		Ring 3, 4, C–N
903	985	994	1356	1259	1263	1285	Ring 3, 4; C–N
798	804	816	1198	1186	1164	1166	Ring 1, 2, 3, 4

HF: HFLYP/6-31G(d), DFT: VWN/DZVP, Exp: Experimental frequencies.

erizes radically. The general formula and structure of polyaniline is described in Figure 1b. The empirical formula corresponding to polyaniline is $C_{24}H_{20}N_4$, the molecular point group is corresponding to C1. There are 138 calculated genuine vibrations corresponding to this molecule. Both Table 2 and Figure 2 are presenting the IR spectra of polyaniline. The vibrational frequencies of C–N are obtained at 1285 cm^{-1} corresponding to ring 3, 4. Again, at 1493 cm^{-1}, this band corresponding to C–N of the ring 3. Finally the C–N of the ring 4 is observed at 1531 cm^{-1}. C=N of the ring 2 has two vibrational modes at both 1599 cm^{-1} and 1659 cm^{-1} respectively. Another two vibrational modes were noticed for the ring 4 and the ring 1, 2, 3 and obtained at both of 1341 cm^{-1} and 1573 cm^{-1}. The last band which appeared at 1166 cm^{-1} is assigned to the ring 1, 2, 3, 4. The obtained results indicate that, both ab initio calculation HF/6-31G(d) and Density Functional method, VWN/DZVP gives good agreement with the experimental results. Moreover, both are considered to be more accurate as compared with that of semiempirical calculations AM1, PM3, PM5 and MINDO. This is due to the effect of electron correlation which is included in both types of calculation rather than semiempirical methods. It is worth to mention that, this effect of electron correlation is responsible for bringing the semiempirical calculations of aniline in fair agreement with experimental results while that of polyaniline is far from experimental results. The effect of electron correlation for aniline monomer is considered as a little source of error in the calculations while polyaniline has four aniline ring unit so that the error increased and as a result its effect is clear.

From the above results one can observe that, the vibrational calculations of a four-ring unit (emeraldine base:EB) are believed to be a good representation of the polyaniline at Cu(II)-montmorillonite. Furthermore, the presented model could be used to study the possible adsorption of polyaniline on the surface of other metals (mainly transition metals).

Final heat of formation: Heats of formation are relative to the element in their standard state at 298 K. Final heat of formation is calculated at PM3 level

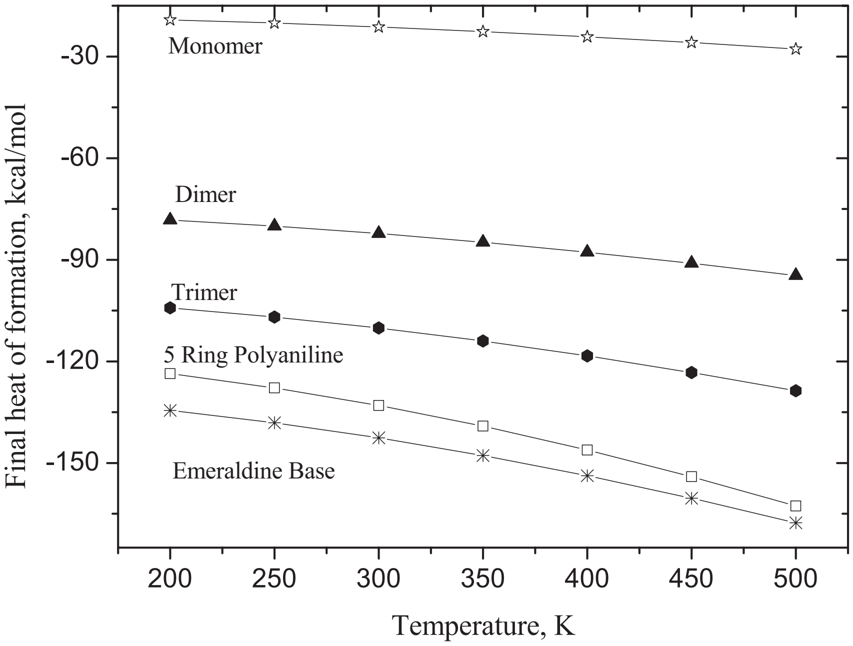

Figure 3. Final heat of formation as a function of temperature which calculated at PM3 level of theory for aniline monomer, dimer, trimer, four ring unit (emeraldine base) and five ring unit polyaniline.

of theory for aniline monomer, dimer, trimer and two structures of polyaniline namely: four ring unit and five ring unit. The final heat of formation is studied as a function of temperature in the range 200 up to 500 K. As seen in Figure 3, and starting with aniline monomer the heat of formation is changed with temperature from –19.2 kcal/mol up to –27.8 kcal/mol in the studied temperature range. Regarding aniline dimer the calculated final heat of formation is changed from –82.1 kcal/mol up to –94.6 kcal/mol. The same behavior is noticed in case of aniline trimer. The heat of formation corresponding to emeraldine base polyaniline which as a function of temperature is changed from –138.1 kcal/mol to –167.7 kcal/mol. Finally, five ring polyaniline shows a change in its final heat of formation and changed from –127.8 kcal/mol to –162.7 kcal/mol.

It is clear that, the final heat of formation is a function of polymerization and decrease from aniline monomer to five-ring unit.

Conclusion

From the comparison of both experimental and calculated frequencies it is concluded that, both scaled Hartree-Fock, HF and Density Functional Theory, DFT, results considered being more accurate than other methods according to electron correlation effect which is of concern in these kinds of calculation rather than semiempirical calculations. Both calculated and experimental data are in good agreement with each other. It is a kind of challenge to perform vibrational analysis for this polymer. So that, the presented data of polyaniline suggest that IR data calculated ab initio on relatively short oligomers (quantum-mechanical oligomer approach) may provide valuable information regarding the interpretation of vibrational spectra of polymers.

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Povzetek

Polimerizacijo anilina s Cu(II) montmorilonitom smo raziskovali s spektroskopijo ATR-FTIR. Experimentalne spektre smo primerjali s spektri, dobljenimi z metodami AM1, PM3, PM5, MINDO, Hartree-Fockovo HF/6-31g(d), kot tudi teorijo gostotnih funkcionalov BLYP/DZVP in B3LYP/6-31g(d,p). Proučevali smo tvorbeno entalpijo kot funkcijo temperature. Rezultati za anilin kažejo, da se frekvence, izračunane z metodo B3LYP/6-31G(d,p), dobro ujemajo z eksperimentalnimi vrednostmi, medtem ko je za polianilin ujemanje optimalno pri uporabi HF/6-31G(d) metode. Menimo, da so vibracijski računi za verige, sestavljene iz štirih obročev, dober približek za polianilin v Cu(II) montmorilonitu. Pokazali smo, da je tvorbena entalpija odvisna od polimerizacije in se spreminja od monomere anilina do petčlenske verige polianilina.