Theoretical study of frequencies modes, energy gap and HOMO –LUMO energies in solvents combinations for

monomer urea

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Abstract

Molecular structure determination for monomer urea as well as their vibrational frequencies have been theoretically investigated by molecular orbital by Ab Initio calculation based on DFT theory level using 6-311G basis set performed by B3LYP method. Assignments for vibrational frequencies were made, and solvent effect on the IR frequencies using eleven solvents: water, Dimethylsulfoxied, Ethanol, Acetone, Aniline, Chlorobenzene, Chloroform, Toluene, Benzene ,Cyclohexane and Heptane. The vibration mode of carbonyl is shifted to lower frequencies while the NH₂ bending increased in polar solvent. The correlation between the dielectric constant and parameters[C=O freq., Energy gap, HOMO and LUMO] in eleven solvents obtained values r² with range 0.890-0.973

Key words: monomer urea, DFT, 6-311G(3dp,3df),HOMO–LUMO

Introduction

Urea, CO(NH₂)₂, has been the subject of extensive theoretical and experimental study in the past three decades, mainly because of its interesting physical and chemical properties. It is one of the simplest biological molecules and one of the simplest diamides used in organic chemistry⁽¹⁾. Urea has the advantage of corresponding to a molecule that contains the classic organic atoms (C, N, O, and H) and both single and double bonds, it is also the only example of a compound containing a carbonyl group involved in four hydrogen bonds

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(the carbonyl O atom shows a particularly unusual hydrogen-bond pattern: it accepts four N–H hydrogen bonds)⁽²⁾.

Urea, first isolated by Rouelle in 1773, was the first organic substance synthesized from inorganic materials in the laboratory by Wöhler in 1828 and so its synthesis demolished the vita list theories that considered biological and nonbiological compounds to be somehow distinct. Since then it has been the subject of interest to investigators in almost every branch of fundamental and applied research^(3,4).

Urea is produced in natural course from ammonia and carbon dioxide by metabolic reactions, known as the urea cycle, in all living beings and excreted from the body so as to avoid the toxic effects of ammonia. Water solutions of urea also show very exceptional, specific properties. These solutions can change the structure of proteins,⁽⁵⁾ increase the solubility of hydrophobic species such as hydrocarbons,⁽⁶⁾ and prevent micelle formation^{.(7)} This makes urea very interesting for researchers in the field of biochemistry.

Its role in pharmaceutical chemistry is well established. A specific drug urea stibamine for Kalaazar is prepared by the interaction of *p*-aminophenyl stibimic acid with urea.⁾⁸⁾ It has also been found that some Pt-urea complexes have antitumor activity, probably due to their square-planar structure (e.g., cis platinum). Moreover, the NH₂ and CO groups should provide enough hydrogen bonding to produce conformational changes in nucleotides and DNA in addition to chemical bonding. This brings us to the importance of urea to coordination chemists. Though urea is a very small molecule, it has three coordination sites (one oxygen and two nitrogen atoms) and it is able to form complexes with different coordination numbers with several metals. To characterize these complexes, researchers use infrared, Raman, UV, and NMR spectroscopy and X-ray diffraction, so spectroscopists and structure chemists are brought together in this field. Quantum chemists also showed their interest in this molecule by performing calculations on the structure and the vibrational spectrum of urea.⁽⁹⁻

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²⁶⁾ The aim of this work was theoretical determination vibration frequencies, energy gap, HOMO–LUMO energies in different solvents and correlation between these properties and dielectric constant.

Computational method

.The urea compound study represented by general formal as shown in fig1



Fig.1. DFT-calculated optimized structures of the urea in gas phase at .B3LYP/6-311G (3dp,3df)

A full quantum mechanical geometry optimization was performed by using PC GAMESS computational program for calculation. The calculations were done at the density functional theory DFT/B3LYP level of theory using the basis set 6-311G(3dp,3df). IR spectrum of urea in non solvent , assuming normal coordinate analysis, at the harmonic approximation was simulation as for molecule in eleven different solvents: water, Dimethylsulfoxied, Ethanol, Acetone, Aniline, Chlorobenzene, Chloroform, Toluene, Benzene ,Cyclohexane and Heptane . Energy band gap (Δ E) and HOMO-LUMO energies calculation has been done using Chermcraft program, correlation drawing throughout the Data fit 9. program. All calculations were performed on the Pentium (R) 4/IPM-PC- CPU 3.000GHz.

Results and discussion

1.Vibrational assignment

The theory study provide certainty of the often speculative assignments of the observed bands of specific molecular vibration modes. The theoretical vibrational frequencies for urea calculated using 6-311G(3dp,3df) basis set is given in table (1). Urea molecule, [H₄N₂CO] has 8 atom which give rise to 18 internal normal mode vibrations 13 (in plane mode) and 5 (out of plane mode). The calculated vibration frequencies for urea molecule using harmonic oscillator approximation in this work, with assignments and the calculated and experimental frequencies from literature.⁽²⁷⁾ The calculated stretching frequencies of carbonyl group is shifted low frequencies in polar solvents compared with non solvent(gas) , on the other hand the stretching of the carbonyl group vibration mode is shifted to low frequency , which are expected. This is attributable to the effects of strong intermolecular hydrogen bonding in polar solvents which decrease the carbonyl stretching frequency. While the stretching of amine group is shifted to high frequencies in polar solvent. The amine bending group is shifted to high frequencies in polar solvent.

HOMO - LUMO energy gap .2

The HOMO, LUMO and HOMO-LUMO energy gap of urea in the DFT level in 6-311G(3dp,3df) basis set has been calculated in table 2 . The HOMO-LUMO energy gap reveals that the chemical activity of the molecule. Molecules with high HOMO (highest occupied molecular orbital energy) values can donate their electrons more easily compared to molecules with low HOMO energy values, and hence are more reactive. Molecules with low LUMO (lowest unoccupied molecular orbital energy) values are more able to accept electrons than molecules with high LUMO energy values. According to the HOMO and LUMO values for the solvents increase the polar of solvent, however, the

HOMO and LUMO coefficients are not equal. The larger HOMO coefficient

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indicates that the electron donating capability of the solvent molecule is more important than its electron accepting ability. Therefore, a solvent with the ability to donate

Table 1. Comparison of the calculated fundamental frequencies urea cm	⁻¹ based on harmonic approximation in non
solvent and eleven solvents with experimental values.	

assignment Solvents	EXP	H ₂ O	DMSO	C ₂ H ₅ OH	C ₃ H ₆ O	C ₆ H ₅ NH ₂	C ₆ H ₅ Cl	CHCl ₃	C ₇ H ₈	C ₆ H ₆	C ₆ H ₁₂	C ₇ H ₁₆	Gas
ⁱ (H _{trans} NCO) v	376	301	239	200	191	249	279	249	151	349	202	255	291
^{ic} (H _{trans} NCO) v	445	377	429	325	433	334	327	326	378	390	392	427	468
$(CNH_2))^i v$	573	433	449	390	488	400	400	401	425	433	420	442	496
CN ₂)) v	483	488	506	473	524	480	476	472	474	511	468	481	524
CNH ₂)) ^{ic} v	582	564	567	553	577	551	523	523	561	542	542	561	581
v (OCN)	635	594	579	579	610	578	572	572	575	576	572	576	605
ONCN))v	759	777	774	776	776	776	776	776	774	778	777	775	774
CN)) ^s v	940	968	978	971	978	971	960	960	964	962	955	965	965
NH ₂)) ^{ic} v	1008	1030	1046	1025	1017	1024	1019	1019	1012	1018	1008	1019	1027
NH ₂)) ⁱ v	1145	1157	1177	1157	1180	1159	1161	1159	1162	1164	1163	1169	1185
CN)) ^{as,} v	1396	1413	1423	1415	1425	1416	1407	1408	1409	1415	1404	1413	1416
\mathbf{NH}_2)) ⁱ v	1587	1596	1608	1599	1586	1604	1597	1598	1607	1607	1604	1614	1629
NH ₂)) ^{ic} v	1591	1606	1618	1615	1625	1619	1613	1612	1622	1626	1620	1628	1643
v(C=O)	1752	1662	1688	1692	1690	1696	1698	1699	1725	1705	1732	1736	1789
NH ₂)) ^{s,ic} v	3436	3570	3531	3553	3532	3554	3571	3570	3559	3572	3576	3545	3511
NH ₂)) ^{s,i} v	3463	3583	3550	3569	3535	3571	3593	3592	3568	3589	3598	3565	3535
NH ₂)) ^{as,ic} v	3543	3696	3643	3671	3644	3671	3691	3690	3681	3692	3695	3662	3626
NH ₂)) ^{as,i} v	3573	3736	3668	3722	3663	3717	3738	3737	3709	3729	3718	3686	3646

s and as stand for symmetric and asymmetric; i and ic stand for in-phase and in-counter phase

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electrons easily and accept electrons with difficulty should be used in order to increase the polar solvents. Similarly the polar solvent is increased when the monomer LUMO becomes increasingly negative. This correlates well with the high HOMO values predicted for the solvent molecules and supports the importance for strong interactions between solvent and urea if a high polar solvent is desired.

Solvent	Mode	Energy gap	Energy gapHOMOLUMO		Dipol.moment	.Exp
	wiouc	(ev)	(ev)	(ev)	(Debye)	3
H ₂ O		7.2682184	7.627411-	0.359193-	5.782893	80.1
DMSC)	7.246449	7.61653-	0.37008-	5.717426	46.7
C ₂ H ₅ O	Н	7.246449	7.61925-	0.3728-	5.664399	26
C ₃ H ₆ C)	7.219237	7.60292-	0.38368-	5.660061	20.7
C ₆ H ₅ NI	\mathbf{I}_2	7.145766	7.57299-	0.42722-	5.455142	7.06
C ₆ H ₅ C	1	7.121276	7.5621-	0.44083-	5.352367	5.69
CHCI	3	7.096785	7.55122-	0.45443-	5.307957	5.2
C7H8		6.928073	7.48319-	0.55512-	4.955984	2.38
C ₆ H ₆		6.884535	7.45326-	0.56872-	4.950887	2.283
C ₆ H ₁₂	2	6.870929	7.45598-	0.58505-	4.791285	2.02
C ₇ H ₁₀	i	6.846439	7.44509-	0.59866-	4.806558	1.9
Gas		6.557996	7.32808-	0.77009-	4.247184	-

Table 2. Calculated energy gap ,HOMO,LUMO and dipole momentof studied molecule (in ev and Debye)

3. Correlation between experimental dielectric constant for solvents and C=O vibrational frequencies, Energy gap, HOMO and LUMO energies for monomer urea

The correlation between dielectric constant of solvents and vibration frequencies of carbonyl, as it can be seen in fig 2. The dielectric constants are decrease as vibrational frequencies of carbonyl values increase due to less of polar for solvents. This means that there is an inverse relationship between dielectric constant and vibrational frequencies of carbonyl. While correlation coefficient is very good (r² .= 0.890)



Fig. 2. correlation between the experimental dielectric constant for solvents and C=O frequency in urea in eleven solvents obtained by the DFT method

While noted in fig. 3 that an increase of the energy gap increases the value of the determination of the dielectric constant for the solvents, this means that there is a direct correlation, also notes the increasing value of the correlation coefficient ($r^2 = 0.961$).



Fig. 3. correlation between the experimental dielectric constant and Energy gap in eleven solvents obtained by the DFT method

While in fig 4 and 5 are noted that the relationship between the dielectric constants and values HOMO are inversely related, while in the case of the values LUMO of the direct correlation.



Fig. 4 correlation between the experimental dielectric constant and HOMO in eleven solvents obtained by the DFT method



Fig. 5 correlation between the dielectric constant and LUMO in eleven solvents obtained by the DFT method

Conclusion

The calculation of normal mode frequencies for urea and their assignments from the scaled ab initio force field have given a reasonable interpretation of the vibrational spectra, and helped to eliminate some inconsistencies in the several experimental assignments available for this molecule. Evidence is presented for large frequency shifts in carbonyl and hydrogen-involving vibrations due to intermolecular hydrogen bonding and vibrational coupling in the condensed phase and, appropriately, the theoretical frequencies are compared in the present work with the frequencies of the matrix isolated species. In addition to the presence of link relationships between a variety of variables and dielectric constant for solvents.

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دراسة نظرية لنمط الترددات وفجوة الطاقة وطاقات HOMO و LUMO في مجموعة من المذيبات لمومنر اليوريا وسام عبد الحسن راضي قسم الكيمياء، مركز أبحاث البوليمر ، جامعة البصرة

المستخلص

يتضمن البحث در اسة نظرية باستعمال نظرية دالية الكثافة الالكترونية بطريقة B3LYP وعند مستوى المجموعة الاساس 6-311G(3dp,3df) لمونمر اليوريا اضافة إلى حسابات الترددات التذبذبية للجزيئة وتشخيص الترددات مع الاطياف العملية وكذلك در اسة تاثير المذيبات المختلفة على ترددات تحت الحمراء لمونمر اليوريا. وكذلك در اسة علاقات الارتباط بين مغير ات معينة وثابت ثنائي العزل الكهربائي العملي للمذيبات المستخدمة في الدر اسة.