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Vibrational and theoretical studies of urea and magnesium-urea complexes

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Abstract. The molecular structure and IR spectra of urea, H_2NCONH_2, in gas phase and in acetonitrile solution, as well as of the two complexes $[MgU_4Cl_2]$ and $[MgU_6]Cl_2$ have been observed. The influence of environmental changes to geometry and spectra are shown. Various basis sets have been employed to safeguard the validity of the reported findings, using polarization functions for all calculations to get the correct pyramidal amide configuration. The erroneous low energy of the C_{2v} symmetry group, after the addition of the ZPVE correction, is discussed. For the solvated urea molecule a reduction of the energy barrier, compared to the gas phase urea, between the two minimum configurations, C_2 and C_s, and the planar geometry, is observed. The lowest energy minimum in acetonitrile is found to be the C_2 symmetry group, while for the two complexes, the local symmetry of urea is C_s or C_2 depending on the complex, or even on the coordination position of urea in the complex. The wagging motion of the amide group is also discussed in all the studied urea species. The computed geometries and most of the spectroscopic results are in good agreement with the available experimental data.

Introduction

The presence of urea in the products of human metabolism and its small size, due to which accurate quantum mechanical calculations can be easily performed, are some of the factors due to which this molecule attracts the interest of both chemists and biologists. It is also known that urea forms a variety of complexes with metal atoms [1] by using the lone pair of either oxygen or nitrogen. Some of these complexes are known to have antimicrobial and antiviral properties [1].

The paper is divided into three parts. In the first, we focus on the geometry and IR spectra of the isolated molecule. One of the urea topics, which have been discussed by several authors, is its equilibrium structure. Older calculations with small basis sets predicted a planar geometry [2, 3], while more elaborate computations with larger basis sets have shown that the planar isomer was a second-order saddle point, and the global minimum had a C_2 symmetry with the NH_2 groups in pyrimidal form [4]. We first demonstrate that the methods we employ can correctly predict the equilibrium structure of urea in the gas phase. We also discuss the effect of anharmonicity of the vibrations of urea molecule by calculating the fundamental frequencies using third- and fourth-order derivatives of the energy, reporting for the first time the anharmonic corrections at the SCF and MP2 level.

The second part deals with the solvated urea in acetonitrile. We discuss how this solvent affects the geometry and IR spectrum. Our results are also compared with the available experimental data for the parent and deuterated molecule [7].

In the last part, the results for the geometry of two urea complexes with Mg are given. The first magnesium complex has four urea molecules and two chlorine atoms in its inner coordination sphere. The second complex has six urea molecules in the inner coordination sphere of the Mg^{2+} ion and two Cl^- as counter ions. In this way a comprehensive study will be reported of the geometry changes and IR shifts which are observed when urea is studied in the gas phase, in solution, and in coordination complexes with the magnesium ion.

Computational methods

For the computations the basis sets developed by Pople and his group [8–10] have been used. These include the split valence 6-31G basis set as well as the triple split, 6-311G basis set, extended with polarization and diffuse functions. The specified variety of basis sets was used to safeguard the validity of the reported findings.

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The supplementary Tables mentioned in the text are available in electronic form on Springer Verlag's server at http://link.springer.de/link/service/journals/00214index.htm

No data, neither experimental nor theoretical, are available in the literature for the geometry of urea solvated in acetonitrile. Thus, to reduce uncertainties associated with small basis sets, we have extended the series of basis used for the gas phase molecule to include a much larger one, 6-311G++3pd3df. With this basis set the calculation of urea in acetonitrile consists of 256 GTFs.

For the urea complexes, due to their sizes, it was not possible to use larger basis sets than 6-31G*. Even this set involves 465 GTFs for the $[MgU_6]Cl_2$ complex.

The geometry and harmonic IR frequency calculations have been performed using the PC GAMESS version [11] of the GAMESS (US) QC package [12]. Of the methods for which analytical second-order derivatives were not available, that is at the MP2 level and for the solvation models, numerical second-order derivatives, with two displacements in each Cartesian direction were used to improve the accuracy.

The calculations of urea in acetonitrile solvent have been performed by employing the Onsager [13] continuum solvation model with the solute embedded in a spherical cavity whose radius is 3.32 Å. The cavity radius was calculated at the MP2/6-31G** level, using the Gaussian 98 [14].

The third- and fourth-order energy derivatives were calculated at the SCF level analytically using CADPAC [15], version 5.2, while at the MP2 level the third-order energy derivative was determined numerically from analytical second-order derivatives. The fundamental frequencies have been calculated using SPECTRO [16], version 3.0.

Results and discussion

Gas phase urea molecule

Structure Early theoretical studies [17] found that the optimized geometry of urea was planar. This result was due to an inappropriate basis set. It is known from the early 1970s from the work of Attanasio et al. [18] that, in order to describe the behavior of the lone pair of the nitrogen atom and its participation in the C-N bond, d-polarization functions should be included in the basis set for the description of the nitrogen atom. This was taken into account in many accurate ab initio calculations [4–6], giving as the equilibrium geometry the C_2 symmetry isomer (Fig. 1A) with the C_s isomer (Fig. 1B) also being a true minimum, with zero imaginary frequencies, but a

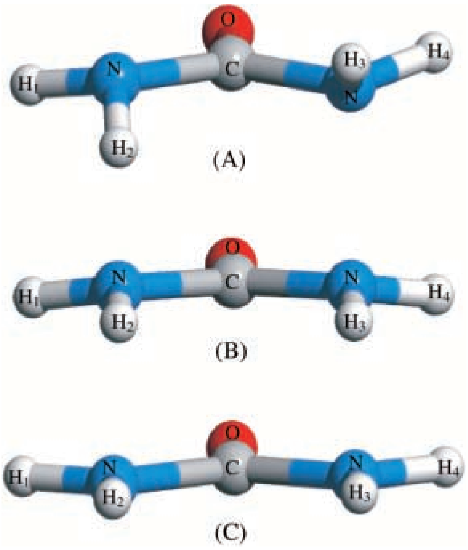

Fig. 1. Molecular structure of the gas phase and solvated urea molecule. The C_2, C_s and C_{2v} symmetry groups of urea, are indicated with (A), (B) and (C), respectively

Table 1. Comparison of the calculated geometry of the C_2 symmetry urea molecule, with the experimental one

Bonds	Present work				Exper.[a]
	6-31G**		6-311G**		
	SCF	MP2	SCF	MP2	
C = O	1.198	1.225	1.191	1.214	1.221
C-N	1.371	1.390	1.374	1.393	1.378
$N-H_1$	0.995	1.008	0.995	1.010	1.021
$N-H_2$	0.994	1.008	0.994	1.010	0.998
Av. Dev.	0.015	0.010	0.016	0.011	
Bond angles					
OCN	122.9	123.5	123.1	123.8	122.6
NCN	114.2	112.9	113.8	112.5	114.7
CNH_1	113.7	111.9	113.5	111.6	112.8
CNH_1	118.2	116.0	117.6	115.1	119.2
H_1NH_2	115.3	113.6	114.8	113.2	118.6
Av. Dev.	1.2	2.4	1.5	2.8	
Dihedral angles					
$OCNH_1$	−11.8	−13.7	−13.0	−14.8	−10.8
$OCNH_2$	−151.7	−146.3	−150.9	−145.5	−156.9
$NCNH_1$	168.2	166.3	167.0	165.2	169.2
Av. Dev.	2.4	5.5	3.5	6.5	

[a] Experimental data from a microwave study [19]

Table 2. Energies and energy differences computed with two basis sets. Energy is in a.u., energy differences in kcal/mol and dipole moments (μ) in debye (D)[a]

Method	Sym	I.F.	μ	E	ΔE	$\Delta\Delta H_0$
HF						
6-31G**	C_{2v}	2	4.59	−223.998600	1.15	0.00
	C_2	0	3.94	−224.000430	0.00	0.10
	C_s	1	4.51	−223.998765	1.04	0.25
6-311G**	C_{2v}	2	4.58	−224.053366	1.40	0.09
	C_2	0	3.88	−224.055591	0.00	0.00
	C_s	0	4.43	−224.053806	1.12	0.35
MP2						
6-31G**	C_{2v}	2	4.23	−224.641395	2.41	1.05
	C_2	0	3.33	−224.645238	0.00	0.00
	C_s	0	3.97	−224.642763	1.55	1.05
6-311G**	C_{2v}	2	4.16	−224.746903	3.25	1.70
	C_2	0	3.21	−224.752076	0.00	0.00
	C_s	0	3.84	−224.749498	1.62	1.23
Exp.			3.83[b]			

[a] Sym = Symmetry of the conformer
I.F. = Imaginary Frequencies
ΔE = relative energy
$\Delta\Delta H_0$ = relative energy including ZPE correction from harmonic frequencies scaled by 0.92 for HF calculations and by 0.97 for MP2 calculations [20]

[b] Experimental value from [24]

little higher in energy. In these studies the planar geometry (Fig. 1C) was a second-order saddle point.

In the present work four basis sets, at the SCF and MP2 levels, have been used for the study of the structure. Our results show that the methods used give geometries which do not show remarkable differences and all the basis sets, although varying in size, give bond lengths and angles of similar accuracy. In Tables 1 and 2 we present the results associated with the 6-31G** and 6-311G** basis sets. Tables with the results of all four basis sets used are given in the supplementary material (Tables S1 and S2).

We observe (Table 2) that at the SCF level the split valence basis set predicts the C_s structure to be a transition state, while at the MP2 level both basis sets correctly predict that the C_s structure is a true minimum. It is observed that the energy difference between the C_2 and the C_{2v} structures increases with the inclusion of correlation. This is an indication of the inversion barrier of the amide group. We should note, however, from the findings of Godfrey et al. [19], that there is another intermediate way to go from the C_2 to the C_s structure without proceeding though C_{2v} intermediate, but through an energy barrier that is four times lower in

Table 3. Gas-phase calculated frequencies (cm^{-1}) for the parent and deuterated urea molecule[a]

Assignment	6-31G**		6-311G**		Experiment			
	SCF	MP2	SCF	MP2	[25]	[26]	[27][b]	[27][c]
	H_2NCONH_2, present work							
$\nu_a(NH_2)$	3555	3560	3524	3505	3548	3545	3450	
$\nu_a(NH_2)$	3555	3560	3524	3505	3548	3545	3450	
$\nu_s(NH_2)$	3445	3439	3424	3393	3440	3440	3345	
$\nu_s(NH_2)$	3442	3437	3420	3391	3440	3440	3345	
$\nu(CO)$	1795	1753	1775	1737	1734	1740	1680	1655
$\delta_a(NH_2)$	1610	1577	1607	1549	1605	1590	1610	1590
$\delta_s(NH_2)$	1603	1568	1599	1541	1594	1590	1600	1545
$\nu_a(CN)$	1391	1365	1376	1340	1394	1393	1470	1480
$\rho_s(NH_2)$	1160	1135	1162	1131	1153	1145	1150	1180
$\rho_a(NH_2)$	1036	1019	1034	1009	1014	1004	1060	1020
$\nu_s(CN)$	932	913	922	901	960	940	1005	
$\omega(CO)$	788	744	794	760	790	785	790	
$\delta(CO)$	565	616	567	651	578	580	720	
$\omega_s(NH_2)$	547	562	563	569	552	543	560	550
$\omega_a(NH_2)$	527	527	527	533	542	500		
$\delta(CN)$	464	447	464	451	485	479	490	490
$\tau_a(NH_2)$	428	431	429	435				
$\tau_s(NH_2)$	368	384	366	381		233	370	380
Av. Dev.[d]	13	22	17	37				
	15	20	19	35				
	D_2NCOND_2, present work							
$\nu_a(ND_2)$	2633	2632	2608	2591	2648	2650		
$\nu_a(ND_2)$	2630	2630	2606	2590	2648	2650		
$\nu_s(ND_2)$	2491	2486	2476	2453	2505	2500		
$\nu_s(ND_2)$	2488	2483	2471	2450	2505	2500		
$\nu(CO)$	1775	1733	1754	1719	1723	1730		
$\nu_a(CN)$	1409	1547	1388	1346	1408	1405		
$\delta_s(ND_2)$	1226	1193	1221	1172	1223	1221		
$\delta_a(ND_2)$	1142	1121	1142	1103	1155			
$\rho_s(ND_2)$	976	946	974	939	1000			
$\rho_a(ND_2)$	847	822	850	820				
$\nu_s(CN)$	829	819	824	810	845	840		
$\omega(CO)$	756	713	759	720	776	767		
$\delta(CO)$	510	490	513	509	517	517		
$\omega_s(ND_2)$	429	481	441	493				
$\delta(CN)$	392	415	393	427				
$\omega_a(ND_2)$	389	380	392	384				
$\tau_a(ND_2)$	324	322	324	324				
$\tau_s(ND_2)$	263	275	261	274				
Av. Dev.[d]	17	38	23	46				
	14	34	21	42				

[a] The SCF and MP2 frequencies have been scaled using the factors [20] 0.90 and 0.94, respectively

[b] Experimental data from FT-IR experiment

[c] Experimental data from Raman experiment

[d] The values in the first and second line are average deviations from the experimental results reported by King [25] and Li et al. [26], respectively. The wagging frequency of 233 cm^{-1} is not included for the calculation of the average deviation

Table 4. Comparison between vibrational frequencies obtained in the harmonic approximation with fundamental frequencies using cubic and quadratic force constants. The results presented are from the C_2 isomer

Assignment	SCF/6-31G**++			MP2/6-31G**++		
	Harmonic frequencies	Fundamental frequencies	Anharmonic correction [28]	Harmonic frequencies	Fundamental frequencies	Anharmonic correction [28]
$\nu_a(NH_2)$	3951	3803	−148	3780	3613	−167
$\nu_a(NH_2)$	3951	3801	−150	3780	3612	−168
$\nu_s(NH_2)$	3828	3700	−128	3650	3502	−148
$\nu_s(NH_2)$	3823	3695	−128	3647	3499	−148
$\nu(CO)$	1957	1910	−47	1817	1774	−43
$\delta_a(NH_2)$	1787	1747	−40	1676	1631	−45
$\delta_s(NH_2)$	1781	1751	−30	1667	1628	−39
$\nu_a(CN)$	1538	1512	−26	1441	1460	19
$\rho_s(NH_2)$	1284	1246	−38	1201	1161	−40
$\rho_a(NH_2)$	1144	1092	−52	1075	859	−216
$\nu_s(CN)$	1034	1018	−16	970	952	−18
$\omega(CO)$	866	920	54	780	731	−49
$\delta(CO)$	626	617	−9	640	530	−110
$\omega_s(NH_2)$	573	511	−62	595	554	−41
$\omega_a(NH_2)$	573	376	−197	563	550	−13
$\delta(CN)$	516	518	2	480	482	2
$\tau_a(NH_2)$	466	366	−100	469	437	−32
$\tau_s(NH_2)$	388	319	−69	385	357	−28

Table 5. Energy and energy differences computed using a series of basis sets for urea in acetonitrile solvent. Energies are in a.u., energy differences in kcal/mol and dipole moments (μ) in debye (D), respectively[a]

Basis set	Sym	I.F.	μ	E	ΔE
6-31G*	C_{2v}	2	5.29	−223.989504	0.50
	C_2	0	4.84	−223.990305	0.00
	C_s	0	5.29	−223.989916	0.24
6-31G**	C_{2v}	2	5.29	−224.005894	0.26
	C_2	0	4.96	−224.006316	0.00
	C_s	0	5.28	−224.006050	0.17
6-31G**++	C_{2v}	2	5.63	−224.017249	0.09
	C_2	0	5.43	−224.017390	0.00
	C_s	0	5.62	−224.017297	0.06
6-311G**	C_{2v}	2	5.29	−224.060642	0.42
	C_2	0	4.89	−224.061312	0.00
	C_s	0	5.26	−224.060988	0.20
6-311G++3df3pd	C_{2v}	2	5.44	−224.090448	0.22
	C_2	0	5.16	−224.090801	0.00
	C_s	0	5.41	−224.090655	0.09

[a] Sym = Symmetry of the conformer
I.F. = Imaginary Frequencies
ΔE = relative energy

energy. Experimental evidence is given to demonstrate this [19].

In order to increase the accuracy of the calculated energies, the zero-point vibrational energies (ZPVE) have also been computed, within the harmonic approximation [20].

The ZPVE has been scaled using the factors 0.92 and 0.97 for the SCF and MP2 values, respectively [20]. It is observed that the planar (C_{2v}) geometry, at the SCF/6-31G** level, has lower energy than the C_2 and C_s symmetry structures, although it is a second-order saddle point. These surprising data are due to:

- The two imaginary frequencies are excluded from the ZPVE calculation for the planar geometry. Now the sum of frequencies added to give the ZPVE is 16 instead of 18. These frequencies are 393i and 217i at the SCF/6-31G** level of theory.
- The harmonic approximation is used to compute the ZPVE. It is known that the force field of molecules containing the $-NH_2$ group (e.g., NH_3 [21] or formamide [22]) is highly anharmonic. Thus the ZPVE computed from the harmonic approximation is of limited accuracy.

A further argument in support of the view that the gas phase structure of urea is not planar has been provided by Masunov and Dannenberg [23], who noted that the urea dipole moment [24] value is too high to be compatible with the C_{2v} symmetry, while the C_2 symmetry gives the correct dipole moment.

IR spectrum The results for the gas-phase calculated frequencies for the parent and the deuterated urea molecule are given in Table 3. The scaling factors [20] used to estimate fundamental frequencies from theoretical harmonic frequencies are 0.90 cm^{-1} and 0.94 cm^{-1} for SCF and MP2, respectively. Even with a single scale factor for the whole range of frequencies the average deviation errors from the experimental results for the parent and deuterated molecules are 13 cm^{-1} and 17 cm^{-1}, respectively, compared with King's experimental data [25], but 15 cm^{-1} and 14 cm^{-1} with those as determined by Li et al. [26], respectively, (Table 3). Also included in the same Table are results from FT-IR and Raman experiments from the work of Anastassopoulou et al. [27]. The above errors are for the results computed at the SCF level with the 6-31G** basis set, while those at the MP2 level are a little higher. We note that the results of Rousseau et al. [28], which were obtained at the SCF level using two different scaling factors, have errors very close to the ones found in this paper, that is 9 cm^{-1} and 15 cm^{-1}.

Work is currently in progress to compute the anharmonic corrections of various nitrogen-containing compounds. The results for urea taken from the study [29] are shown in Table 4. We have computed analytically the third- and fourth-order energy derivatives of urea at the SCF/6-31G**++ level analytically. For this reason the third-order derivative was calculated numerically, using as an input analytically determined second-order energy derivatives, and the fourth-order derivative was computed at the SCF level using the MP2 optimized of theory. At the MP2/6-31G**++ level these derivatives were not available geometry [30, 31]. The Fermi [32], Coriolis and Darling-Dennison [33] resonances were calculated and taken into account automatically by SPECTRO.

The present results provide evidence for the large effect of the anharmonicity on the IR vibrational spectrum of urea. For the SCF results, it should be noted, that the much shortened bond lengths predicted at this level, together with the absence of correlation, leads to considerable error in comparison with the experimental results. This is also clear from the two positive anharmonic corrections, one for ω_{12} and the other for ω_{16} harmonic vibrations. The inclusion of correlation improves considerably the agreement between theory and experiment, with the greatest discrepancy arising from the ω_a (NH_2) mode, which is in error by 155 cm^{-1}, while the other differences are in the range 2–66 cm^{-1}. The largest fractions of these errors are believed to be associated with the limitations of method and basis set, something that is also clear from the discrepancy of the MP2 optimized geometry from the experiments [21, 34].

Urea in acetonitrile solvent

The results from the geometry optimization of urea in acetonitrile solvent are summarized in Tables 5 and 6. We observe that the energy difference between the different isomers (C_{2v}, C_2, and C_s) is reduced. This is because the dipole-dipole interaction, introduced by the Onsager model, favors the stabilization of the isomers with the larger dipole moments ($\mu_{C_{2v}} > \mu_{C_s} > \mu_{C_2}$). The results from the calculation using the 6-311G + + 3pd3df basis set show that the energy difference between the two real minima is only 0.09 kcal/mol and the energy difference between the C_2 and C_{2v} isomers is 0.22 kcal/mol. These values are very small and they show that the conclusion drawn on the gas phase molecule also applies to the solvated urea molecule, that is, the C_s isomer appears to be a small minimum in a large amplitude motion of the C_2 conformer [19]. The C_{2v} symmetry is a second-order saddle point in all the calculations while both C_2 and C_s symmetry species are always true minima. The reduction of the energy barrier has also been observed by Wong et al. [35]. These authors studied the 1,2-dichloromethane conformers in various solvents among which was acetonitrile, using the Onsager model. The energy difference that includes the ZPVE correction is not presented for the reasons explained earlier.

In Table 6 the geometric characteristics of urea in the acetonitrile solvent are given. The numbering of the hydrogen atoms is given in Fig. 1. The bond lengths and angles show only a small change as the basis set used increases in size. Only the dihedral angles show a larger change.

The average deviation given in Table 6, is the deviation of the geometry with respect to the planar one. Ignoring for a moment the results obtained by the 6-311G + + 3pd3df basis set, it seems that by adding polarization and diffuse functions, the geometry is getting flatter, as can be seen from the average deviation of the dihedral angles. In order to clarify this matter, the 6-311G + + 3pd3df basis set was used. It is observed that the $-NH_2$ groups were still holding their shallow pyrimidal configuration. A comparison with the gas phase geometry together with the geometry of urea in the Mg-Urea complexes will be given later.

Table 6. The geometry of urea in acetonitrile, calculated using a series of basis sets and the average deviation from the planar configuration

Bonds	6-31G*			6-31G**			6-31G**++			6-311G**			6-311G++3pd3df		
	C_{2v}	C_2	Cs	C_{2v}	C_2	Cs	C_{2v}	C_2	Cs	C_{2v}	C_2	C_S	C_{2v}	C_2	C_S
CO	1.210	1.206	1.208	1.210	1.208	1.209	1.214	1.213	1.214	1.204	1.201	1.202	1.205	1.203	1.203
CN	1.355	1.363	1.361	1.355	1.360	1.358	1.354	1.357	1.356	1.356	1.364	1.362	1.352	1.358	1.356
NH_1	0.992	0.994	0.994	0.990	0.992	0.992	0.991	0.992	0.992	0.990	0.992	0.992	0.988	0.990	0.990
NH_2	0.994	0.996	0.995	0.992	0.994	0.993	0.993	0.994	0.993	0.991	0.994	0.993	0.990	0.991	0.991
Av. Dev		0.004	0.003		0.003	0.002		0.001	0.001		0.004	0.003		0.003	0.002
Bond angles															
OCN	122.4	122.7	122.4	122.4	122.6	122.4	122.2	122.3	122.2	122.5	122.7	122.5	122.3	122.5	122.3
NCN	115.1	114.7	115.1	115.2	114.8	115.2	115.6	115.4	115.6	115.0	114.5	114.9	115.4	115.1	115.3
CNH_1	117.8	115.3	115.8	117.6	115.7	116.3	117.8	116.6	117.0	117.7	115.4	115.8	117.9	116.1	116.4
CNH_2	123.7	120.2	121.5	123.6	120.9	122.1	123.4	121.8	122.5	123.4	120.1	121.2	123.2	120.8	121.6
H_1NH_2	118.4	115.7	116.3	118.9	116.8	117.4	118.8	117.4	117.9	118.9	116.2	116.7	118.9	116.9	117.3
Av. Dev		1.9	1.3		1.5	0.9		0.9	0.5		1.8	1.3		1.3	1.0
Dihedral angles															
$OCNH_1$	0.0	−13.0	−14.4	0.0	−11.3	−11.5	0.0	−9.6	−9.3	0.0	−13.1	−14.1	0.0	−11.9	−12.5
$OCNH_2$	180.0	−159.2	−165.1	180.0	−161.8	−168.1	180.0	−166.1	−170.8	180.0	−160.1	−165.5	−180.0	−163.5	−167.4
$NCNH_1$	180.0	167.0	168.7	180.0	168.7	171.0	180.0	170.4	172.8	180.0	166.9	169.0	180.0	168.1	170.2
Av. Dev		15.6	13.5		13.6	10.8		11.0	8.6		15.4	13.2		13.4	11.6

Table 7. Harmonic frequencies (cm^{-1}) for urea in acetonitrile solvent. Results are presented for the parent and deuterated molecule[a]

Assignment	6-31G**	6-311G + + 3df3pd	Exper.[b]
	H_2NCONH_2, present work		
$\nu_a(NH_2)$	3578	3543	3503
$\nu_a(NH_2)$	3578	3542	3503
$\nu_s(NH_2)$	3462	3434	3390
$\nu_s(NH_2)$	3455	3426	3390
$\nu(CO)$	1740	1687	1695
$\delta_a(NH_2)$	1609	1600	1614
$\delta_s(NH_2)$	1604	1594	1614
$\nu_a(CN)$	1397	1376	1419
$\rho_a(NH_2)$	1145	1138	1167
$\rho_s(NH_2)$	1016	1010	
$\nu_s(CN)$	948	939	969
$\omega(CO)$	775	782	
$\delta(CO)$	561	563	576
$\tau_s(NH_2)$	518	519	
$\delta(CN)$	472	473	509
$\tau_a(NH_2)$	427	406	
$\omega_a(NH_2)$	317	310	
$\omega_s(NH_2)$	314	293	
Av. Dev.	39	29	
	D_2NCOND_2, present work		
$\nu_a(ND_2)$	2651	2625	2623
$\nu_a(ND_2)$	2648	2622	2623
$\nu_s(ND_2)$	2505	2484	2474
$\nu_s(ND_2)$	2498	2476	2474
$\nu(CO)$	1719	1662	1678
$\nu_a(CN)$	1420	1394	1448
$\delta_s(ND_2)$	1235	1227	1239
$\delta_a(ND_2)$	1140	1134	1152
$\rho_s(ND_2)$	978	971	991
$\nu_s(CN)$	835	829	862
$\rho_a(ND_2)$	822	819	833
$\omega(CO)$	760	767	
$\delta(CO)$	504	507	522
$\delta(CN)$	397	399	429
$\tau_s(ND_2)$	379	379	
$\omega_a(ND_2)$	325	306	
$\tau_a(ND_2)$	242	228	
$\omega_s(ND_2)$	230	222	
Av. Dev.	23	17	

[a] The calculated frequencies were scaled by 0.90 [20]
[b] Experimental data from [36]

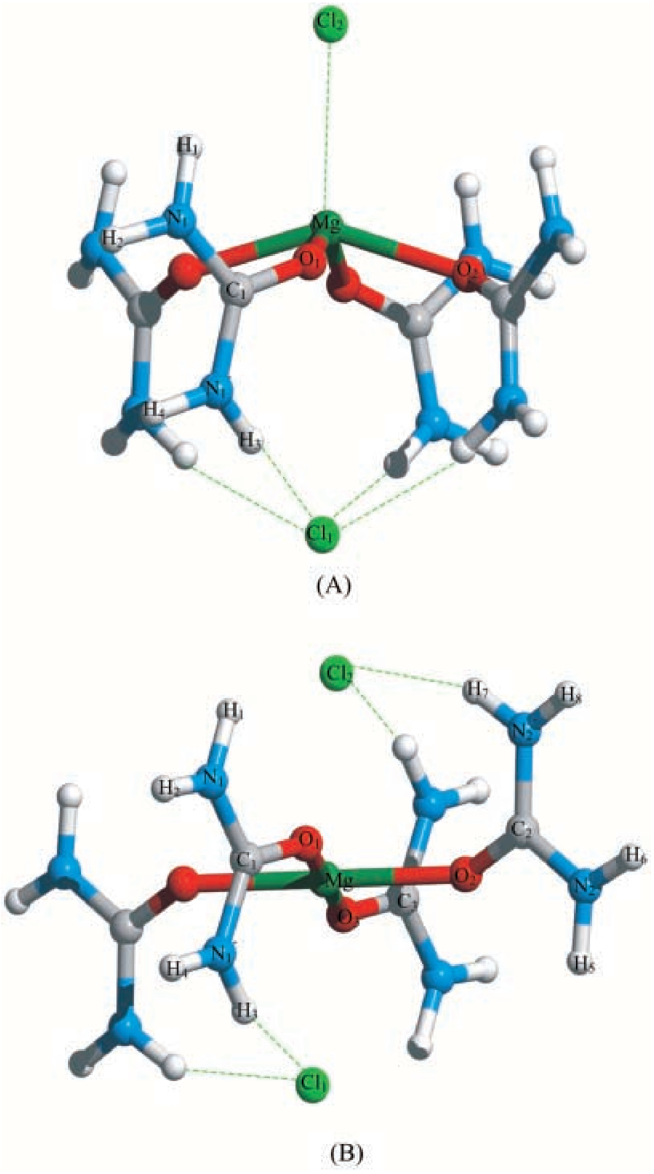

Fig. 2. The structures of the two minima (A) and (B) of the $[MgU_4Cl_2]$ complex

The IR frequencies and assignments of urea and deuterated urea in acetonitrile are given in Table 7 (the IR spectra with the whole set of basis sets are given in the supplementary material as Table S3). As can be seen, our results, especially the ones on deuterated urea, are in very good agreement with the experimental values reported by Hadži et al. [36]. The average deviation error from the experimental values is 29 cm^{-1} and 17 cm^{-1} for the parent and deuterated molecules, respectively, using the 6-311G + +3dp3pd basis set. However, the much smaller set 6-31G** gives equally good results. Overall it is observed that the effect of the basis set is rather small on the computed frequencies. It is interesting to note that the vibrations that describe the wagging motion of the $-NH_2$ groups now have lower frequencies compared to the gas phase. The other vibrations do not show any significant change.

Complexes of urea with magnesium

The structures and IR spectra of $[MgU_4Cl_2]$ and $[MgU_6]Cl_2$ are presented and discussed in this section. The reason for choosing the magnesium complexes is the availability of experimental IR spectra [37, 38]. There are also structural data for the analogous complex of hexakis(urea)magnesium bromide [39]. It is noted, however, that the available data for the metal complexes of urea are for the solid phase. Nevertheless, we are confident of the validity of our findings for the studied complexes, since our results for urea (Tables 1 and 3) and urea in acetonitrile (Table 7) are consistent with the available experimental data.

Geometry For the complex $[MgU_4Cl_2]$, two different minima were found at the SCF/6-31G level of theory (Fig. 2), of which the umbrella-like minimum (A) had the lower energy. With the extension of the basis set with d polarization functions (6-31G*), the two minima have collapsed to one having the umbrella-like structure (Fig. 2A).

The calculated structure of $[MgU_6]Cl_2$ is shown in Fig. 3. The structure is consistent with the geometry of the crystal: "The Mg^{2+} ion coordinates to six O atoms of the urea molecules at the vertices of a slightly distorted octahedron..." [39]. In Table 9 are presented, for comparison, the most important distances and angles of both complexes, together with the corresponding distances of the gas and solvated urea molecules. A complete list of geometric data is given in the supplementary material (Tables S4 and S5).

The bond lengths and angles given in Table 8, have been computed with the 6-31G* basis set. It is observed from Table 8 that the geometry of urea in the two considered phases (gas and liquid) and in the two complexes changes very little and the more significant of these changes is associated with the CN and CO bond distance.

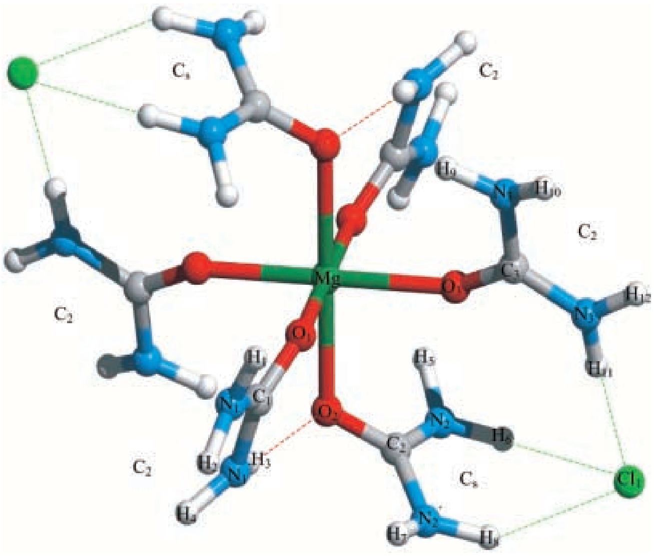

Fig. 3. The structure of the $[MgU_6]Cl_2$ complex together with the symmetry of each coordinated urea molecule. The *dotted lines* denote H-bonds

It is worth commenting on the local symmetry of urea molecules in the two complexes. The symmetry of all urea molecules in the first complex (Fig. 2) is C_s. One notes the difference with the results of urea in the gas and liquid phase where the minimum configuration has C_2 symmetry (Tables 2 and 5). The CO length of the urea molecules of the complexes is larger than the corresponding bond length of urea in the gas phase, as it was expected, because of the oxygen also being in the coordination sphere of Mg, and as a consequence the CN bond is shortened. It is observed that both the mean NH length and the OCNH dihedral angle, which is a measure of the pyramidal structure of the amide group, do not show any significant changes.

Two urea molecules in $[MgU_6]Cl_2$ (Fig. 3) have C_s local symmetry, while the other four have a C_2 symmetry. The above complex has three different types of urea molecules, each having different hydrogen bonds and slightly different geometric characteristics. Thus, it is rather difficult to describe in detail the geometry of this complex. More details may be found in the submitted supplementary material (Table S5).

IR spectra The studied structures of $[MgU_4Cl_2]$ and $[MgU_6]Cl_2$, due to their complexity, gave very rich IR spectra. The vibrational frequencies of the spectra of the above complexes that are needed for comparison with the gas and solvated urea spectra are given in Table 9.

Agreement of our gas phase IR spectrum of the $[MgU_4Cl_2]$ complex with the experimental data from the crystal structure is rather poor. Possible reasons for this discrepancy can be associated with differences in geometry (between the gas and solid phase), or a bad assignment of the bands in the experimental paper [37]. However, the IR spectrum of the $[MgU_6]Cl_2$ complex seems to be in much better agreement with the experimental data.

Table 8. Bond lengths and angles of urea molecule into gas phase, in solution, and into complexes $[MgU_4Cl_2]$ and $[MgU_6]Cl_2$, computed using the 6-31G* basis set. The hydrogen denoted as H_1 is the one closer to the carbon atom. The bond distances and angles are in Angstroms and degrees, respectively

Bonds	Present work				Experiment[a]
	Gas phase	Solvated	$[MgU_4Cl_2]$	$[MgU_6]Cl_2$[b]	$[MgU_6]Br_2$[b]
C = O	1.197	1.206	1.232	1.239	1.252
C-N	1.373	1.363	1.342	1.340	1.338
N-H_1	0.996	0.994	1.001	0.999	0.89
N-H_2	0.996	0.996	0.994	0.998	
Bond angles					
OCN	123.0	122.7	120.8	121.1	121.1
NCN	114.0	114.7	118.4	117.8	117.8
CNH_1	113.4	115.3	116.0	116.6	
CNH_2	117.7	120.2	120.6	119.7	
H_1NH_1	114.4	115.7	116.7	117.3	
Dihedral angles					
$OCNH_1$	−12.6	−13.0	−16.2	−11.3	
$OCNH_2$	−150.0	−159.2	−167.0	−165.2	
$NCNH_1$	167.4	167.0	168.0	169.9	

[a] Crystal geometry from [39]
[b] These are mean values

Table 9. Frequencies (cm^{-1}) for the two Mg-Urea complexes, computed with the 6-31G* basis set[a]

Assignment	$[MgU_4Cl_2]$[b]		$[MgU_6]Cl_2$[c]	
	Calculated	Experiment[d]	Calculated	Experiment[e]
$\nu_a(NH_2)$	3550		3532, 3544	
$\nu_a(NH_2)$	3527	3450	3519, 3524	
$\nu_s(NH_2)$	3441	3351	3392, 3424	
$\nu_s(NH_2)$	3331	3223	3239, 3333	
$\nu(CO)$	1694	1658	1707	1659
$\delta_s(NH_2)$	1642		1679, 1698	
$\delta_a(NH_2)$	1616	1605	1636, 1646	1578
$\nu_a(CN)$	1467	1465	1458, 1479, 1482	1465
$\rho_a(NH_2)$	1164	1153	1161, 1162, 1179	
$\rho_s(NH_2)$	1053		1051, 1060, 1111	
$\nu_s(CN)$	995	1020	985, 997, 1005	1008
$\omega(CO)$	801		782, 790, 824	
$\tau_s(NH_2)$	678	780	682, 732	
$\tau_a(NH_2)$			598, 636	
$\delta(CO)$	566		567, 576, 582	
$\delta(CN)$			495, 508, 15, 523	
$\omega_s(NH_2)$			393, 453, 469	
$\nu_a(OMgO)$			332	
$\omega_a(NH_2)$	527		311	
$\delta(CN)$	500			
$\omega_s(NH_2)$	478			
$\nu(MgCl)$	347			
$\nu_a(OMgO)$	341			
$\tau_a(NH_2)$	298			
$\nu_s(OMgO)$	258		247	
$\nu_a(OMgO)$	213			
Low frequency motions	196–23		224–17	

[a] The calculated frequencies were scaled with 0.90 [20]

[b] The umbrella like structure (Fig. 2A)

[c] Only the more significant vibrations with the largest IR intensities are presented here

[d] $[MgU_4Cl_2]$ experimental IR frequencies from [37]

[e] $[MgU_6]Cl_2$ experimental IR frequencies from [38]

The shifting of some vibrations is obvious and expected (Table 9). For example, the CO stretching vibration has a lower frequency than that of the urea molecule in the gas phase, because the CO bond distance is bigger. In addition, the CN stretching and scissoring vibrations moved towards a higher frequency, because of the bond length, which is smaller in comparison to that in the gas phase.

Especially interesting vibrations are those of the NH_2 group and in particular the wagging and twisting vibrations. In the case of the considered complexes, they are shifted in a somewhat lower frequency. The above observation could be considered as an indication that the transformation between the C_2 and C_s local symmetries is much easier. The frequencies below 200 cm^{-1} describe the complicated movement of the skeleton of the complex and lattice vibrations.

Conclusions

In this paper we have studied the structure and the IR spectra of urea in three different states. The main findings of our work are the following:

- The gas phase isolated urea molecule has a C_2 symmetry, while the C_{2v} planar structure is a second-order saddle point.
- The ZPVE calculation for a saddle point gives invalid results, due to the necessary exclusion of the imaginary frequencies. The positive ZPVE correction for the saddle point is erroneously low, giving for the C_{2v} structure of urea, which has two imaginary frequencies (SCF/6-31G**), an energy that is lower than the true minimum.
- The results of the geometry optimization of urea in acetonitrile solvent show that H_2NCONH_2 has the same symmetry with that found in the gas phase (C_2), with energy barriers between the two minima (having C_2 and C_s symmetries) and the C_{2v} saddle point significantly lower.
- In the two complexes which we have studied, the local symmetry of urea is either C_2 or C_s, depending on the complex or the coordinated position of urea in the complex.

The IR vibrational frequencies of the studied species have been calculated and reported. Analysis of the anharmonic corrections to the frequencies of urea, reported for the first time, shows the expected large anharmonicity of the vibrations, and the improvement on the agreement between theory and experiment. The harmonic IR frequencies for the solvated urea molecule and for the complexes show that the wagging vibration is shifted towards a lower frequency.

References

1. Theophanides T, Harvey PD (1987) Coord Chem Rev 76: 237
2. van Alsenoy C, Williams JO, Schaefer L (1981) J Mol Struct (THEOCHEM) 76: 179
3. Attanasio A, Gunthard HH, Ha T-K (1972) Mol Phys 24: 215
4. Ha TK, Puebla C (1994) Chem Phys 181: 47
5. Meier RJ, Coussens B (1992) J Mol Struct (THEOCHEM) 253: 25
6. Gobbi A, Frenking G (1993) J Amer Chem Soc 115: 2362
7. Hadži D, Kidriè J, Kneževic ŽV, Barliè B (1976) Spectr Acta 32A: 693
8. Hehre WJ, Ditchfield R, Pople JA (1972) J Chem Phys 56: 2257
9. Krishnan R, Binkley JS, Seeger R, Pople JA (1980) J Chem Phys 72: 650; Frisch MJ, Pople JA, Binkley JS (1984) J Chem Phys 80: 3265; Clark T, Chandrasekhar J, Schleyer PVR (1983) J Comp Chem 4: 294
10. Hariharan PC, Pople JA (1973) Theoret Chimica Acta 28: 213
11. Granovsky AA http://www.classic.chem.msu.su/gran/gamess/index.html
12. Schmidt MW, Baldridge KK, Boatz JA, Elbert ST, Gordon MS, Jensen JJ, Koseki S, Matsunaga N, Nguyen KA, Su S, Windus TL, Dupuis M, Montgomery JA (1993) J Comput Chem 14: 1347–1363
13. Onsager L (1936) J Am Chem Soc 58: 1486
14. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Andres JL, Head-Gordon M, Replogle ES, Pople JA (1998) Gaussian 98 (Revision A.7) Inc Pittsburgh PA
15. Amos RD, Alberts IL, Andrews JS, Colwell SM, Handy NC, Jayatilaka D, Knowles PJ, Kobayashi R, Koga N, Laidig KE, Maslen PE, Murray CW, Rice JE, Sanz J, Simandiras ED, Stone AJ, Su M-D (1992) CADPAC, The Cambridge Analytic Derivatives Package issue 5, Cambridge UK
16. Willetts A, Gaw JF, Green WH, Handy NC (1991) SPECTRO: a program for spectroscopic constants. In: Bowman JM, Ratner MA (eds) Advances in molecular vibrations and collision dynamics. Greenwich, CT JAI Press, vol 1B
17. Vijay A, Sathyanarayana DN (1993) J Mol Struct 295: 245
18. Attanasio A, Gunthard HH, Ha T-K (1972) Mol Phys 24: 215
19. Godfrey PD, Brown RD, Hunter AN (1997) J Mol Struct 413/414: 405
20. Scott AP, Radom L (1996) J Phys Chem 100: 16,502
21. Martin JML, Lee TJ, Taylor PR (1992) J Chem Phys 97: 8361
22. Bouø P, Bednárová L (1995) J Phys Chem 99: 5961
23. Masunov A, Dannenberg JJ (1999) J Phys Chem A 103: 178
24. Brown RD, Godfreym D, Storey J (1975) J Mol Spectrosc 58: 445
25. King ST (1972) Spectr Acta 28A: 165
26. Li X, Stotesbury SJ, Jayasooriya UA (1987) Spectr Acta 43A: 1595
27. Anastassopoulou J, Ganguli PK, Theophanides T (1989) Inorg Chim Acta 159: 237
28. Rousseau B, van Alsenoy C, Keuleers R, Desseyn HO (1998) J Phys Chem A 102: 6540
29. Papadopoulos MG, Raptis SG, unpublished results
30. Klatt G, Willetts A, Handy NC, Tarroni R, Palmieri P (1996) J Mol Spectrosc 176: 64
31. Klatt G, Willetts A, Handy NC (1996) Chem Phys Let 249: 272
32. Fermi E (1931) Phys Z 71: 250
33. Darling BT, Dennison DM (1940) Phys Rev 57: 128
34. Klatt G, Willetts A, Handy NC, Degli Esposti C (1995) Chem Phys Lett 237: 273
35. Wong MW, Frisch MJ, Wiberg KB (1991) J Am Chem Soc 113: 4776
36. Hadži D, Kidriè J, Kneževic ŽV, Barliè B (1976) Spectr Acta 32A: 693
37. Antonenko NS, Nuger YA (1966) Rus J Inorg Chem 11: 578
38. Hussain I, Goodgame M (1994) Jour Chem Soc Pak 16: 95
39. Lebioda L, Stadnicka K, Sliwinski J (1979) Acta Cryst B35: 157