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The intrinsic basicity of urea. An experimental (FT ICR) and theoretical (G2) study¹

Rafael Notario^a, Obis Castaño^b, Marta Herreros^a, José-Luis M. Abboud^{a,*}

^a*Instituto de Química Física “Rocasolano”, C.S.I.C. c/ Serrano, 119, E-28006 Madrid, Spain*

^b*Departamento de Química Física, Universidad de Alcalá de Henares, E-28871 Alcalá de Henares, Madrid, Spain*

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Abstract

The gas phase basicity of urea (**1**), GB(**1**), [i.e. the standard Gibbs energy change for the reaction $\text{1H}^+(\text{g}) \rightleftharpoons \text{1}(\text{g}) + \text{H}^+(\text{g})$] has been determined experimentally for the first time. This was achieved by means of Fourier Transform Ion Cyclotron Resonance Spectroscopy (FT ICR). **1** and 1H^+ have been treated at the G2 level. This study suggests that **1**(g) is very nearly a 1:1 mixture of two conformers of C_2 and C_s symmetries. **1**(g) is an oxygen base. The calculated and experimental values of GB(**1**) are in excellent agreement. An equally excellent agreement also exists between the experimental and calculated standard enthalpies of formation of **1**(g). The vibrational frequencies of the conformers of **1** and of 1H^+ have been calculated. This information, as well as the structures optimized at the MP2(FULL)/6-31G(d) level have been examined and compared to the available experimental data. The results thus obtained shed light on the mechanism of the stabilizing effect of $\text{1H}^+(\text{g})$ provided by the amino groups.

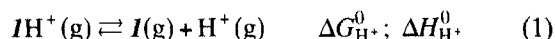
Keywords: Intrinsic basicity; FT ICR; Ab initio; Structure; Stability

1. Introduction

We are presently involved in the study of the intrinsic reactivity (i.e. reactivity in the absence of solvent) of small molecules of biological interest [1–4]. Urea, $\text{OC}(\text{NH}_2)_2$, (**1**), is particularly appealing because of:

1. Its importance as a metabolite produced by many terrestrial vertebrates and its role in prebiotic chemistry [5,6] and its usefulness as a model for the study of non-linear optical properties [7]

2. The fact that, to our knowledge, neither the gas phase basicity GB (the standard Gibbs energy change for reaction (1) in the gas phase) nor the proton affinity PA (the standard enthalpy change for reaction (1)) are known for this compound,

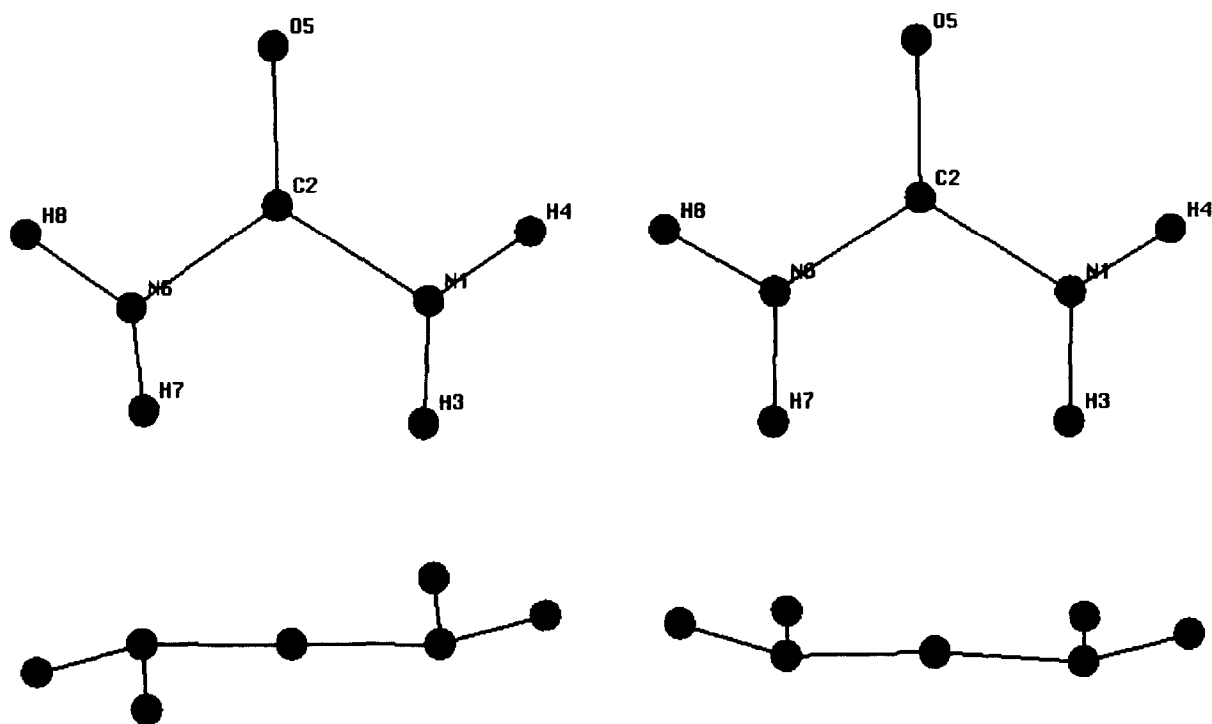


3. The recent report by Olah and coworkers of the existence and properties of mono- and di-protonated urea in solution [8]
4. The recent work by Dixon and Matsuzawa [7] on the structure and energetics of **1**.

These workers used methods based on density functional theory (DFT). At the BP TZVP⁻¹ level

* Corresponding author.

¹ Dedicated to Professor J. Bertrán on the occasion of his 65th birthday.



Scheme 1. Structures **1a** (C_s) and **1b** (C_2) for neutral urea. MP2(FULL)/6-31G(d) optimized structures.

they found that this compound presents two stable conformations, with symmetries C_s (**1a**) and C_2 (**1b**). They are portrayed in Scheme 1. It is remarkable that their electronic energies were found to be extremely close, **1a** being $1.41 \text{ kcal mol}^{-1}$ above **1b**. Inclusion of the zero-point energies reversed the order, **1b** being now $0.09 \text{ kcal mol}^{-1}$ above **1a**. The fully planar C_{2v} structure turned out not to be a minimum on the potential energy surface of urea. In both **1a** and **1b** the amino groups present floppy pyramidal structures. Their fate under the strong electron demand induced by protonation in the gas phase seems a matter worth exploring.

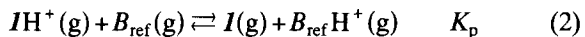
From a practical standpoint, **1** is a relatively small molecule. This allows the use of ab initio quantum-mechanical methods of a substantial level.

Here we report for the first time the experimental value of GB(**1**) as well as the results of an ab initio study at the G2 level of **1**(g) and 1H^+ (g). This information provides the basis for the discussion of relevant properties of these species and of some aspects of the reactivity of carbonyl compounds.

2. Experimental

The experimental determination of GB(**1**) was carried out by means of Fourier Transform Ion Cyclotron Resonance Spectroscopy (FT ICR) [9–11]. The experiments were performed on a modified Bruker CMS-47 spectrometer used in previous studies [1–4]. Ref. [11] provides a detailed description of the most relevant features of this instrument. The experimental method is outlined in Ref. [1–4] and described in detail in Ref. [12].

Briefly stated, we determined in these experiments the equilibrium constants K_p pertaining to the proton exchange reactions between **1** and several reference bases, B_{ref} in the gas phase, reaction (2):



For each reference base, the gas phase basicity of **1**, GB(**1**) is given by equation (3):

$$\text{GB}(\text{1}) = \text{GB}(B_{\text{ref}}) + \delta\Delta G_{\text{H}^+} \quad (3)$$

Table 1

Experimental determination of the gas phase basicity of urea (**1**). All values in kcal mol⁻¹^a

Reference	GB(<i>B</i> _{ref}) ^b	ΔΔ <i>G</i> _{H⁺} (g)	GB(1)	GB(1) (av.)
<i>n</i> -Bu ₂ S	200.9	0.11	201.01	201.0 (SD = 0.2)
Pyrazine	201.4	-0.69	200.71	
<i>i</i> -Pr ₂ S	201.9	-0.77	201.13	

^a Values of ΔΔ*G*_{H⁺}(g) and GB(**1**) are given with two decimal figures in order to avoid round-off errors.^b See text.

where

$$\Delta\Delta G_{H^+} = -RT \ln K_p \quad (4)$$

The experimental values are presented in Table 1.

The values of GB(*B*_{ref}) used in this work have been determined in Prof. Taft's laboratory and are reported in Ref. [13]. They have been anchored to the most recent value of GB(NH₃), 195.3 kcal mol⁻¹ [14].

From the data given in Table 1 we obtain GB(**1**) = 201.0 ± 0.3 kcal mol⁻¹ at the 95% confidence level.

3. Computational methods

The ab initio molecular orbital treatment of **1**, and its protonated form, **1H**⁺, has been carried out at the G2 level. As defined by Pople and co-workers [15,16], G2 theory is a composite procedure based on Møller–Plesset perturbation theory at second and fourth orders (MP2 and MP4) and on quadratic configuration interaction theory including single, double and triple excitations (QCISD(T)). G2 theory uses MP2(FULL)/6-31G(d) geometries, including all electrons in the correlation treatment (MP2 = FULL). Energies are

calculated at the MP4SDTQ/6-311G(d,p) level (complete fourth-order Møller–Plesset perturbation theory) with corrections from higher level calculations. The final total energies obtained in G2 theory corresponds effectively to QCISD(T)/6-311+G(3df,2p)//MP2/6-31G(d) calculations with HF/6-31G(d) scaled (0.8929) zero-point vibrational energies.

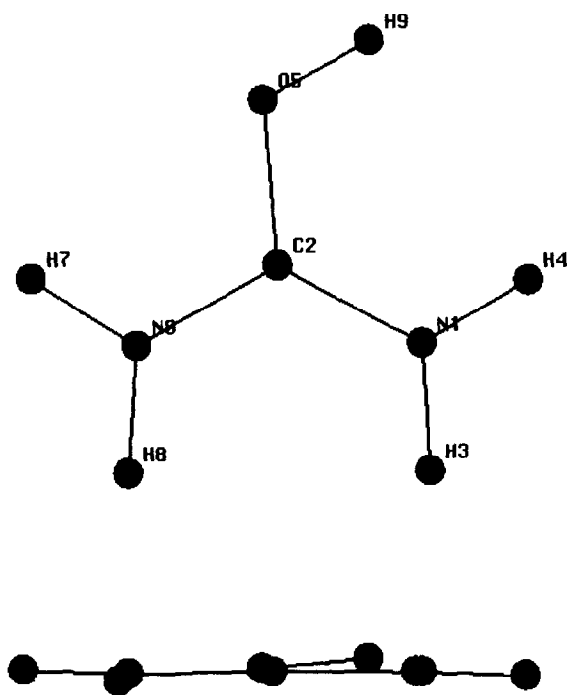
The optimization of the structure **1b** involved no particular difficulties. In the process of implementing the G2 calculations on **1a** within the GAUSSIAN 94 package [17], it was found that at the 6-31G(d) level this structure appeared as a transition state, with a single imaginary frequency (91i cm⁻¹) associated to an inversion of the pyramidal amino groups leading to structure **1b**. At the MP2(FULL)/6-31G(d) level, however, **1a** appeared as a local minimum, all frequencies being real. A gradient optimization at the 6-31G(d) level finally led to an extremely close *C_s* structure which is a true local minimum. The frequencies thus obtained were used to generate the ZPE and entropy values used in the standard G2 calculations (Table 2). In the case of **1H**⁺, frequency calculations on the geometry optimized at the MP2(FULL)/6-31G(d) level led to one imaginary frequency

Table 2

Calculated G2(MP2), G2 and G2(ZPE = MP2) enthalpies of **1a**, **1b** and **1H**⁺ (in hartrees). Proton affinities (PA) and gas phase basicities (GB) of **1a** and **1b** (in kcal mol⁻¹)

	G2(MP2) enthalpies		G2 enthalpies		G2(ZPE = MP2) enthalpies	
	0 K	298 K	0 K	298 K	0 K	298 K
(NH ₂) ₂ CO(C ₂) 1b	-244.932586	-244.927186	-224.938922	-244.933521	-244.941563	-224.936162
(NH ₂) ₂ CO(C _s) 1a	-224.932450	-224.927143	-224.938789	-224.933483	-224.940909	-224.935603
(NH ₂) ₂ COH ⁺ 1H ⁺	-225.262963	-225.257078	-225.269121	-225.263236	-225.272308	-225.266423
PA (1b) ^a	207.3	208.5	207.2	208.4	207.5	208.7
PA (1a) ^a	207.3	208.5	207.3	208.4	208.0	209.1
GB (1b) ^{a,b}	200.8	202.0	200.7	201.9	201.0	202.2
GB (1a) ^{a,b}	200.3	201.5	200.31	201.4	201.0	202.1

^a All values in kcal mol⁻¹.^b GBs calculated from PA values using for reaction (1); *T*Δ*S* = 6.5 and 7.0 kcal mol⁻¹ for structures **1b** and **1a** respectively at 298 K.



Scheme 2. Protonated urea, 1H^+ . MP2(FULL)/6-31G(d) optimized structure.

($16i\text{ cm}^{-1}$) corresponding to an out-of-plane bending of the O–H bond. Again, a gradient optimization was carried out at this level that led to a true minimum. The remaining steps of the G2 calculation were carried out one-by-one on this optimized structure. In terms of bond lengths and bond angles, the two structures are extremely similar. The most relevant difference originates in the O–H bond (see structure 1H^+ , Scheme 2). Thus, while the uronium ion is found to be completely planar at the HF/6-31G(d) level, all the frequencies being real, the most refined calculation leads to a structure in which all the heavy atoms and the four amino hydrogens lie in the same plane but the “hydroxylic” hydrogen is slightly out of it (3.9°). $1(\text{g})$ behaves as an oxygen base. Thus, calculation of the energetics of nitrogen-protonated structure shows this ion being substantially less stable than the oxygen-protonated one.

Although G2-calculated energy changes for reaction (1) are generally referred to 0 K, we have also carried out the temperature correction leading to ΔG_{298}^0 in order to directly compare the result with our experimental value. To this end, the scaled

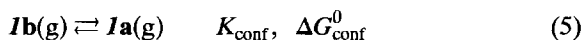
vibrational frequencies were used [18,19]. Calculations have been performed for structures **1a** and **1b**.

We have also calculated the total energies at the G2(MP2) level [20], in which the basis-set-extension corrections in G2 theory are replaced by a single correction obtained at the MP2 level; and at the G2(ZPE = MP2) level [21], in which the zero-point energies used in the calculations are obtained at the MP2(FULL)/6-31G(d) level and scaled by 0.9646 [22].

The total energies (enthalpies) of **1a**, **1b** and 1H^+ at the G2(MP2), G2 and G2(ZPE = MP2) levels of theory are listed in Table 2, together with the corresponding PAs and GBs, at 0 and 298 K.

4. Discussion

At the highest computational level of this study, ΔG_{conf}^0 , the standard Gibbs energy change for reaction (5), i.e. the conformational equilibrium between structures **1a** and **1b**, amounts to $-0.1\text{ kcal mol}^{-1}$.



Thus, the equilibrium constant K_{conf} at 298 K equals 1.2. As discussed in Refs. [7] and [23], as well as by Gobbi and Frenking [24], the energy barriers (including the ZPE correction) for rotation around the C–NH₂ bonds are very low (ca. 7 kcal mol^{-1} above the **1b** structure at the MP4/6-311G(d,p) and BP/TZVP levels). Hence, it seems reasonable to infer that the actual sample of **1(g)** studied in this work at a nominal temperature close to 298 K, was actually a rapidly interconverting mixture of **1a(g)** (55%) and **1b(g)** (45%).

The computed GB values for the conformers **1a(g)** and **1b(g)** amount respectively to 202.1 and 202.2 kcal mol^{-1} (Table 2). Combining these values with the molar fractions of these species [25], one predicts a GB value of 201.7 kcal mol^{-1} for 1 mole of the mixture, in extremely good agreement with the experimental value of $201.0 \pm 0.3\text{ kcal mol}^{-1}$. Agreements of such high quality are becoming usual when comparing experimental and G2-calculated gas phase basicities [see, e.g. [12] and references therein].

The experimental standard enthalpy of formation of **1(g)** recommended by NIST is $-58.8 \pm 0.5\text{ kcal mol}^{-1}$ [26]. Using the G2 energies computed for **1a(g)** and

Table 3

Calculated and experimental vibrational frequencies of urea, in cm^{-1} . Values in parentheses are infrared intensities in km mol^{-1}

C_2			C_s			Expt. ^c
Species	MP2(FULL)/6-31G(d) ^a	BP/TZVP ^b	Species	MP2(FULL)/6-31G(d) ^a	BP/TZVP ^b	
A	411 (79)	357 (67)	A''	191 (32)	184 (34)	228(s)–233(s)
B	461 (48)	440 (109)	A'	457 (218)	409 (320)	408(m)
A	480(4.6)	453 (2.6)	A''	467 (125)	410 (70)	442(w)
B	565 (37)	528 (28)	A'	507 (145)	463 (32)	500(w)
B	606 (309)	565 (214)	A'	566 (127)	539 (58)	580(w)
A	672 (131)	572 (67)	A''	574 (36)	545 (25)	608(m)–616(m)
B	803 (174)	774 (68)	A'	774 (60)	736 (20)	759(w)
A	973 (6.6)	922 (7.6)	A'	980 (10)	927 (9.4)	940(m)
B	1093 (21)	1003 (27)	A''	1053 (19)	975 (25)	1004(m)
A	1215 (2.3)	1136 (2.7)	A'	1211 (3.2)	1131 (3.2)	1145(vw)
B	1460 (194)	1371 (209)	A''	1465 (197)	1374 (211)	1386(s)–1393(s)
A	1680 (0.1)	1577 (0.9)	A''	1676 (214)	1565 (201)	1590(s)
B	1687 (206)	1577 (180)	A'	1689 (22)	1579 (14)	1590(s)
A	1868 (332)	1738 (406)	A'	1860 (360)	1728 (422)	1740(s)
B	3599 (58)	3470 (37)	A''	3619 (54)	3474 (36)	3440(m)
A	3602 (4.2)	3476 (2.6)	A'	3627 (14)	3485 (7)	3440(m)
B	3721 (41)	3591 (34)	A''	3747 (35)	3607 (41)	3545(m)
A	3721 (31)	3591 (27)	A'	3749 (43)	3609 (30)	3545(m)

^a This work.^b Calculated vibrational frequencies using DFT, from Ref. [7].^c Observed IR frequencies of urea isolated in a solid argon matrix, from Ref. [27].

1b(g) with the ZPE terms at the MP2(FULL)/6-31G(d) level and the appropriate thermal corrections together with the G2 energies for the isolated atoms, taken from Ref. [15] and the standard enthalpies of formation of the isolated atoms [26], we calculate the standard enthalpies of formation of **1a(g)** and **1b(g)** as -57.7 and $-58.0 \text{ kcal mol}^{-1}$ respectively. The computed standard enthalpy of formation of 1 mole of the gaseous mixture is then $-57.9 \text{ kcal mol}^{-1}$, again in truly excellent agreement with the experimental datum.

The computed vibrational frequencies at the MP2(FULL)/6-31G(d) level for **1a(g)** and **1b(g)** are presented in Table 3. Also given are the experimental frequencies determined by Li and co-workers in an argon matrix [27] and the values computed in Ref. [7]. For a given conformer, the agreement between our results and the BP/TZVP values is seen to be quite satisfactory. Furthermore, the calculated frequencies for **1a(g)** and **1b(g)** are generally very close. A very important exception is the lowest fundamental frequency, namely 411 cm^{-1} for **1b(g)** and 191 cm^{-1} for **1a(g)**. Li [27] reports two strong bands at 228 and 233 cm^{-1} . These values are quite compatible with

the computed value for **1a(g)**. Interestingly, King and co-workers [28] in older experiments using a similar technique only detected a strong band at 227 cm^{-1} . Clearly, more experimental information is necessary. Dixon and Matsuzawa [7] have suggested that these spectra are best understood as originating in a mixture of the C_2 and C_s conformers. Our results regarding the value of K_{conf} and its weak dependence on temperature strongly support this contention.

The structural parameters computed for **1a(g)** and **1b(g)** are presented in Table 4, together with the data obtained at the MP2/6-311G+(d) level in Ref. [8] and BP/TZVP level in Ref. [7] as well as the experimental values determined in the solid state.

We shall not elaborate on these results, as they are quite similar to those given in Refs. [7] and [8]. We only mention that they are significantly different from those obtained in the solid state, wherein **1** has a C_{2v} symmetry and conjugation between the electronic lone pairs on the amino nitrogens and the π -electron system of the carbonyl group is important. It has been suggested [7,8] that these differences originate in extensive self-association through hydrogen bonding in the crystal. Our results agree with these vistas.

Table 4

Calculated and experimental geometry parameters of urea (**1**). Bond lengths in Å and bond angles in degrees

	C_2			C_s		C_{2v}		
	MP2(FULL)/6-31G(d) ^a	MP2/6-311 + G(d) ^b	BP/TZVP ^c	MP2(FULL)/6-31G(d) ^a	BV/TZVP ^c	Expt. ^d	Expt. ^e	Expt. ^f
$r(\text{C}-\text{O})$	1.225	1.219	1.231	1.227	1.233	1.243	1.260	1.246
$r(\text{C}-\text{N})$	1.390	1.390	1.395	1.384	1.391	1.351	1.352	1.333
$r(\text{N}_1-\text{H}_4)$	1.013	1.009	1.017	1.011	1.016	0.988	0.998	1.004
$r(\text{N}_1-\text{H}_3)$	1.013	1.009	1.017	1.011	1.016	0.995	1.003	1.005
$\theta(\text{O}-\text{C}-\text{N})$	123.5	123.4	123.0	122.7	122.4	121.5	121.7	121.9
$\theta(\text{N}-\text{C}-\text{N})$	113.0	113.2	114.0	114.4	115.0	117.0		116.2
$\theta(\text{C}-\text{N}_1-\text{H}_4)$	111.9	112.5	113.0	113.2	113.9	118.1	119.0	119.9
$\theta(\text{C}-\text{N}_1-\text{H}_3)$	116.2	116.6	117.7	119.7	120.6	119.8	120.2	120.6
$\theta(\text{H}_4-\text{N}_1-\text{H}_3)$	113.5		113.9	115.0	115.9	122.1		119.5
$\omega(\text{H}_4-\text{N}_1-\text{C}-\text{O})$	13.5	12.8		17.0		0	0	0
$\omega(\text{H}_3-\text{N}_1-\text{C}-\text{O})$	146.0	147.1		157.7		0	0	0

^a This work. ^b From Ref. [8]. ^c From Ref. [7]. ^d Neutron diffraction data from Ref. [29]. ^e Neutron diffraction data from Ref. [30]. ^f Neutron diffraction data from Ref. [31].

Table 5 portrays the rotational constants determined in this study as well as in Refs. [7] and [32]. The experimental values determined by Brown using microwave spectroscopy [33] are also given for comparison purposes. It is clear that, in general, the agreement between the experimental and calculated constants is very good (generally within 1% or better), even with those determined at the 6-31G level, although at this level a planar structure is obtained. It is also important to emphasize that Brown already stated that the microwave data suggested a non-planar structure for **1(g)**.

Olah and co-workers [8] have reported the computed geometry at the MP2/6311 + G(d) level for **1H⁺(g)**. The structural parameters obtained by these workers are shown in Table 6 together with our own results and the experimental data obtained by means of neutron diffraction studies [34,35] of uronium salts. Our results are quite similar to Olah's and are in fair agreement with the experimental data. The most significant

difference lies in the fact that the "hydroxylic" hydrogen is found slightly out of the plane defined by all the other atoms of the ion. The experimental structures are fully planar. They were determined in the solid state, however, and this prevents us from concluding about the origin of this specific feature.

The experimental dipole moment for **1(g)** as determined by Brown [33] is 3.83 D (12.8×10^{-30} Cm). At the MP2(FULL)/6-31G(d) level we find 3.85 and 4.60 D for structures **1b** and **1a**, respectively. Although the experimental value is nearly the same as that computed for **1b**, and significantly lower than that calculated for **1a**, we feel that this is no sufficient evidence for us to entirely rule out the existence of a mixture of both conformers in the gas phase.

The calculated vibrational frequencies for **1H⁺(g)** are given in Table 7. Protonation of **1** generates three new normal modes of vibration. As in the cases of **1a** and **1b** [32], there is an extensive degree of coupling of the various modes. We nevertheless emphasize the

Table 5

Rotational constants for urea in MHz

	C_2		C_s		C_{2v}	
	MP2(FULL)/6-31G(d) ^a	BP/TZVP ^b	MP2(FULL)/6-31G(d) ^a	BP/TZVP ^b	HF/6-31G(d) ^c	Expt. ^d
A	10991.6	11176.6	11107.6	11265.6	11263.1	11233.3
B	10393.5	10818.4	10331.7	10751.3	10563.6	10369.4
C	5402.8	5547.4	5386.8	529.4	5451.1	5416.7

^a This work. ^b From Ref. [7]. ^c From Ref. [32]. ^d Microwave data from Ref. [33].

Table 6

Calculated and experimental geometry parameters of uronium ion (1H^+). Bond lengths in Å and bond angles in degrees

	C_1	C_s	Expt. ^c	Expt. ^d
	MP2(FULL)/6-31G(d) ^a	MP2/6-311 + G(d) ^b		
$r(\text{C}-\text{O})$	1.316	1.310	1.302	1.298
$r(\text{C}-\text{N}_1)$	1.326	1.321	1.297	1.312
$r(\text{C}-\text{N}_6)$	1.319	1.319	1.315	1.315
$r(\text{O}-\text{H})$	0.977	0.967	0.99	1.006
$r(\text{N}_1-\text{H}_4)$	1.013	1.009	0.85	1.005
$r(\text{N}_1-\text{H}_3)$	1.015	1.009	1.04	1.013
$r(\text{N}_6-\text{H}_7)$	1.015	1.010	0.85	1.000
$r(\text{N}_6-\text{H}_8)$	1.013	1.008	1.10	1.014
$\theta(\text{O}-\text{C}-\text{N}_1)$	122.6	122.7	122.0	121.7
$\theta(\text{O}-\text{C}-\text{N}_6)$	114.5	144.5	116.3	116.7
$\theta(\text{H}-\text{O}-\text{C})$	114.3	115.4	119	113.6
$\theta(\text{H}_4-\text{N}_1-\text{C})$	122.0	122.2	117	123.1
$\theta(\text{H}_3-\text{N}_1-\text{C})$	121.5	121.5	127	119.1
$\theta(\text{H}_7-\text{N}_6-\text{C})$	118.8	118.8	123	119.1
$\theta(\text{H}_8-\text{N}_6-\text{C})$	122.9	123.0	119	120.8
$\omega(\text{H}-\text{O}-\text{C}-\text{N}_1)$	3.9	0	0	0

^a This work. ^b From Ref. [8]. ^c Neutron diffraction data of uronium nitrate, from Ref. [34]. (d) Neutron diffraction data of uronium nitrate, from Ref. [35].

Table 7

Calculated vibrational frequencies of uronium ion, in cm^{-1} . Values in parentheses are infrared intensities in km mol^{-1}

Species	MP2(FULL)/6-31G(d) ^a
A	77 (8.3)
A	401 (35)
A	492 (89)
A	506 (166)
A	517 (546)
A	548 (13)
A	640 (2.6)
A	723 (1.0)
A	1044 (12)
A	1072 (21)
A	1137 (1.1)
A	1233 (172)
A	1633 (21)
A	1644 (115)
A	1738 (216)
A	1812 (578)
A	3592 (372)
A	3610 (65)
A	3716 (32)
A	3724 (181)
A	3727 (333)

^a This work.

following: (i) the highest fundamental frequency (3727 cm^{-1}) corresponds to a “nearly pure” stretching of the O–H group, (ii) The lowest fundamental frequency, 77 cm^{-1} , is essentially a combination of the out-of-plane bending of the O–H group and the torsion of the amino groups, (iii) The in-plane O–H bending mode appears as “nearly pure” at 1233 cm^{-1} . Other important modes, including the C–O and C–N stretchings are too mixed to lead to straightforward conclusions.

As pointed out by Wiberg [36], the main role of the carbonyl oxygen in amides and other carbonyl compounds is to polarize the C–O bond, leading to an electron-deficient carbon. The interaction between this carbon and the lone pairs of the substituents, notably the amino groups in amides and urea have been discussed in detail by Wiberg [37] and Frenking [24] respectively and shall not be discussed further. The case of 1H^+ is related to that of protonated ketones and amides [7]. It has been shown for the latter [36] that protonation of the carbonyl oxygen implies a significant charge transfer to the incoming proton. Oxygen recovers a large part of this charge, because of the higher electronegativity of oxygen relative to carbon. This takes place through an electronic depopulation of the C=O bond, which becomes

weaker and longer (ca., 0.08 Å in the case of **1** and 1H^+). As a result, the s character of the carbon hybrid involved in the C=O bond must decrease and, by orthogonality, the s character of the two other hybrids must increase. This brings about a substantial widening (ca. 10°) of the C–N–C angle upon protonation. Furthermore, the electronic depopulation of the carbonyl carbon strongly favors the transfer of charge from the lone pairs of the substituents to the carbon center. This leads to a significant shortening of the C–N bond lengths (some 0.07 Å on going from **1** to 1H^+). This interaction becomes more favorable when the amino groups are planar, as indicated above. It is interesting that a similar behavior has been found in the case of amides, even in cases of significantly strained systems [38]. With respect to the latter, the shortening of the C–N bond is less important in the case of 1H^+ [a detailed discussion of the structures of protonated amides is given in Ref. [38]] as a consequence of the mutual attenuation of the electron demand on each of the amino groups.

It is clear from the above that the quantum-mechanical treatment of the protonation of urea has led to an extremely good agreement between the experimental and computed thermodynamic properties of the neutral and protonated species. Several important conclusions have been reached. As the situation stands now, it seems that a “finer tuning” of these data and concepts requires more fresh experimental data, particularly structural, for **1(g)** and $1\text{H}^+(\text{g})$.

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