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Vibrational Analysis of Urea

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Although a lot of work has been done on the vibrational analysis of urea, there still remain some contradictions and uncertainties, mainly due to interpretation of the vibrational spectrum of crystalline urea based on force field calculations on isolated urea instead of on urea in its crystal phase. We have shown that this approach is not allowed in the case of urea. The vibrational spectrum of urea was interpreted by measuring the solid state infrared spectra of eight isotopomers of urea at room temperature and at −196 °C, and Raman spectra at room temperature and at −120 °C, and of a urea−water solution. Force field calculations from our recently published article on isolated urea and on urea in its crystal structure, at the Hartree−Fock level with a 6-31++G** basis set, were also used. We have also shown that high-pressure measurements using a "diamond anvil cell" are not useful by performing a vibrational analysis.

I. Introduction

Urea, first isolated by Rouelle in 1773, was the first organic substance synthesized from inorganic materials in the laboratory by Wöhler in 1828[1] and so its synthesis demolished the vitalist 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.

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,[2] increase the solubility of hydrophobic species such as hydrocarbons,[3] and prevent micelle formation.[4] 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.[5] It has also been found that some Pt−urea complexes have antitumor activity,[6] probably due to their square-planar structure (e.g., cisplatinum). Moreover, the NH_2 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.[6] 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.[7−24]

Urea is also important for applied research. It is an easy source of nitrogenous food to the vegetable kingdom through a simple enzymatic hydrolysis with the aid of urease, which is abundantly present in the soil.[5] The importance of urea as a fertilizer was recognized as late as 1950 and since then it occupies a significant place in the world nitrogen supply. The possible technical applications of urea and its derivatives, particularly in the field of fertilizer, resins, plastic, and pharmaceuticals are embodied in extensive patent literature. Since the year 1920 with the advent of John's patent[25] of urea resin, various types of resin have come on the market.[5] Urea is also a useful nonlinear optics material for applications in the UV spectral region.[26]

Though urea is a simple molecule, it gave rise to a lot of discussion in the literature on several topics.

In the early fifties, the planar structure of urea in the solid state was proven by using infrared spectra obtained by directing plane-polarized radiation through orientated urea crystals.[27−28] It was known from X-ray data that the heavy atoms C, N, and O of each molecule lie in a plane and have C_{2v} symmetry, whereas the position of the hydrogen atoms, too light to scatter X-rays, had to be inferred.[29−35] Though results from dipole measurements[36−38] and considerations concerning the CN length from X-ray measurements predict approximately 20% double bond character of the CN-linkages, favoring an entirely planar structure, the only published vibrational analysis till then by Kellner[39] has employed a model in which the hydrogen atoms lie in a plane perpendicular to the plane of the remaining atoms. The planar structure of the urea molecule in the solid state has later been confirmed by several neutron diffraction studies.[40−43]

A second point of discussion, which was only solved in the nineties, was the geometry of the urea molecule in the gas phase. A number of quantum chemical calculations on urea in the gas phase, both geometry optimizations and frequency calculations, have appeared in the literature. The earlier calculations[7−10,17] predicted a planar structure whereas experimental data[23,44−46] and more recent calculations[12−16] have shown it to be nonplanar.

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The problems in the earlier calculations originated either in the use of inadequate methods or the use of too small basis sets.

Although a lot of work has been done on the vibrational analysis of urea, there still exist some contradictions and uncertainties about the interpretation of the vibrational spectrum. In part, these problems originated from the fact that the interpretation of the solid state spectrum of urea was based on gas phase calculations, a way of interpreting which, as we will show, is not allowed in the case of the urea molecule. A thorough study on the vibrational analysis of urea was necessary and is performed successfully by measuring solid state infrared spectra at room temperature, at −196 °C and at an elevated pressure up to 1 GPa, of urea and its ^{13}C, $^{15}N_2$, ^{18}O isotopomers and their deuterated analogues, just as Raman spectra of the solid state at room temperature and at −120 °C, and of a urea−water solution. Force field calculations on the gas phase and the solid state of urea were performed at the Hartree−Fock level with a 6-31++G** basis set. Details on these calculations have recently been published.[24] The definite experimental vibrational analysis will be described in this article.

II. Experimental Section

1. General Information. The normal urea used was a pure commercial product, available at Aldrich (U270-9) just as [d_4]-urea (17, 608-7), [^{13}C]urea (29, 935-9), and [1,3-$^{15}N_2$]urea (31, 683-0). [^{18}O]urea was synthesized according to the method used by Korn[47] and Laulicht.[48] Deuterated [^{13}C]urea, [1,3-$^{15}N_2$]urea, and [^{18}O]urea were prepared by dissolving the products in D_2O. Partially deuterated urea were prepared by dissolving urea in the corresponding H_2O/D_2O mixtures. The solutions were evaporated to dryness in vacuo. This procedure was repeated three times.

The infrared spectra were recorded on a Bruker IFS 113v Fourier transform spectrometer, using a liquid nitrogen cooled MCT detector with a resolution of 1 cm^{-1}. For each spectrum 100 scans were recorded and averaged. The low-temperature measurements were performed with a laboratory designed liquid nitrogen cooled cryostat, consisting of a copper sample holder with a small container that can be filled with liquid nitrogen. This is surrounded by a jacket with KBr windows and placed under vacuum. From the sample a pellet with a KBr matrix was made. High-pressure measurements were performed by using the "Diacell B-05" diamond anvil cell. Far-infrared spectra were recorded using a DTGS detector with a resolution of 4 cm^{-1}. For each spectrum 250 scans were recorded and averaged.

The Fourier transform Raman spectra were recorded on a Bruker IFS 66v interferometer equipped with a FT Raman FRA106 module. The molecules were excited by the 1064 nm line of a Nd:YAG laser operating at 200 mW. For each spectrum 1000 scans were recorded and averaged. The low-temperature Raman spectra were recorded on a SPEX 1403-0.85 m double beam spectrometer. The molecules were excited by the Spectra Physics Model 2000 Ar^+ laser. A Miller−Harney cell was used to cool the sample. The spectra were recorded with a spectral slit width of 4 cm^{-1}. For each spectrum three scans were recorded and averaged.

2. Theoretical Model and Computational Procedure. Molecular crystals can be studied either by the periodic Hartree−Fock method[49] or by molecular cluster methods.[50−53] The former has the advantage that the periodicity of the system is included directly in the wave function. The latter, however, has the advantage of its conceptual simplicity and the fact that existing quantum mechanical codes can be used, in which analytical gradients are available. Numerous successful calculations[50,54−58] have shown that the cluster method allows efficient and accurate studies of molecular crystals. In the molecular cluster methods two models are frequently used: the point charge model (PC model)[50,54−55] and the supermolecule model (SM model).[56−58] In the PC model a molecule described by a wave function is surrounded in accordance with the symmetry of the crystal by point charges. In the SM model a cluster is constructed from a molecule and its nearest neighbors, described by a wave function, and surrounded by point charges.

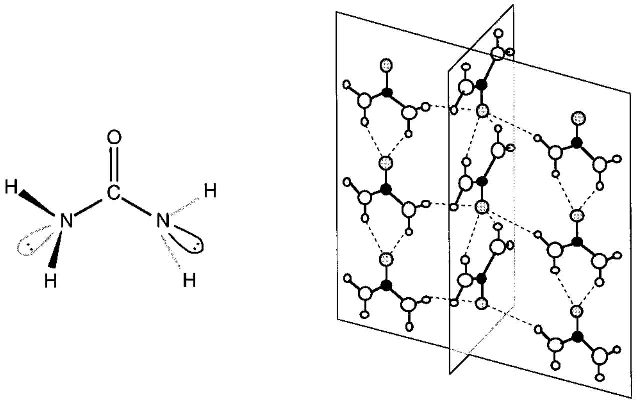

Figure 1. Structure of urea in the gas phase (left) and in the crystalline state (right).

The combination of the SM model with conventional Hartree−Fock methods requires prohibitively expensive calculations even for medium sized molecules. To allow calculations on large systems, the MIA approach[59,60] was developed and implemented in the quantum chemical program package BRABO.[60] This approach, which scales linearly with the size of the system,[61] is an efficient combination of the direct SCF method[62] and the "multiplicative integral approximation" (MIA approximation).[59] For more details on this approximation we refer to the literature.[24]

In this study the $P\bar{4}2_1m$ crystal phase of urea[29−35,40−43] was modeled using the SM approach, in which the supermolecule was constructed from a central molecule surrounded by its 14 nearest neighbors. This supermolecule was surrounded by molecules, represented by Mulliken point charges,[63] having an atom nearer to any central-molecule-atom than 20 Å, yielding 664 neighboring molecules (5312 pointcharges). A 6-31++G** basis set was chosen to describe the gas phase and the 15 molecule cluster. Use of this basis set resulted in a total of 100 basis functions describing the single molecule and 1500 basis functions describing the supermolecule used in this study.

For a detailed description of the procedure used to optimize the structure of these clusters we refer to the literature.[54−58] For further details on the geometry optimization and the numerical force field calculation we refer to our previous article.[24]

III. Geometry of Urea in the Gas Phase, in a Urea−Water Solution and in Its $P\bar{4}2_1m$ Crystal Phase

Although earlier quantum chemical calculations on urea in the gas phase predicted a planar structure,[7−10,17] more recent calculations[12−16] have shown it to be nonplanar (Figure 1). This nonplanar geometry is also confirmed by microwave spectroscopy[23,45] and low-temperature matrix isolation studies.[44,46] We tried to confirm this nonplanar geometry by means of "electron diffraction", but the compound was not volatile enough[64−68] at room temperature to obtain a diffraction pattern and at higher temperature it gave rise to decomposition products.[69−72]

The planar structure of urea in the solid state has already been proven in the early fifties by using infrared spectra obtained

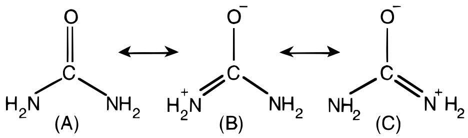

Figure 2. Resonance forms of urea.

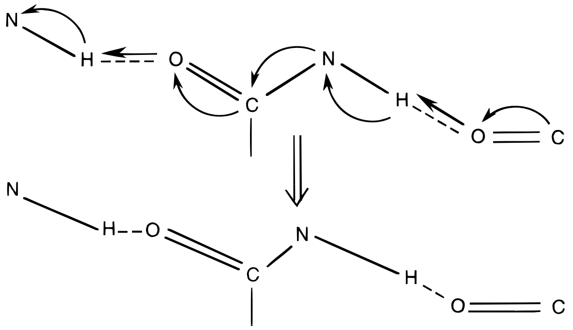

Figure 3. Effect of hydrogen bonding on the NH, CO, and CN strength.

by directing plane-polarized radiation through orientated urea crystals.[27−28] At that time it was already known from X-ray data that the heavy atoms C, N, and O of each molecule lie in a plane and have C_{2v} symmetry.[29−35] The planarity of the hydrogen atoms was later confirmed by several neutron diffraction studies[40−43] and by our recently published ab initio calculation on the solid state.[24] The planarity of the urea molecule in the solid state is mainly due to an extensive network of hydrogen bonds (Figure 1).

The different conformation of the nitrogen atoms of urea in the solid state ($sp^2 + p$) and in the gas phase (sp^3) is very important for the vibrational analysis of urea and probably the reason for a lot of misunderstanding in the literature concerning the interpretation of the vibrational spectrum.

Figure 2 shows the resonance forms of urea. Because of the ($sp^2 + p$) conformation of the nitrogen atoms in the solid state, the free electon pairs of these nitrogen atoms are more conjugated with the CO double bond and, consequently, the ionic resonance forms B and C become more important in comparison with the gas phase.

Consequently, the CO bond has less and the CN bonds have more double bond character in the solid state compared to the gas phase and the CO and CN stretching vibrations shift to a lower and a higher frequency, respectively, in going from the gas phase to the solid state spectrum.

The hydrogen bonds have an effect similar to that of the different conformation on the shifts of the CO and the CN stretching vibrations. This is explained in Figure 3 by regarding the hydrogen bond as a donor−acceptor complex.[73] In this case the oxygen atom acts as a donor and the hydrogen atom as an acceptor. Because of the “pile-up” and “spill-over” effects in this donor−acceptor complex, the CO bond becomes longer and the CN bonds become shorter and the corresponding stretching vibrations will shift to lower and higher wavenumbers, respectively, which is in total agreement with the shifts predicted by the structural difference between the gas phase and the solid state. The NH bond becomes longer as well and the corresponding NH_2 stretching vibrations will also absorb at lower wavenumbers. These hydrogen bonds also have an influence on the frequency of other vibrations, i.e., the NH_2 rocking vibrations will shift to a lower frequency in contrast with the NH_2 deformation and the CO wagging vibrations, which will shift to a higher frequency at increasing strength of hydrogen bonding, as will be shown later in this article.

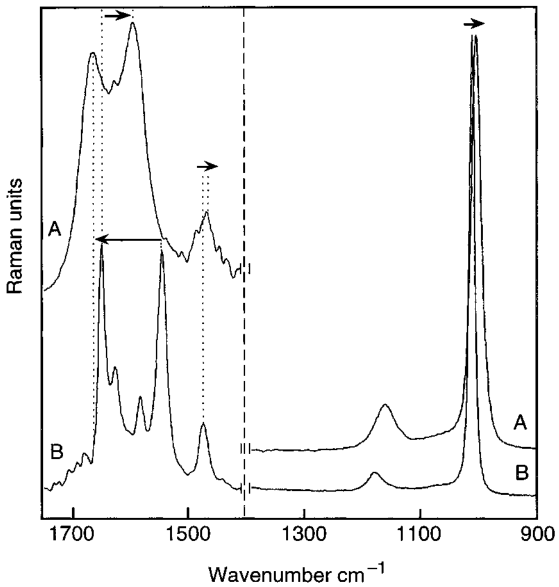

Figure 4. Raman spectra of a urea−water solution (A) and of solid urea (B).

The influence of both effects results in the fact that the vibrational spectra of this compound in the solid state and the spectrum of the gas phase are very different and certainly not comparable.

As we are not able to study the gas phase of urea, we studied a urea−water solution. Urea appears as a strictly planar molecule in the solid state due to an extensive network of intermolecular hydrogen bonds.[24,29−35,40−43] These intermolecular interactions are absent in the gas phase and the urea molecule exhibits the nonplanar configuration.[12−16,23−24,44−46] In aqueous solutions these intermolecular urea−urea hydrogen bonds are also nonexisting,[74,75] so a nonplanar configuration of the urea molecules is very well possible. Of course hydrogen bonds with the solvent water molecules exist, but it is not necessary that these hydrogen bonds make the urea molecules planar as the intermolecular urea−urea hydrogen bonds do in the solid state. So it could be that a urea−water solution, in view of the spectroscopic effects described above, can be regarded as an intermediate state between the gas phase and the solid state and then the shifts described above must be observed.

As an example we show the Raman spectra of solid urea and of a urea−water solution in Figure 4. In the gas phase the CO stretching vibration is calculated to absorb at 1731 cm^{-1}.[24] In the solution spectrum this vibration is assigned to the band at 1664 cm^{-1}, which appears at lower frequency (1540 cm^{-1}) in the solid state spectrum, a shift that is in total agreement with the spectroscopic effects described above. The Raman bands at 1647 and 1623 cm^{-1} in the solid state spectrum are assigned to the NH_2 deformation vibrations and appear, as expected, at lower wavenumbers in the solution spectrum (1626 and 1593 cm^{-1}) and are calculated at even lower frequencies in the gas phase (1600 and 1589 cm^{-1}).[24] The Raman bands at 1466 and at 1010 cm^{-1} in the solid state spectrum, assigned to the antisymmetrical and the symmetrical CN stretching vibrations, respectively, are shifted, as expected, to lower wavenumbers (1461 and 1003 cm^{-1}) in the solution spectrum and again at even lower frequencies in the gas phase spectrum (1386 and 934 cm^{-1}).[24]

From the examples given above it can be concluded that a urea−water solution is indeed, in view of the spectroscopic effects described above, an intermediate state between the solid state and the gas phase. All these spectral differences indicate that the Raman spectra and, consequently, the vibrational analyses of solid urea, of a urea–water solution, and of the gas phase of urea, are not comparable. These differences in the Raman spectra were already observed by Stewart in 1957[76] without further explanation.

In the literature, several interpretations of the vibrational spectrum of solid urea are based on force field calculations on the gas phase and consequently resulted in contradictions between these calculations and the solid state experiments. As we have shown, this approach of interpretation is not allowed in the case of urea due to the effect of the conformational difference and the different extent of hydrogen bonding between the solid state and the gas phase (urea–water solution), on the internal force constants and consequently on the frequencies and the "potential energy distributions" (PEDs) of urea.

IV. Vibrational Spectrum of Urea

The urea molecule has eight atoms, which leads to 24 degrees of freedom. Taking into account the six nongenuine motions (three translations + three rotations), 18 internal modes of vibration are to be considered. Urea has C_{2v} point group symmetry in the solid state,[24,27–38,40–43] giving rise to seven A_1, two A_2, three B_1, and six B_2 modes. The two A_2 vibrations are infrared inactive. All the vibrational modes are Raman active. Urea has C_2 point group symmetry in the gas phase[12–16,23–24,44–46] resulting in nine A and nine B modes. All these vibrations are infrared and Raman active.

A. Gas Phase Spectrum. To our knowledge, up till now only two matrix isolation spectra[44,46] and one gas phase spectrum[77] have appeared in the literature of urea. Li[46] did not give any assignments, while the assignments of Langer[77] are rather doubtful in view of the data presented in our previous article.[24] Our calculated frequencies and assignments[24] are in excellent agreement with the spectrum of King,[44] as reassigned by Vijay[17] and Spoliti.[22] Further on in this article we will use our calculated frequencies for describing the gas phase because not all experimental frequencies are given in the literature and the published frequencies are in excellent agreement with our calculations: the overall (parent and deuterated isotopomer) rms deviation and the maximum difference are only 14 and 28 cm^{-1}, respectively.[24]

B. Crystal Phase Spectrum. The first vibrational spectral data of urea is given by Kohlrausch and Pongratz[78] in 1934, but they measured the Raman spectrum of an aqueous solution. Kellner[39] was the first to report infrared data on the solid state in 1941 together with a theoretical calculation assuming a nonplanar structure for the urea molecule. However, in the early fifties the planarity of the urea molecule in the solid state has been proven,[27,28] and consequently, the approach by Kellner[39] seemed to be invalid. In 1955 Angell[79] investigated the infrared spectrum of urea by comparing the spectrum with that of the guanidinium ion, but the first normal coordinate analysis of urea assuming the new established planar structure was by Yamaguchi,[80] which included infrared and Raman data on normal and deuterated urea. Since then several vibrational analyses on urea were published. However, some data are based on force field calculations of the gas phase and, as already mentioned, gave a lot of contradictions with experimental data. Further on we will discuss the different parts of the vibrational spectrum, indicating the points of discussion. By combining our experimental results with the results from our calculations on the solid state of urea,[24] a definite assignment has been obtained.

NH Stretching Modes. Stewart[76] observed two strong bands and one shoulder on the low-frequency side of the lowest band in the 3500–3000 cm^{-1} region of the infrared spectrum of urea, which he assigned to the NH_2 stretching vibrations. Other authors[17,48,81–87] also observed these two bands and the shoulder but only assigned the two bands to the NH_2 stretching modes. Laulicht[48] explained the shoulder observed at about 3270 cm^{-1} as being a combination band of the symmetrical NH_2-deformation and the CO-stretching vibration. Robinson[88] observed four bands at 3460, 3436, 3353, and 3346 cm^{-1}, respectively, by determining infrared absorption spectra from reflection measurements.

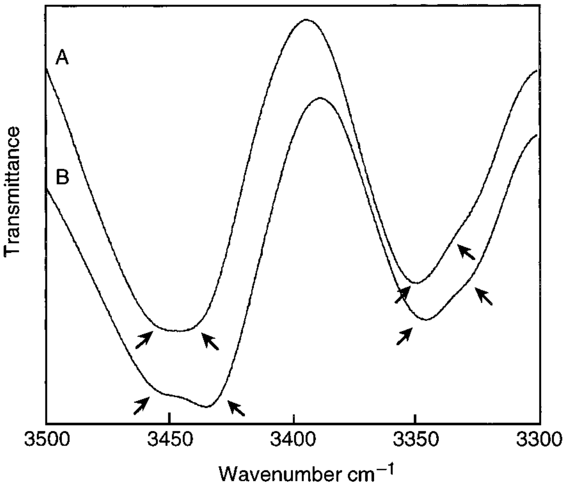

Figure 5. NH_2 stretching vibrations in the room temperature (A) and −196 °C (B) infrared spectrum of urea.

We observed these two strong bands at 3444 and 3349 cm^{-1}, respectively, and the shoulder observed by Stewart[76] appears as a weak peak in our spectra at 3264 cm^{-1}. Figure 5 shows that on these two strong bands two other bands are superimposed as shoulders at 3450 and 3341 cm^{-1}, respectively. These shoulders are even more visible at the low-temperature spectrum of urea (Figure 5). As these bands only appear as shoulders, their real maximum is difficult to determine. This explains the small differences between the observed frequencies of the ^{12}C and ^{13}C analogues, which theoretically must coincide. From our force field calculations on the solid state[24] we found that the antisymmetrical NH_2 A_1 and B_2 vibrations appear at 3453 and 3445 cm^{-1} and the symmetrical analogues at 3340 and 3320 cm^{-1}, respectively. Consequently, we also assign the band at 3264 cm^{-1} as a combination band of the symmetrical NH_2 deformation and the CO stretching vibration observed at 1683 and 1601 cm^{-1}, respectively, as will be discussed later in this article.

The NH_2 stretching vibrations shift to a lower frequency upon lowering the temperature from room temperature to −196 °C due to the smaller intermolecular distances, and consequently stronger hydrogen bonds, at lower temperature (Figure 3).

As expected, these frequencies disappear on deuteration and for the ^{15}N-isotopomer. All experimental infrared frequencies (room temperature and −196 °C) for urea and its isotopomers are given in Table 1. The average ratio $\nu(NH_2)/\nu(ND_2) \approx 1.35$ indicates the pure character of these vibrations, as confirmed by the PED values from our force field calculation on the solid state.[24] The same effects are observed in the Raman spectra.

1700–1400 cm^{-1} Region in the Infrared Spectrum of Urea. In this region four absorptions are expected: the ν(CO) and the ν_{as}(CN) stretching vibrations and the symmetrical and antisymmetrical NH_2-deformation vibrations.

We assign the bands at 1625 and 1466 cm^{-1} to the $\delta_{as}(NH_2)$ and to the ν_{as}(CN) vibrations, respectively, which is in total agreement with the literature.[16–17,20,22,48,76,80–89]

TABLE 1: Infrared $\nu(NH_2)$ Frequencies (cm^{-1}) of Urea and Its Isotopomers

		urea		urea ^{13}C		urea $^{15}N_2$		urea ^{18}O		urea-d_4	
		20 °C	−196 °C	20 °C	−196 °C	20 °C	−196 °C	20 °C	−196 °C	20 °C	−196 °C
$\nu_{as}(NH_2)$	(A1)	3450	3448	3454	3454	3443	3437	3450	3447	2601	2595
$\nu_{as}(NH_2)$	(B2)	3444	3435	3443	3433	3435	3422	3445	3434	2593	2584
$\nu_s(NH_2)$	(A1)	3349	3345	3344	3337	3341	3334	3347	3343	2440	2439
$\nu_s(NH_2)$	(B2)	3341	3330	3340	3326	3320	3317	3330	3328	2433	2431

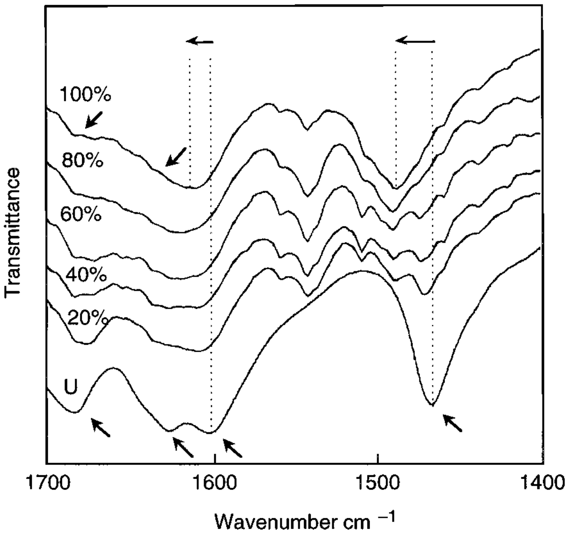

Figure 6. Infrared spectra of partially deuterated urea.

Hitherto there is no agreement in the literature about the relative position of the $\nu(CO)$ and the $\delta_s(NH_2)$ vibrations. Two unassigned bands remain in this region of the spectrum, namely at 1683 and 1601 cm^{-1}. While Stewart[76] assigned the band at 1683 cm^{-1} to the CO stretching vibration, according to a normal coordinate analysis by Yamaguchi[80] the $\nu(CO)$ character of this frequency amounts to ca. 20% only. Besides, ca. 60% $\delta_s(NH_2)$ character is calculated for this band. The band at 1601 cm^{-1} consists of ca. 40% $\nu(CO)$ and only of ca. 40% $\delta_s(NH_2)$ character according to the same calculation. So the reversed assignment is proposed by Yamaguchi.[80] This calculation[80] has been confirmed by Laulicht[48] and Arenas[82] measuring infrared and Raman spectra of the ^{18}O and ^{15}N isotopomers, respectively. Derreumaux[89] has used a modified Urey−Bradley−Shimanouchi intramolecular potential energy function and a rather sophisticated intermolecular energy function to reproduce infrared and Raman frequencies. They assigned the $\delta_s(NH_2)$ and the $\nu(CO)$ vibrations to the bands at 1683 and 1601 cm^{-1}, respectively, and consequently support Yamaguchi's calculation.[80] This calculation[80] has also been confirmed by other normal coordinate analyses by Duncan,[81] Saito,[83] Shteinberg,[84] and Diaz.[86] Only Hadzi[85] assigned the two bands in reversed order, supporting Stewart's assignment,[76] using his normal coordinate analysis but he also calculated a coupling between the two vibrations. This coupling had already been stated by Laulicht[48] and Arenas.[82] Rajalakshmi[87] also followed the assignment of Stewart[76] by using the characteristic frequency values and the infrared structural correlation chart. Vijay[17] and Ha[16] tried to assign the solid state spectrum by using their Hartree−Fock and MP2 calculations, respectively, on the isolated urea molecule. They assigned the band at higher wavenumber to the CO stretching vibration, supporting Stewart's assignment,[76] and calculated no coupling between the two vibrations. Dixon[20] and Spoliti[22] calculated on the isolated molecule at the DFT level and Notario[90] at the MP2 level, but they only compared their results with the gas phase spectrum of urea.[44,46,77]

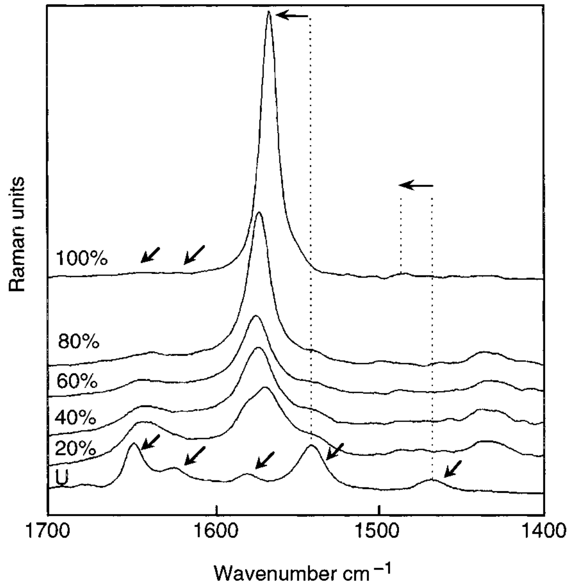

Figure 7. Raman spectra of partially deuterated urea.

TABLE 2: Infrared Frequencies (cm^{-1}) of Urea and Its ^{13}C, $^{15}N_2$, and ^{18}O Isotopomers in the 1700−1400 cm^{-1} Region

		urea	urea ^{13}C	urea $^{15}N_2$	urea ^{18}O
$\delta_s(NH_2)$	(A1)	1683	1673	1676	1675
$\delta_{as}(NH_2)$	(B2)	1625	1622	1613	1625
$\nu(CO)$	(A1)	1601	1573	1600	1592
$\nu_{as}(CN)$	(B2)	1466	1434	1460	1465

We assign the band at 1683 cm^{-1} to $\delta_s(NH_2)$ and the band at 1601 cm^{-1} to the $\nu(CO)$ vibration, but we will show by experimental data and by results of our force field calculations on the solid state[24] that these two vibrations are strongly coupled.

We reject the assignment of Vijay[17] and Ha[16] because they based their assignment on gas phase calculations and we have already proven earlier in this article that this approach is not allowed in the case of urea.

Regarding the infrared spectra of partially deuterated urea (Figure 6), the two bands at 1683 and 1625 cm^{-1}, respectively, dissappear on deuteration, supporting our assignment of the $\delta(NH_2)$ vibrations. We also see the band at 1601 cm^{-1} shifting to higher wavenumber (1608 cm^{-1}), indicating a coupling between the $\nu(CO)$ and the $\delta_s(NH_2)$ vibrations. The band at 1466 cm^{-1} also shifts to a higher wavenumber on deuteration, which indicates that this $\nu_{as}(CN)$ vibration is coupled with the $\delta_{as}(NH_2)$ vibration. The same effects are observed in the Raman spectra of partially deuterated urea (Figure 7). The bands at 1647 and 1623 cm^{-1} disappear on deuteration, and the bands at 1540 and 1466 cm^{-1} shift to higher wavenumbers, supporting our assignments.

Table 2 shows the infrared frequencies of urea and its ^{13}C, $^{15}N_2$, and ^{18}O isotopomers. The bands at 1683 and 1601 cm^{-1} both appear at a lower frequency in the case of the ^{13}C and ^{18}O isotopomer, indicating that both bands have CO stretching character. The ^{13}C changes are almost a factor 3 greater for the band at 1601 cm^{-1}, indicating that the lower band has more

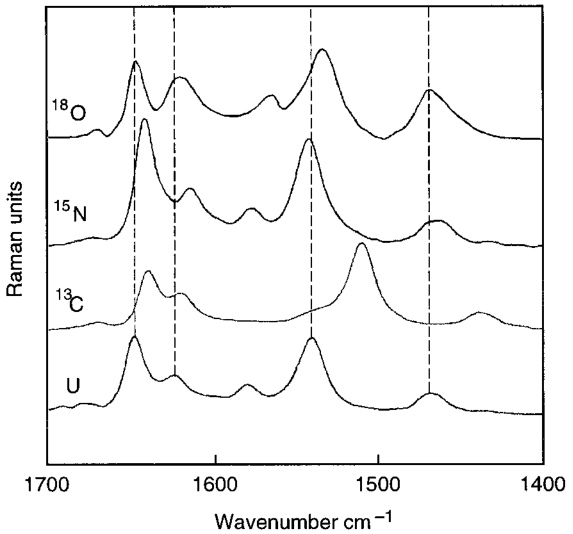

Figure 8. Raman spectra of urea and its ^{13}C, ^{15}N$_2$, and ^{18}O isotopomers in the 1700−1400 cm^{-1} region.

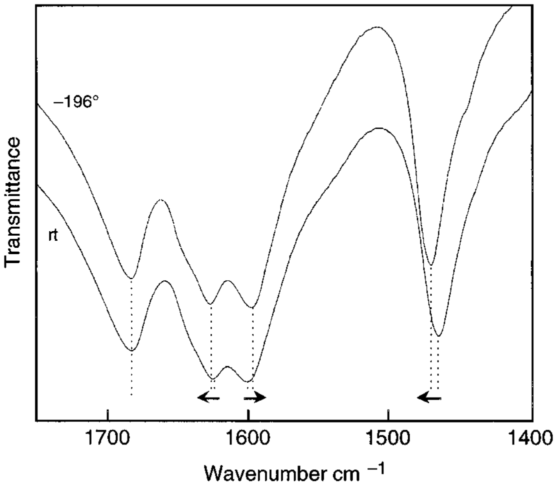

Figure 9. Low-temperature shifts in the 1700−1400 cm^{-1} region of the infrared spectrum of urea.

CO character. The band at 1683 cm^{-1} appears at 1676 cm^{-1} in the case of the ^{15}N$_2$ analogue, while the band at 1601 cm^{-1} almost stays invariant, indicating that the higher frequency band has more NH$_2$ deformation character. The band at 1625 cm^{-1} has a great change on the ^{15}N$_2$ substitution, only a small change on ^{13}C substitution and stays invariant on ^{18}O substitution, indicating a nearly pure NH$_2$ deformation vibration. The band at 1466 cm^{-1} disappears on ^{13}C and ^{15}N$_2$ substitution and appears at 1434 and 1460 cm^{-1}, respectively, indicating a CN stretching vibration. The same changes are also observed in the Raman spectra of these isotopomers (Figure 8). The band at 1647 cm^{-1} appears at lower wavenumber at ^{13}C and ^{15}N$_2$ substitution, indicating that this band has both ν(CO) and δ_s(NH$_2$) character. The band at 1540 cm^{-1} shows great changes on ^{13}C and ^{18}O substitution, indicating that this band has mainly ν(CO) character. The changes of the bands at 1623 and 1466 cm^{-1} on isotopic substitution are also similar to those observed in the infrared spectra.

Low-temperature measurements also confirm our assignments. At lower temperatures the CO stretching vibration shifts to a lower wavenumber in contrast with the CN stretching and the NH$_2$ deformation vibrations due to a strengthening of the hydrogen bonds, as discussed earlier in this article.

As can be seen from Figure 9, the band at 1601 cm^{-1} shifts to a lower frequency upon lowering the temperature, so this band must exhibit high CO stretching character. The band at 1686 cm^{-1} is not shifted. This indicates that this band exhibits both ν(CO) and δ_s(NH$_2$) character. The lowering of this band due to the ν(CO) character is exactly compensated by the expected shift to higher wavenumber due to the δ_s(NH$_2$) character. The bands at 1625 and 1466 cm^{-1} shift to higher wavenumbers, which is in agreement with our assignment to the antisymmetrical NH$_2$ deformation and CN stretching vibrations, respectively. The same results are observed in the low-temperature Raman spectrum (Figure 10). The band at 1540 cm^{-1} shifts to a lower wavenumber, indicating that this band has mainly ν(CO) character. The band at 1647 cm^{-1} is not shifted, indicating a coupling between the δ_s(NH$_2$) and the ν(CO) vibrations. The bands at 1623 and 1466 cm^{-1} show the same shifts as the corresponding bands in the infrared spectra, supporting our assignment to the δ_{as}(NH$_2$) and the ν_{as}(CN) vibrations, respectively.

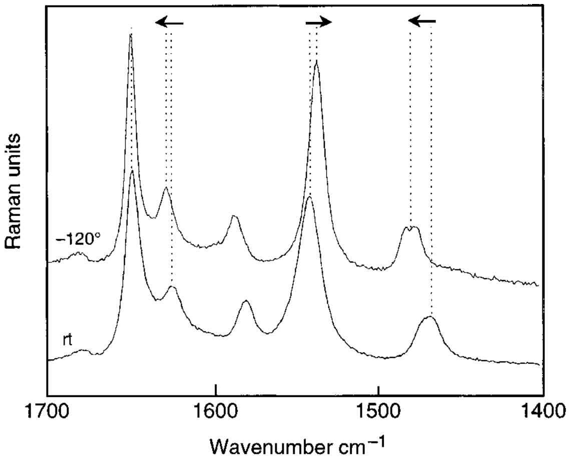

Figure 10. Low-temperature shifts in the 1700−1400 cm^{-1} region of the Raman spectrum of urea.

TABLE 3: Frequency Changes (cm^{-1}) of the ν(CO) Vibration on Complexation

	$\Delta\nu_{as}$(CN) + $\Delta\nu_s$(CN)	$\Delta\nu$(CO) if ν(CO) = 1601 cm^{-1}	$\Delta\nu$(CO) if ν(CO) = 1683 cm^{-1}
MnU$_1$Cl$_2$	42	20	102
MnU$_2$Cl$_2$	25	25	107
MnU$_4$Cl$_2$	26	32	114
MnU$_2$Br$_2$	24	29	111
MnU$_4$Br$_2$	29	22	104
MnU$_6$Br$_2$	26	31	113
MnU$_6$I$_2$	25	25	107

We have prepared several oxygen-bonded Mn−urea complexes.[91] Regarding the resonance forms in urea (Figure 2), the ν(CO) frequency change of the complex compared to the free ligand must be of the same magnitude as the sum of the frequency changes of the symmetrical and the antisymmetrical CN stretching vibrations. Regarding the results given in Table 3, we can see that it is more reasonable to assign the band at 1601 cm^{-1} to the CO stretching vibration because in this case the magnitude of the frequency change of the ν(CO) vibration is comparable to the sum of the ν_{as}(CN) and ν_s(CN) vibrations.

Table 4 shows the PED values of our recently published force field calculation on the solid state of urea.[24] This calculation confirms our experimental assignments and the coupling of the CO stretching and the symmetrical NH$_2$ deformation vibrations.

So we can, on the basis of our experimental and theoretical results, assign the band at 1686 cm^{-1} to the δ_s(NH$_2$) vibration and the band at 1601 cm^{-1} to the ν(CO) vibration. Both vibrations, however, are not pure but strongly coupled. The

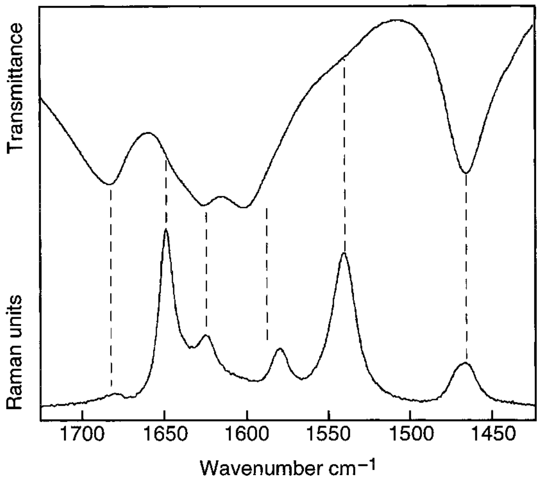

Figure 11. Infrared and Raman spectrum of urea in the 1700−1400 cm^{-1} region.

TABLE 4: PED's in the 1700−1400 cm^{-1} Region of the IR Spectrum of Urea

	IR	R	RHF/ 6-31++G**	PED
1	1683	1647	1663	51% $\delta_s(NH_2)$ + 21% $\nu(CO)$ + 19% $\nu_s(CN)$
2	1625	1623	1636	72% $\delta_{as}(NH_2)$ + 24% $\nu_{as}(CN)$
3	1601	1540	1602	41% $\nu(CO)$ + 33% $\delta_s(NH_2)$ + 10% $\rho_s(NH_2)$
4	1466	1466	1473	54% $\nu_{as}(CN)$ + 21% $\delta_{as}(NH_2)$ + 15% $\delta(CO)$

infrared absorptions at 1625 and 1466 cm^{-1} are assigned to the $\delta_{as}(NH_2)$ and $\nu_{as}(CN)$ vibrations, respectively, which is in total agreement with the literature.[16−17,20,22,48,76,80−87,89]

1700−1400 cm^{-1} Region in the Raman Spectrum of Urea. Figure 11 shows the infrared and Raman spectrum of urea in the 1700−1400 cm^{-1} region. In this region of the Raman spectrum of urea the same four absorptions are expected as in the infrared spectrum. The problem is that not four but six bands are clearly visible in this part of the Raman spectrum (Figure 11), and to our knowledge, this problem has not been mentioned in the literature. However when we look more severely at the infrared spectrum of urea, the same six absorptions are observable although two of them only appear as shoulders (Figure 11) and were, at the beginning, believed to be overtones or combination bands.

The $\delta_{as}(NH_2)$ and $\nu_{as}(CN)$ vibrations are relatively intense bands at 1625 and 1466 cm^{-1}, respectively, in both the Raman and infrared spectrum of urea. These bands can undoubtedly be assigned.

The band at 1683 cm^{-1} appears as a very strong band in the infrared spectrum and as a very weak band in the Raman spectrum of urea, in contrast with the band at 1648 cm^{-1}, which is very strong in the Raman but only appears as a shoulder in the infrared. The same effect is observed with the bands appearing at 1601 and 1540 cm^{-1}. Because the absorptions in the infrared and Raman spectrum must occur at the same wavelengths in the case of urea, and because of the relative intensity change in the infrared and Raman spectrum as described above, one cannot assign two of these four absorptions to combination bands or overtones. The only explanation we have at this time are crystal field splittings, which have, to our knowledge, not been observed in the powder infrared and Raman spectra of urea at this time. Liapis[92] and Durman[93] already observed this effect in the single-crystal Raman spectra of urea. Regarding the X-ray structure of urea (Figure 1) a splitting of the A_1 and A_2 vibrations is expected when the factor group symmetry (D^3_{2d}) of urea is considered instead of its site symmetry (C_{2v}). The B_1 and B_2 vibrations remain unaffected. Looking at the 1700−1400 cm^{-1} region, six bands are indeed expected: splitting of the two A_1 (C_{2v}) vibrations in two A_1 (D^3_{2d}) and two B_2 (D^3_{2d}) vibrations and the two B_2 (C_{2v}) vibrations which become two E (D^3_{2d}) vibrations. All these D^3_{2d} vibrations are Raman active, resulting in the six clearly observable Raman bands. The A_1 (D^3_{2d}) modes are infrared inactive and consequently only appear as shoulders, and only four absorptions are clearly visible in the infrared spectrum. As bands, split due to crystal field effects, have the same vibrational character, this splitting keeps the vibrational analysis, performed on one single band, unaffected. These splittings, which are also observed in other parts of the vibrational spectrum of urea, will be further investigated by performing ab initio calculations.

Effect of Deuteration on the Relative Intensity of the Symmetrical CN Stretching Vibration and the NH_2 Rocking Vibrations. There also exist some contradictions in the assignment of these vibrations. Stewart[76] and Arenas[82] assigned the bands at 1153 and 1057 cm^{-1} to the symmetrical and antisymmetrical NH_2 rocking vibrations, respectively. Yamaguchi[80] preferred to assign the band at 1153 cm^{-1} to both vibrations. They also found[80] that bands with considerable contributions of both the ND_2 rocking vibrations coincide at 889 cm^{-1} in the vibrational spectrum of deuterated urea, but also calculated that both bands at 1001 and 889 cm^{-1} possess a considerable amount of symmetrical ND_2 rocking character. Duncan[81] supported the initial assignment of Stewart[76] considering the NH_2 rocking modes and assigned the $\rho_{as}(ND_2)$ mode to the band at 853 cm^{-1}. Hadzi[85] supported the assignment of Yamaguchi[80] for nondeuterated urea but a different assignment was proposed for the deuterated compound. Yamaguchi[80] assigned the band at 889 cm^{-1} in deuterated urea to the $\nu_s(CN)$ mode and calculated a coupling with the $\rho_s(ND_2)$ mode, whereas Hadzi[85] assigned the band at 853 cm^{-1} to the $\nu_s(CN)$ vibration. Diaz[86] assigned the band at 1001 cm^{-1} in deuterated urea to the $\nu_s(CN)$ vibration and the band at 889 cm^{-1} to both the $\rho_s(ND_2)$ and $\rho_{as}(ND_2)$ vibrations. A coupling between the $\nu_s(CN)$ and the $\rho_s(ND_2)$ vibrations is calculated. Annamalai[94] followed the assignments of Stewart[76] and Hadzi[85] for their CNDO force field calculation on urea and deuterated urea, respectively. Derreumaux[89] supported the assignment of Hadzi.[85] Vijay[17] and Ha[16] performed HF and MP2 calculations, respectively, on the isolated urea molecule, and they assigned the bands at 1001, 889, and 853 cm^{-1} to the $\rho_s(ND_2)$, the $\nu_s(CN)$, and the $\rho_{as}(ND_2)$ vibrations, respectively. Vijay[17] also calculated a coupling between the two symmetrical vibrations.

If we look at Figure 12 exhibiting the infrared spectra of partially deuterated urea, we clearly see that the very strong band at 1153 cm^{-1} and the weak band at 1057 cm^{-1} disappear on deuteration. The small bands that remain after 100% dilution are caused by the partial exchange of deuterium atoms of the fully deuterated urea by hydrogen atoms of water molecules adsorbed by the hygroscopic KBr matrix by the preparation of the pellet.

These bands also appear at a lower wavenumber when urea is compared with the ^{15}N isotopomer. As a consequence, these bands can be assigned to the NH_2 rocking vibrations. The weak band at 1003 cm^{-1} is assigned to the symmetrical CN stretching vibration. Our force field calculation on crystalline urea[24] shows no coupling between the symmetrical NH_2 rocking and the

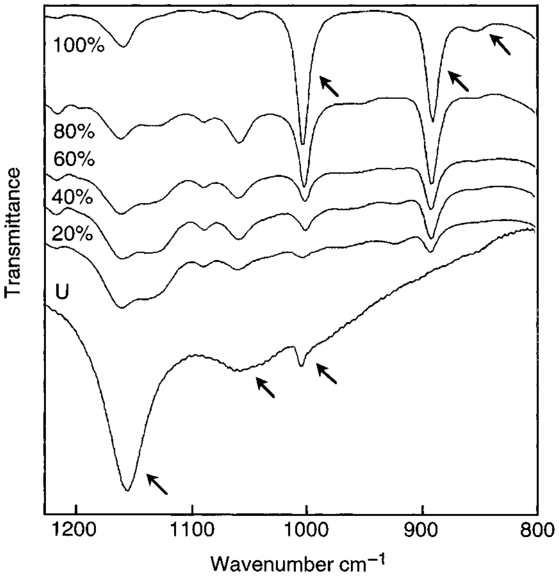

Figure 12. Infrared spectra of partially deuterated urea in the 1200−800 cm^{-1} region.

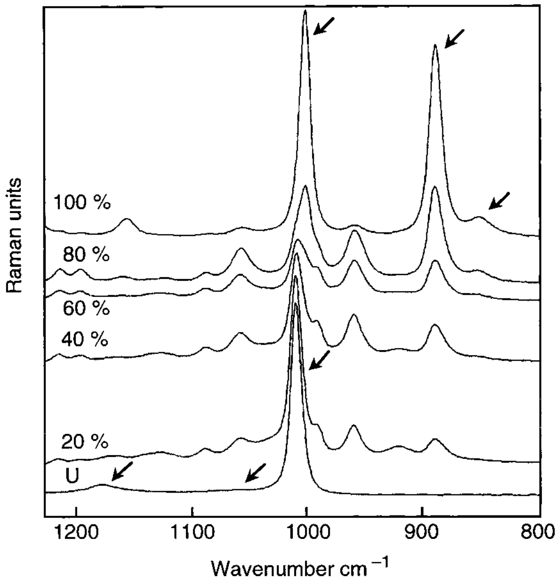

Figure 13. Raman spectra of partially deuterated urea in the 1200−800 cm^{-1} region.

TABLE 5: Experimental and Calculated Frequencies and PED's of Urea in the 1200−800 cm^{-1} Region

	IR	R	RHF/ 6-31++G**	PED
urea	1153	1177	1156	70% $\rho_s(NH_2)$ + 28% $\nu(CO)$
	1057	1056	1065	81% $\rho_{as}(NH_2)$ + 19% $\nu_{as}(CN)$
	1003	1010	1016	84% $\nu_s(CN)$
urea-d_4	1001	1001	994	37% $\rho_s(ND_2)$ + 24% $\nu(CO)$ + 19% $\nu_s(CN)$
	889	890	887	45% $\nu_s(CN)$ + 38% $\rho_s(ND_2)$ + 12% $\delta_s(ND_2)$
	853	852	845	76% $\rho_{as}(ND_2)$ + 15% $\nu_{as}(CN)$

TABLE 6: Infrared Absorptions (cm^{-1}) of Urea in the Gas Phase, at Room Temperature, at −196 °C and at Elevated Pressure

		gas phase (theoretical)		20 °C		−196 °C	P↑
$\nu_{as}(NH_2)$	(A1)	3548	←	3450	←	3348	3450
$\nu_{as}(NH_2)$	(B2)	3548	←	3444	←	3435	3444
$\nu_s(NH_2)$	(A1)	3442	←	3349	←	3345	3356
$\nu_s(NH_2)$	(B2)	3437	←	3331	←	3330	3330
$\delta_s(NH_2)$	(A1)	1592	→	1683	=	1683	1712
$\delta_{as}(NH_2)$	(B2)	1603	→	1625	→	1627	1660
$\nu(CO)$	(A1)	1735	←	1601	←	1598	1605
$\nu_{as}(CN)$	(B2)	1388	→	1466	→	1471	1479
$\rho_s(NH_2)$	(A1)	1155	←	1153	←	1149	1179
$\rho_{as}(NH_2)$	(B2)	1029	→	1057	←	1055	1086
$\nu_s(CN)$	(A1)	936	→	1003	→	1008	1017
$\pi(CO)$	(B1)	786	→	789	→	790	771
$\tau_{as}(NH_2)$	(B1)	517	→	721	→	727	679
$\delta(CO)$	(B2)	568	→	569	→	573	574
$\delta(CN)$	(A1)	467	→	530	→	532	540
$\omega_{as}(NH_2)$	(B1)	423	→	509	←	508	518

symmetrical CN stretching vibrations (Table 5). If we look at the infrared spectrum of deuterated urea (Figure 12), we see that a relative band intensity change has occurred: the two weak bands and the intense band of the normal urea have been converted into two intense bands and one weak band on deuteration. This indicates that a coupling between the ν_s(CN) and the $\rho_s(ND_2)$ vibrations must exist; otherwise, the relative band intensity would have been maintained. The same relative band intensity change is observed in the Raman spectra of partially deuterated urea (Figure 13): the two weak bands at 1177 and 1056 cm^{-1} and the intense band at 1010 cm^{-1} in the Raman spectrum of urea are converted on deuteration into two intense bands and one weak band, again indicating that a coupling between the ν_s(CN) and the $\rho_s(ND_2)$ vibrations must exist.

This is also confirmed by our force field calculation (Table 5) on crystalline urea[24] where indeed a coupling is calculated between the ν_s(CN) and the $\rho_s(ND_2)$ vibrations.

CO and CN Deformation and the Out-of-Plane Vibrations of Urea. The band at 789 cm^{-1} shows a small shift to a higher wavenumber upon lowering the temperature and clearly appears at a lower wavenumber for the ^{13}C and the ^{18}O isotopomers. We assign this band to the π_{CO} vibration. As this band also appears at a lower wavenumber on deuteration, a coupling with the antisymmetrical NH_2 torsional mode must occur.

On the basis of our force field calculation, we assign the bands at 569 and 530 cm^{-1} to the CO and CN deformation vibrations, respectively.

The antisymmetrical NH_2 torsional and wagging modes absorb at 727 and 508 cm^{-1}, respectively, and appear at 550 and 376 cm^{-1} on deuteration. The symmetrical modes are infrared inactive and the Raman bands are too weak so that they cannot be experimentally observed.

V. Use of Low-Temperature and High-Pressure Measurements in the Vibrational Analysis of Urea

Table 6 shows the frequencies of all the infrared active vibrations of urea at room temperature, at −196 °C and at elevated pressure up to ca. 1 GPa, and of our force field calculation on the urea molecule in the gas phase.

If we look at the sequence of the urea molecule in the gas phase, at room temperature and at −196 °C, we expect the molecules to come closer to each other, with stronger hydrogen bonding as a consequence. We expect to see our frequencies shift gradually on going from the gas phase to the solid state to −196 °C and if we look at Table 6 we see that this is experimentally confirmed. The only two exceptions are the antisymmetrical rocking NH_2 and the antisymmetrical wagging NH_2 vibrations. These exceptions are a consequence of differences in the PED values of the gas phase and the solid state because of the difference in structure and the absence of hydrogen bonding in the gas phase (see section III).

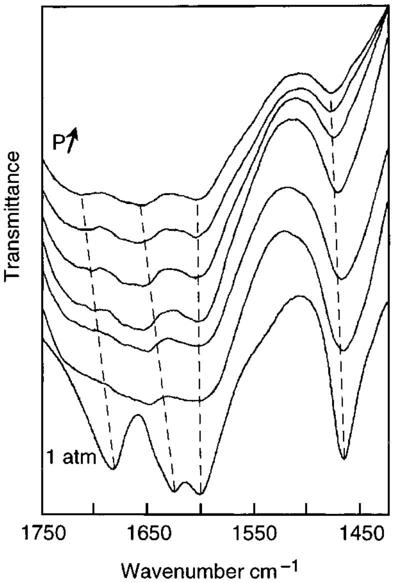

Figure 14. High-pressure measurements of the 1700−1400 cm^{-1} region in the infrared spectrum of urea.

Considering the high-pressure measurements, we see that all the in plane vibrations shift to higher wavenumbers. We also observed this effect at other types of molecules such as oxamides and dithiooxamides.[95] As an example, we show the results of our high-pressure measurements of the 1700−1400 cm^{-1} region in the infrared spectrum of urea (Figure 14).

The only explanation we have for this effect at this time is that because of the very high pressure (up to 1 GPa) not only the intermolecular distances become smaller but also the interatomic distances decrease with an increase of the corresponding wavenumbers as a consequence. This hypothesis will be further investigated soon by performing ab initio calculations on the structure of urea at normal and at elevated pressure. As we see this increase in frequencies already at the smallest amount of pressure possible with our experimental design, we think we can conclude it is not useful to make use of a “diamond anvil cell” when you are performing a vibrational analysis, because both the intermolecular and interatomic distances change and consequently the effect of hydrogen bonding can no longer be studied. Lowering the temperature only results in a decrease of the intermolecular distances, so this technique is suitable to study the effect of hydrogen bonding.

VI. Conclusions

Although a lot of work has been done on the vibrational analysis of urea, there still remains a lot of contradictions and uncertainties about the interpretation of the vibrational spectrum. These contradictions and uncertainties are caused by interpretations of the vibrational spectrum based on force field calculations on isolated urea instead of on urea in its crystal structure. We have shown that this approach of interpretation is not allowed in the case of urea due to the conformational difference and the different extent of hydrogen bonding between the solid state and the gas phase.

We have interpreted the vibrational spectrum of urea by measuring the solid state infrared spectra of eight isotopomers of urea at room temperature and at −196 °C, just as Raman spectra at room temperature and at −120 °C, and of a urea−water solution. We have also performed force field calculations at the Hartree−Fock level with a 6-31++G** basis set, on the isolated urea molecule and on the urea molecule in its crystal structure.

We observed that infrared and Raman frequencies are different. The only explanation we have at this time is crystal field splittings. This hypothesis will be tested soon by performing ab initio calculations.

In the last part of this article we have shown that high-pressure measurements making use of a “diamond anvil cell” are not as straightforward by performing a vibrational analysis as the low-temperature measurements where the spectroscopic shifts can be explained only by the change of the hydrogen bonding effect.

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References and Notes

(1) Wöhler, F. *Ann. Phys. Chem.* **1828**, *12*, 253.
(2) Brandts, J. F.; Hunt, L. *J. Am. Chem. Soc.* **1967**, *89*, 4826.
(3) Wetlaufer, D. B.; Malck, S. K.; Stoller, L.; Coffin, R. I. *J. Am. Chem. Soc.* **1964**, *86*, 508.
(4) Shick, M. J. *J. Phys. Chem.* **1964**, *68*, 3585.
(5) Banerjee, B. K.; Srivastava, P. C. *Fertilizer Technol.* **1979**, *16*, 264.
(6) Theophanides, T.; Harvey, P. D. *Coord. Chem. Rev.* **1987**, *76*, 237.
(7) Elbert, S. T.; Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 857.
(8) Van Alsenoy, C.; Williams, J. O.; Schäfer, L. *J. Mol. Struct. (THEOCHEM)* **1981**, *76*, 179.
(9) Koizumi, M.; Tachibana, A.; Yamabe, T. *J. Mol. Struct. (THEOCHEM)* **1988**, *164*, 37.
(10) Williams, M. L.; Gready, J. E. *J. Comput. Chem.* **1989**, *10*, 35.
(11) Dovesi, R.; Causa, M.; Orlando, R.; Roetti, C.; Saunders: V. R. *J. Chem. Phys.* **1990**, *92*, 7402.
(12) Meier, R. J.; Coussens, B. *J. Mol. Struct. (THEOCHEM)* **1992**, *253*, 25.
(13) Ramondo, F.; Bencivenni, L.; Rossi, V.; Caminito, R. *J. Mol. Struct. (THEOCHEM)* **1992**, *277*, 185.
(14) Kontoyianni, M.; Bowen, J. P. *J. Comput. Chem.* **1992**, *13*, 657.
(15) Gobbi, A.; Frenking, G. *J. Am. Chem. Soc.* **1993**, *115*, 2362.
(16) Ha, T. K.; Puebla, C. *Chem. Phys.* **1994**, *181*, 47.
(17) Vijay, A.; Sathyanarayana, D. N. *J. Mol. Struct.* **1993**, *295*, 245.
(18) Gatti, C.; Saunders, V. R.; Roetti, C. *J. Chem. Phys.* **1994**, *101*, 10686.
(19) Starikov, E. B. *Biopolymers* **1994**, *34*, 921.
(20) Dixon, D. A.; Matsuzawa, N. *J. Phys. Chem.* **1994**, *98*, 3967.
(21) Meier, R. J.; Maple, J. R.; Hwang, M.-J.; Hagler, A. T. *J. Phys. Chem.* **1995**, *99*, 5445.
(22) Spoliti, M.; Pieretti, A.; Bencivenni, L.; Sanna, N. *Electron. J. Theor. Chem.* **1997**, *2*, 149.
(23) Godfrey, P. D.; Brown, R. D.; Hunter, A. N. *J. Mol. Struct.* **1997**, *413−414*, 405.
(24) Rousseau, B.; Keuleers, R.; Desseyn, H. O.; Van Alsenoy, C. *J. Phys. Chem. A* **1998**, *102*, 6540.
(25) John, H. U.S. Patent **1920**, *355*, 834.
(26) Halbout, J. M.; Tang, C. L. Properties and Applications of Urea. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987.
(27) Keller, W. E. *J. Chem. Phys.* **1948**, *16*, 1003.
(28) Waldron, R. D.; Badger, R. M. *J. Chem. Phys.* **1950**, *18*, 566.
(29) Wyckoff, R. W. G. *Z. Kristallogr.* **1932**, *81*, 102.
(30) Wyckoff, R. W. G.; Corey, R. B. *Z. Kristallogr.* **1934**, *89*, 462.
(31) Vaughan, P.; Donohue, J. *Acta Crystallogr.* **1952**, *5*, 530.
(32) Sklar, N.; Senko, M. E.; Post, B. *Acta Crystallogr.* **1961**, *14*, 716.
(33) Caron, A.; Donohue, J. *Acta Crystallogr.* **1964**, *17*, 544.
(34) Caron, A.; Donohue, J. *Acta Crystallogr.* **1969**, *B25*, 404.
(35) Swaminathan, S.; Craven, B. M.; Spackman, M. A.; R. F. Stewart, R. F. *Acta Crystallogr.* **1984**, *B40*, 398.
(36) Bergmann, E.; Weizmann, A. *Trans. Faraday Soc.* **1938**, *34*, 783.
(37) Kumler, W. D.; Fohlen, G. M. *J. Am. Chem. Soc.* **1942**, *64*, 1944.
(38) Gilkerson, W. R.; Srivastava, K. K. *J. Phys. Chem.* **1960**, *64*, 1485.
(39) Kellner, L. *Proc. R. Soc. (London)* **1941**, *A177*, 456.
(40) Worsham, J. E., Jr.; Levry, H. A.; Peterson, S. W. *Acta Crystallogr.* **1957**, *10*, 319.
(41) Pryor, A. W.; Sanger, P. L. *Acta Crystallogr.* **1970**, *A26*, 543.
(42) Guth, H.; Heger, G.; Klein, S.; Treutmann, W.; Scheringer, C. *Z. Krystallogr.* **1980**, *153*, 237.

(43) Swaminathan, S.; Craven, B. M.; McMullan, R. K. *Acta Crystallogr.* **1984**, *B40*, 300.

(44) King, S. T. *Spectrochim. Acta* **1972**, *A28*, 165.

(45) Brown, R. D.; Godfrey, P. D.; Storey, J. *J. Mol. Spectrosc.* **1975**, *58*, 445.

(46) Li, X.; Stotesbury, S. J.; Jayasooriya, U. A. *Spectrochim. Acta* **1987**, *A43*, 1595.

(47) Korn, E. D. In *Methods in Enzymology*; Colowick, S., Kaplan, N. O., Eds.; Academic Press: New York, 1957; Vol. IV, p 623.

(48) Laulicht, I.; Pinchos, S.; Petreanu, E.; Samuel, D. *Spectrochim. Acta* **1965**, *21*, 1487.

(49) Pisani, C.; Dovesi, R.; Roetti, C. *Hartree−Fock Ab Initio Treatment of Crystalline Systems*; Lecture Notes in Chemistry, Vol. 48; Springer-Verlag: Berlin, 1988.

(50) Sæbø, S.; Klewe, B.; Samdal, S. *Chem. Phys. Lett.* **1983**, *97*, 499.

(51) Ángyán, J. G.; Silvi, B. *J. Chem. Phys.* **1987**, *86*, 6957.

(52) Bridet, J.; Fliszár, S.; Odiot, S.; Pick, R. *Int. J. Quantum Chem.* **1983**, *24*, 687.

(53) Sugano, S.; Shulman, R. G. *Phys. Rev.* **1963**, *130*, 517.

(54) Popelier, P.; Lenstra, A. T. H.; Van Alsenoy, C.; Geise, H. J. *J. Am. Chem. Soc.* **1989**, *111*, 5658.

(55) Lenstra, A. T. H.; Van Alsenoy, C.; Verhulst, K.; Geise, H. J. *Acta Crystallogr.* **1994**, *B50*, 96.

(56) Peeters, A.; Van Alsenoy, C.; Lenstra, A. T. H.; Geise, H. J. *Int. J. Quantum Chem.* **1993**, *46*, 73.

(57) Peeters, A.; Van Alsenoy, C.; Lenstra, A. T. H.; Geise, H. J. *J. Mol. Struct. (THEOCHEM)* **1994**, *304*, 101.

(58) Peeters, A.; Van Alsenoy, C.; Lenstra, A. T. H.; Geise, H. J. *J. Chem. Phys.* **1995**, *103*, 6608.

(59) Van Alsenoy, C. *J. Comput. Chem.* **1988**, *9*, 620.

(60) Van Alsenoy, C.; Peeters, A. *J. Mol. Struct. (THEOCHEM)* **1993**, *286*, 19.

(61) Van Alsenoy, C.; Rousseau, B. To be published.

(62) Almlöf, J.; Faegri, K.; Korsell, K. *J. Comput. Chem.* **1982**, *3*, 385.

(63) Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

(64) Suzuki, K.; Onishi, S.; Koide, T.; Seki, S. *Bull. Chem. Soc. Jpn.* **1956**, *29*, 127.

(65) Trimble, L. E.; Voorhoeve, R. J. H. *Analyst* **1978**, *103*, 759.

(66) De Wit, H. G. M.; Van Miltenburg, J. C.; De Kruif, C. G. *J. Chem. Thermodynam.* **1983**, *15*, 651.

(67) Ferro, D.; Barone, G.; Della Gatta, G.; Piacente, V. *J. Chem. Thermodynam.* **1987**, *19*, 915.

(68) Krasulin, A. P.; Kozyro, A. A.; Kabo, G. Ya. *J. Appl. Chem. USSR* **1987**, *60*, 96.

(69) Khattab, F. I.; Al-Ragehy, N. A.; Ahmad, A. K. S. *Thermochim. Acta* **1984**, *73*, 47.

(70) Wynne, A. M. *J. Chem. Educ.* **1987**, *64*, 180.

(71) Stradella, L.; Argentero, M. *Thermochim. Acta* **1993**, *219*, 315.

(72) Paorici, C.; Zha, M.; Zanotti, L.; Attolini, G.; Traldi, P.; Catinella, S. *Cryst. Res. Technol.* **1995**, *30*, 667.

(73) Gutmann, V. *The Donor−Acceptor Approach to Molecular Interactions*, Plenum Press: New York and London, 1978.

(74) Hoccart, X.; Turrell, G. *J. Chem. Phys.* **1993**, *99*, 8498.

(75) Lee, C.; Stahlberg, E. A.; Fitzgerald, G. *J. Phys. Chem.* **1995**, *99*, 17737.

(76) Stewart, J. E. *J. Chem. Phys.* **1957**, *26*, 248.

(77) Langer, J.; Schrader, B.; Bastian, V.; Jacob, E. *Fresenius J. Anal. Chem.* **1995**, *352*, 489.

(78) Kohlrausch, K. W. F.; Pongratz, A. *Monatsh. Chem.* **1937**, *70*, 226.

(79) Angell, C. L.; Sheppard, N.; Yamaguchi, A.; Shimanouchi, T.; Miyazawa, T.; Mizushima, S. *Trans. Faraday Soc.* **1957**, *53*, 589.

(80) Yamaguchi, A.; Miyazawa, T.; Shimanouchi, T.; Mizushima, S. *Spectrochim. Acta* **1957**, *10*, 170.

(81) Duncan, J. L. *Spectrochim. Acta* **1971**, *A27*, 1197.

(82) Arenas, J.; Parellada, R. *J. Mol. Struct.* **1971**, *10*, 253.

(83) Saito, Y.; Machida, K.; Uno, T. *Spectrochim. Acta* **1971**, *A27*, 991.

(84) Shteinberg, B. Ya.; Mushkin, Yu. I.; Finkelstein, A. I. *Opt. Spectrosc.* **1972**, *33*, 589.

(85) Hadzi, D.; Kidric, J.; Knezevic, Z. V.; Barlic, B. *Spectrochim. Acta* **1976**, *A32*, 693.

(86) Diaz, G.; Campos, M. *Spectrosc. Lett.* **1981**, *14*, 365.

(87) Rajalakshmi, T.; Fareed, R. S. Q.; Dhanasekaran, R.; Ramasamy, P.; Thomas, J.; Srinivasan, K. *Mater. Sci. Eng.* **1996**, *B39*, 111.

(88) Robinson, T. S.; Price, W. C. *Proc. Phys. Soc.* **1953**, *B66*, 969.

(89) Derreumaux, P.; Vergoten, G.; Lagant, P. *J. Comput. Chem.* **1990**, *11*, 560.

(90) Notario, R.; Castaño, O.; Herreros, M.; Abboud, J.-L. M. *J. Mol. Struct. (THEOCHEM)* **1996**, *371*, 21.

(91) Keuleers, R.; Desseyn, H. O. Submitted for publication.

(92) Liapis, K.; Jayasooriya, U. A.; Kettle, S. F. A.; Eckert, J.; Goldstone, J. A.; Taylor, A. D. *J. Phys. Chem.* **1985**, *89*, 4560.

(93) Durman, R.; Jayasooriya, U. A.; Kettle, S. F. A. *J. Phys. Chem.* **1988**, *92*, 620.

(94) Annamalai, A.; Singh, S. *J. Chem. Phys.* **1982**, *77*, 860.

(95) Keuleers, R.; Clou, K.; Miao, M. S.; Van Doren, V.; Desseyn, H. O. To be published.