Coriolis Coupling Constants and Inertia Defect of Urea

M. Campos-Vallette, C. A. Acevedo-Gonzalez, G. Diaz F.*, and R. Peña C.**

Universidad de Chile, Facultad de Ciencias, Departamento de Química,
Casilla 653, Santiago, Chile

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Coriolis coupling constants and the inertia defect for urea have been calculated using force constants obtained by the iterative consistency method. The Coriolis coupling constants are very sensitive to the force constant variation and the value of the inertia defect is calculated to be 0.0119 umaÅ^2.

Introduction

Several papers dealing with the vibrational spectra and normal coordinate analysis of urea have appeared [1–6]. Duncan [1] computed a 21 parameter symmetry valence force field and Puranik et al. [2] have considered the molecule as a four body problem using a general quadratic potential function. Moreover Annamalai et al. [3] have performed symmetry force field calculations for the planar vibrations of urea using CNDO/Force method and Saito et al. [4] have employed a general valence force field for the non planar ones. It seems, however, that the assignment of the non planar vibrations of urea have not definitely been settled to date. A normal coordinate analysis and the calculation of both Mean Amplitudes and Centrifugal Distortion constants for urea and urea-d_4 were performed from a symmetry force field [5]; this study was partially continued for the series including selenourea, thiourea and urea by reporting the force field in internal coordinates for the in plane molecular vibrations, and the corresponding mean amplitudes [6]. In order to complete this study we carried out, for the first time, a normal coordinate analysis in internal coordinates for the out of plane vibrations. This treatment which permits to make a more confidence theoretical assignment using the L matrix, allowed the evaluation of Compliance Constants, Coriolis coupling constants and Inertia Defect of Urea.

Experimental

Commercially available urea was recrystallized several times from ethanol. The purified urea was converted into urea-d_4 by the usual exchange reaction with D_2O obtained from Merck AG, 99.7% purity. In order to make the deuteration as complete as possible, the exchange reaction was repeated three times. The infrared spectra from 4000 to 250 cm^{-1} were recorded on a Perkin-Elmer 621 spectrophotometer. The measurement was made for the crystal dispersed in Nujol and KBr mulls. The spectra are similar to those recorded by Saito et al. [4].

Calculations

Normal coordinate analysis

The molecular model and the internal coordinates of urea are shown in Figure 1. The group symmetry is C_{2v} and the normal modes are distributed in 13 in plane vibrations: $7A_1 + 6B_1$; and 5 out of plane vibrations: $3B_2 + 2A_2$. The structural parameters were taken from the data of the neutron diffraction analysis of Worsham et al. [7].

a) In plane vibrations

The normal coordinate analysis for the in plane vibrations of urea and urea-d_4 has been carried out using the force field obtained by the iterative con-

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* Academia Superior de Ciencias Pedagógicas de Valparaíso, Departamento de Química, Casilla 34-V, Valparaíso, Chile.

** Academia Superior de Ciencias Pedagógicas de Santiago, Departamento de Química, Macul 743, Santiago, Chile.

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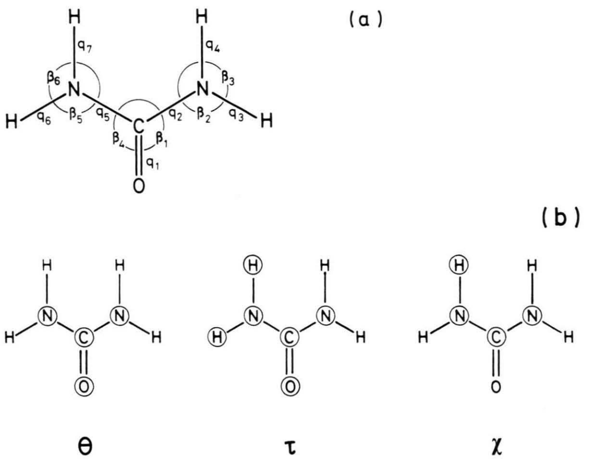

Fig. 1. Model and internal coordinates of urea, a) in plane vibrations, b) out of plane vibrations [11].

sistency method [8]. The reliability of the force constant results given by this method has been tested in series of simple polyatomic molecules [9]. The in plane F matrix is presented in Table 1. The assignment of the calculated fundamental frequencies was discussed and compared with experimental data in [6].

b) Out of plane vibrations

The out of plane fundamental frequencies of urea and urea-d$_4$, which are necessary to calculate the force field using the iterative method were selected from our spectra and reported data [4, 5, 10]. The diagonal values of the F^0 matrix for urea, which allow the initiation of the iterative process, are calculated from the equation $F^0_{ii} = \lambda_i / G_{ii}$ where $\lambda_i = (\omega_i / 1303.16)^2$ and ω_i the i^{th} experimental vibration frequency. The G matrix was constructed by the explicit formulation given by Aroca et al. [11]. The final F matrix obtained after 17 iterative steps is shown in Table 2. The assignment of theoretical and experimental frequencies of urea and urea-d$_4$ made using the L matrix and the Potential Energy Distribution, P.E.D., is given in Table 3.

Compliance constants

The advantages in the determination of compliance constants, F^{-1}, over the more common force constants are well known [12]: the most noteworthy being the simplicity in the exclusion of dependent forces which are conjugate with dependent coordinates. Moreover, the coefficients are determined only by the selection of these forces and are independent of the remainder. This allows the compilation of tables of compliance constants for the structural elements, and simplifies the task of treating molecules with similar structural groups.

The compliance constant matrix for in and out of plane vibrations of urea are displayed in Table 4.

Coriolis coupling constants

A knowledge of the approximate values of Coriolis coupling constants, ζ, which represents a form of vibration-rotation interaction constants, can be useful for preliminary analysis of rotational structure, prediction of band shapes etc. In calculat-

Table 1. Force constants * for the in plane vibrations of urea.

q_1	q_2	q_5	q_3	q_6	q_4	q_7	β_1	β_4	β_2	β_5	β_3	β_6
10.7461	0.7661	0.7661	0.0345	0.0345	0.1168	0.1168	1.1587	1.1587	−0.0470	−0.0470	0.0260	0.0260
	8.0312	0.7321	0.0913	0.0631	−0.0251	−0.0218	−0.2517	−0.8693	0.1387	0.4459	−0.2163	0.0353
		8.0312	0.0631	0.0913	−0.0218	−0.0251	−0.8696	−0.2517	0.4459	0.1387	0.0353	−0.2163
			6.4040	0.0075	−0.0124	−0.0024	−0.0300	−0.0255	0.0250	0.0451	−0.0399	0.0171
				6.4039	−0.0024	−0.0124	−0.0255	−0.0300	0.0451	0.0250	0.0171	−0.0399
					6.3220	−0.0035	0.0021	0.0243	0.1395	−0.0011	−0.1358	−0.0080
						6.3220	0.0243	0.0021	−0.0011	0.1395	−0.0080	−0.1358
							2.7290	1.7152	0.0216	0.0514	0.0183	0.0094
								2.7290	0.0514	0.0216	0.0094	0.0183
									1.3511	−0.0522	0.4564	−0.0909
										1.3511	−0.0909	0.4564
											0.8269	−0.0204
												0.8269

* Units: stretch: mdyn Å^{-1}; stretch-bend: mdyn; bending: mdyn Å.

ing Coriolis coupling constants, we have used the matrix equation of Meal and Polo [13]

$$\zeta = L^{-1} C^{\alpha} \tilde{L}^{-1}.$$

The elements of the C^{α} matrix were evaluated using standard formulae given by Aroca et al. [11] and Ponomariev [14].

Table 2. Force constants in mdyn Å for the non planar vibrations of urea.

$f(\Theta)$	$f(\tau_1)$	$f(\tau_2)$	$f(\chi_1)$	$f(\chi_2)$
0.694	−0.020	0.020	0.028	−0.028
	0.507	−0.021	0.009	0.139
		0.507	0.139	0.009
			0.188	0.023
				0.188

Table 3. Out of plane fundamental frequencies (cm^{-1}) and assignments of urea and urea-d_4.

	Urea			Urea-d_4		
Sym.	$\nu_{exp.}$	$\nu_{cal.}$	assign.	$\nu_{exp.}$	$\nu_{cal.}$	assign.
A_2	719	708	$\tau(NH_2)$	517	511	$\tau(ND_2)$
	555	546	$\chi(NH_2)$	420	419	$\chi(ND_2)$
B_2	785	780	$\Theta(C{=}O)$	776	777	$\Theta(C{=}O)$
	719	709	$\tau(NH_2)$	510	517	$\tau(ND_2)$
	500	491	$\chi(NH_2)$	375	372	$\chi(ND_2)$

Table 5. Coriolis coupling constants of urea.

ζ^X

$(A_1 \times B_2)$			$(B_1 \times A_2)$	
−0.1025	−0.2155	0.6989	0.1778	0.7321
−0.9220	−0.6604	0.2240	0.4533	−0.5497
0.0371	−0.6228	−0.4714	−0.7401	−0.1040
0.9136	−0.1787	0.0838	−0.3162	−0.0802
−0.0004	0.2507	0.1397	−0.3907	−0.1156
0.1838	0.0317	−0.0687	0.1841	−0.2733
−0.3253	0.2160	−0.5547		

ζ^Y

$(A_1 \times B_1)$					
−0.0031	−0.1545	−0.8928	−0.2857	0.3116	0.0210
−0.1679	−0.0064	0.2079	0.2884	0.8708	−0.2213
0.9356	0.2953	0.0147	−0.0092	0.1867	0.0385
−0.0176	0.0998	0.2055	−0.7000	0.0403	−0.6634
0.2818	−0.7666	0.0234	0.1231	−0.1737	−0.3320
−0.1206	0.3357	0.0014	−0.2708	−0.0878	0.1613
−0.0465	0.4233	−0.3377	0.5119	−0.2491	−0.6176

ζ^Z

$(A_1 \times A_2)$		$(B_1 \times B_2)$		
0.5548	0.2097	−0.0115	0.3711	0.4549
−0.6466	−0.1302	−0.0567	0.4753	0.4577
0.5933	−0.2543	−0.5910	0.4862	0.1685
−0.264	0.1188	0.7505	0.3103	0.1560
0.1583	−0.2910	−0.1347	−0.4776	0.5975
−0.0891	0.4475	0.4650	−0.3751	0.0828
−0.2203	0.9236			

Table 4. Compliance constants * of urea.

$C(q_1)$	$C(q_2)$	$C(q_5)$	$C(q_3)$	$C(q_6)$	$C(q_4)$	$C(q_7)$	$C(\beta_1)$	$C(\beta_4)$	$C(\beta_2)$	$C(\beta_5)$	$C(\beta_3)$	$C(\beta_6)$
0.102	−0.014	−0.014	−0.001	−0.001	−0.002	−0.002	−0.030	−0.030	0.016	0.016	−0.011	−0.014
	0.137	−0.009	−0.001	−0.001	0.002	0.002	−0.024	0.065	−0.029	−0.051	0.052	0.013
		0.138	−0.001	−0.001	0.002	0.002	0.065	−0.024	−0.046	−0.034	0.018	0.046
			0.156	−0.000	0.001	0.000	0.002	0.001	−0.997	−0.004	0.010	−0.002
				0.156	0.000	0.001	0.001	0.001	−0.004	−0.007	−0.002	0.011
					0.160	0.000	0.002	−0.000	−0.033	0.001	0.045	−0.001
						0.160	−0.000	0.002	0.001	−0.033	−0.013	0.045
							0.646	−0.395	−0.007	−0.033	−0.013	0.035
								0.647	−0.011	0.011	0.038	−0.018
									0.947	−0.012	−0.541	0.087
										0.955	0.086	−0.530
											1.527	−0.067
												1.541

$C(\Theta)$	$C(\tau_1)$	$C(\tau_2)$	$C(\chi_1)$	$C(\chi_2)$
1.460	−0.007	0.007	−0.255	0.255
	2.488	0.129	0.020	1.860
		2.488	−1.860	0.020
			6.853	−0.820
				6.853

* Units: stretch: Å $mdyn^{-1}$; stretch-bend: $mdyn^{-1}$; bending: $mdyn^{-1}$ $Å^{-1}$. $C(Q)$ represents the generalized force conjugated with the corresponding internal coordinate.

After Jahn's rule [15] for the molecule of urea, we obtain ζ^X: $A_1 \times B_2$ and $B_1 \times A_2$, ζ^Y: $A_1 \times B_1$ and ζ^Z: $A_1 \times A_2$ and $B_1 \times B_2$. In the C^α calculations the Y axis was taken perpendicular to the molecular plane. The C^α and L matrix were reduced by symmetry through a transformation U matrix. For the A_1 and A_2 species, the coefficient of the transformation U_i are the symmetry coordinate S defined by a linear combination of internal coordinates Q:

$$S(Q_i) = Q_i \quad \text{and} \quad S(Q_i, Q_j) = 2^{-1/2}(Q_i + Q_j).$$

For the asymmetric vibrations B_1 and B_2

$$S(Q_i, Q_j) = 2^{-1/2}(Q_i - Q_j).$$

The numerical values of the Coriolis constants for urea are given in Table 5. Another set of Coriolis constants was calculated by Díaz [16] who used a symmetry force field.

Inertia defect

The general formula for the inertial defect is $\Delta = \Delta_{\text{vib}} + \Delta_{\text{cent}} + \Delta_{\text{elec}}$, where Δ_{cent} is the contribution due to centrifugal distorsion and Δ_{elec} is the electronic contribution [17].

The inertia defect due to vibration-rotation interaction, Δ_{vib}, which appears to be the major contribution to the total inertia defect in small molecules, can be obtained from the formula developed by Jeyapandian et al. [17]. That equation relates the fundamental vibrational frequencies with the Coriolis coupling constants.

Discussion

Spectral assignment and force constants for the out of plane vibrations

In the following discussion we shall use the infrared spectra of urea and urea-d$_4$ published by Saito et al. [4]. Below 800 cm^{-1}, we identify as fundamental, the bands at 785, 719 and 500 cm^{-1} for the urea and 776, 510 and 375 cm^{-1} for the urea-d$_4$. The broad band at 510 cm^{-1} could be composed by two absorptions: 508 cm^{-1} assigned to B_1 vibrational species of the skeletal deformation [6, 10] and the 517 cm^{-1}, calculated using the product rule, is assigned to an out of plane vibration.

We have ascribed the bands at 785 and 776 cm^{-1} to C=O out of plane bending Θ(C=O). The bands at 719 and 500 cm^{-1} of urea, which shift by effect of deuteration to 510 and 375 cm^{-1}, are assigned to the torsional vibrational modes $\tau(NH_2)$ and $\chi(NH_2)$ respectively (see Figure 1). The proposed assignment agrees well with published data in urea [4, 5] and acetamide [18].

There is no available data concerning the two out of plane Raman active modes of urea and urea-d$_4$. We have adopted the same frequencies estimated by Saito et al. [4]: 719 and 555 cm^{-1} for urea and 517 and 420 cm^{-1} for urea-d$_4$. These frequencies are consistent with the observed diffusion lines in acetamide and its totally deuterated derivatives [18]. We propose the two higher frequencies as due to the torsional modes $\tau(NH_2)$ and $\tau(ND_2)$ and the 555 and 420 cm^{-1} lines to $\chi(NH_2)$ and $\chi(ND_2)$ in agreement with the experimental assignment in acetamide and acetamide-d$_5$ [18].

The theoretical force field of urea, displayed in Table 2, allowed us to calculate the frequencies of urea, urea-d$_4$ and its partially deuteroderivatives. The proposed assignment for urea, based on the L matrix and the P.E.D., agree well with available experimental data [4, 6] cf. Table 3. The L matrix gives directly the symmetry of the normal modes.

Because of the difference between both the method of calculations used to determine the Force Field and the coordinate definitions for the out of plane vibrations modes in urea, the symmetrized F matrix, can not be compared with those proposed by Saito et al. [4] and Díaz et al. [5].

The theoretical assignment of the calculated frequencies for the urea conformational isomers and partially deuteroderivatives are available upon request to our laboratory.

Coriolis coupling constants

The results of the present work and those obtained by G. Díaz [16] follow the sum rules [19] and the upper and lower limits vary between $-1 \leqq \zeta_{ij}^{\alpha} \leqq +1$ for each constant as is shown in Table 5. The numerical differences between the zeta values of both sets is, in several cases, over 100% of the numerical value. In the case of constants with high numerical values the differences are more than 60% of the full range of variation. The same conclusion was raised by Aroca et al. [20] when they compared the Coriolis constants of trans-dichloroethylene with the values obtained by Jeyapandian et al. [17] using a different force fields. In the present work as well as in that by Aroca et al. [20], the proposed force fields reproduce the experimental frequencies quite well, although the zeta values are substantially different.

Inertia defect

The vibrational inertia defect calculated through the formula given in [17], using the zeta values obtained in the present work, is 0.0119 umaÅ^2. This value gives some orientation about the planarity of urea [21]. The reliability of this result can be measured in this moment only by the resemblance between those values calculated by the procedure proposed in this paper and the experimental ones in other molecules [20]. Moreover, preliminary calculations of the total inertia defect in urea [22], using the formulation proposed by Pierce et al. [23], could indicate that the sum of electronic and centrifugal contributions are not negligeable with respect to the vibrational inertia defect.

Conclusion

The set of force constants for the out of plane vibrational modes reproduce well the urea and urea-d_4 spectra: the calculated frequencies and the assignment proposed on the basis of the L matrix and the P.E.D. are quite similar to the experimental ones.

Since the force constants, in terms of compliance constants for the in plane vibrations, are correlative for the series involving urea, thiourea and selenourea [6] we expect the same tendency to operate for the out of plane vibrations.

The calculated Coriolis coupling constants appear to be very sensitive to the force field approximations.

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