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Force field for planar vibrations of urea: use of CNDO/Force MO calculations

A ANNAMALAI, M KANAKAVEL* and SURJIT SINGH**
Structural Chemistry Group, Department of Chemistry,
Indian Institute of Technology, Madras 600 036
*Present Address: Liquid Propellent Division, Vikram Sarabhai Space Centre, Trivandrum 695 022
**To whom all the correspondence should be addressed

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Abstract. Symmetry force field calculations have been performed for the planar vibrations of urea using CNDO/Force method. The CNDO/Force calculations predict well the signs and the magnitudes of bending and interaction force constants; the stretching force constants are found to be higher in magnitude. The bending and interaction constants obtained from these calculations and the stretching force constants obtained from the literature are considered for the initial force field. Using the observed frequencies for urea and its isotopic analogues, urea-D_4, urea-$^{15}N_2$, urea-$^{15}N_2D_4$ and urea-^{18}O in the solid as well as in the solution phases, the force field is refined by carrying out iterations over the diagonal force constants. In the final stages of the refinement iterations are carried out over all the force constants keeping the signs of the interaction constants unchanged. It is found that the agreement between the calculated and the observed frequencies is excellent. The final force fields in terms of symmetry as well as redundancy free internal valence coordinates are reported. On the basis of the potential energy distribution the vibrational assignments are discussed.

Keywords. CNDO/Force calculation; force field of urea; normal coordinate analysis of urea; optimum geometry of urea

1. Introduction

Several papers dealing with the vibrational spectra and normal coordinate analyses of urea have appeared in the past two decades (Stewart 1957; Waldron and Badger 1957; Yamaguchi *et al* 1957; Laulicht *et al* 1965; Duncan 1971; Arenas and Paralleda 1971; Shteinberg *et al* 1972; Hadzi *et al* 1976). Yamaguchi *et al* (1957) and Hadzi *et al* (1976) calculated the Urey-Bradley force fields for the planar vibrations, while Duncan (1971) computed a 21-parameter symmetry valence force field. However, a number of points in the assignments of characteristic frequencies are still controversial. Stewart (1957), Arenas and Paralleda (1971) and Duncan (1971) assigned the bands* at ~1055 cm^{-1} and ~1155 cm^{-1} to B_2 and A_1 NH_2 rocking modes of vibrations respectively; where as, Yamaguchi *et al* (1957) and Hadzi *et al* (1976) preferred to consider the 1155 cm^{-1} band for both these vibrations. Another controversial point is in the assignment of the bands at ~ 1686 cm^{-1} and ~ 1602 cm^{-1} to CO stretching and A_1 NH_2 bending modes, which will be discussed later in detail. In most of the calculations the initial force field is set up by

*The band at 1055 cm^{-1} has been reported at different positions ranging from 1055 to 1064 cm^{-1}. However, this will be referred to as 1055 cm^{-1} band all through the text for the sake of convenience.

transferring the force constants from chemically equivalent molecules. This type of transference may be alright in the case of diagonal force constants; but it is just not possible to transfer the interaction force constants as interaction force constants are sensitive functions of the geometry of molecules. The magnitude and sign of the interaction constants play an important role in the determination of the vibrational frequencies and the potential energy distribution (PED). Recently, Pulay and Torok (1973) and Kanakavel *et al* (1976), by means of CNDO MO calculations, have evaluated the force fields for a variety of molecules. This method is called CNDO/Force method. Kanakavel (1976) suggested that the interaction force constants, obtained from such calculations, together with the diagonal force constants transferred from chemically equivalent molecules may form a better initial force field. Since urea is an important organic molecule with its significant complexing ability with metals, it is thought of interest to carry out the complete force field calculations for the planar vibrations with the above procedure and discuss the vibrational assignments in the light of PED thus obtained.

2. Mode of calculations, results and discussion

In terms of C_{2v} point group the 18 vibrations of urea factorize according to $7A_1+6B_2+2A_2+3B_1$. Out of them A_1 and B_2 species correspond to the in-plane vibrations to which the calculations in the present work are confined. The set of redundancy free internal valence coordinates and symmetry coordinates, used in our calculations are given in table 1 in terms of the internal valence coordinates shown in figure 1.

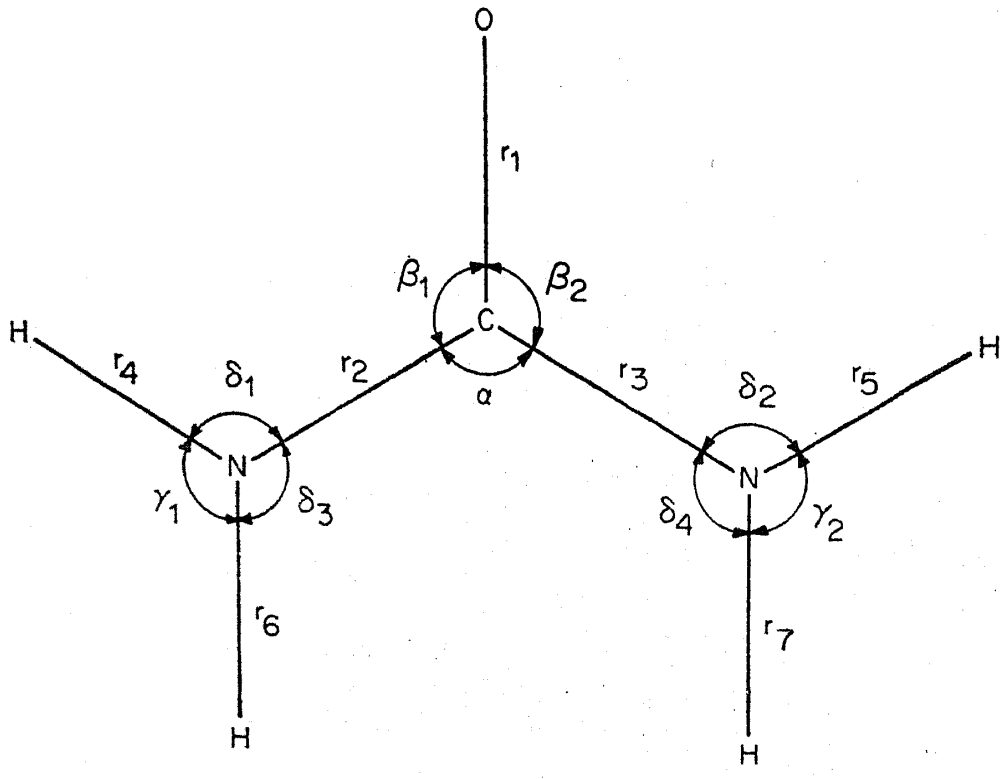

Figure 1. Internal valence coordinates of urea.

Table 1(a). Redundancy free internal valence coordinates (or local symmetry coordinates) of urea*.

Coordinate definition	Vibrational mode	Coordinate definition	Vibrational mode
$s_1 = \Delta r_1$	CO stretch	$s_8 = \frac{1}{\sqrt{6}}(2\Delta\alpha - \Delta\beta_1 - \Delta\beta_2)$	Skel. defor.
$s_2 = \Delta r_2$	CN stretch	$s_9 = \frac{1}{\sqrt{2}}(\Delta\beta_1 - \Delta\beta_2)$	Skel. defor.
$s_3 = \Delta r_3$	CN Stretch	$s_{10} = \frac{1}{\sqrt{6}}(2\Delta\gamma_1 - \Delta\delta_1 - \Delta\delta_3)$	NH_2 bend.
$s_4 = \Delta r_4$	NH stretch	$s_{11} = \frac{1}{\sqrt{6}}(2\Delta\gamma_2 - \Delta\delta_2 - \Delta\delta_4)$	NH_2 bend.
$s_5 = \Delta r_5$	NH stretch	$s_{12} = \frac{1}{\sqrt{2}}(\Delta\delta_1 - \Delta\delta_3)$	NH_2 rock.
$s_6 = \Delta r_6$	NH stretch	$s_{13} = \frac{1}{\sqrt{2}}(\Delta\delta_2 - \Delta\delta_4)$	NH_2 rock.
$s_7 = \Delta r_7$	NH stretch		

Table 1(b). Symmetry coordinates of urea*

A_1 species:

$S_1 = \Delta r_1$

$S_2 = \frac{1}{\sqrt{2}}(\Delta r_2 + \Delta r_3)$

$S_3 = \frac{1}{2}(\Delta r_4 + \Delta r_5 + \Delta r_6 + \Delta r_7)$

$S_4 = \frac{1}{2}(\Delta r_4 + \Delta r_5 - \Delta r_6 - \Delta r_7)$

$S_5 = \frac{1}{\sqrt{6}}(2\Delta\alpha - \Delta\beta_1 - \Delta\beta_2)$

$S_6 = \frac{1}{2\sqrt{3}}(2\Delta\gamma_1 + 2\Delta\gamma_2 - \Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3 - \Delta\delta_4)$

$S_7 = \frac{1}{2}(\Delta\delta_1 + \Delta\delta_2 - \Delta\delta_3 - \Delta\delta_4)$

Redundant:

$S_8 = \frac{1}{\sqrt{3}}(\Delta\alpha + \Delta\beta_1 + \beta_2)$

$S_9 = \frac{1}{\sqrt{6}}(\Delta\gamma_1 + \Delta\gamma_2 + \Delta\delta_1 + \Delta\delta_2 + \Delta\delta_3 + \Delta\delta_4)$

B_2 species:

$S_{10} = \frac{1}{\sqrt{2}}(\Delta r_2 - \Delta r_3)$

$S_{11} = \frac{1}{2}(\Delta r_4 - \Delta r_5 + \Delta r_6 - \Delta r_7)$

$S_{12} = \frac{1}{2}(\Delta r_4 - \Delta r_5 - \Delta r_6 + \Delta r_7)$

$S_{13} = \frac{1}{\sqrt{2}}(\Delta\beta_1 - \Delta\beta_2)$

$S_{14} = \frac{1}{2\sqrt{3}}(2\Delta\gamma_1 - 2\Delta\gamma_2 - \Delta\delta_1 + \Delta\delta_2 - \Delta\delta_3 + \Delta\delta_4)$

$S_{15} = \frac{1}{2}(\Delta\delta_1 - \Delta\delta_2 - \Delta\delta_3 + \Delta\delta_4)$

Redundant:

$S_{16} = \frac{1}{\sqrt{6}}(\Delta\gamma_1 - \Delta\gamma_2 + \Delta\delta_1 - \Delta\delta_2 + \Delta\delta_3 - \Delta\delta_4)$

*The coordinates, given in table 1, involving angle bending displacements are scaled by Å in order to represent all force constants in the same unit, mdyn $Å^{-1}$.

2.1. *CNDO/Force calculations*

The CNDO/Force calculations are performed on urea using a modified form of the computer program of Pople and Beveridge (1970). The force acting on each atom is computed for the experimental geometry of the molecule (Worsham *et al* 1957) by analytically differentiating the total energy, calculated from CNDO wavefunctions, with respect to the nuclear coordinates. Since these forces are always directed towards the equilibrium geometry of the molecule, all atoms are moved in the direction of the force over a small distance, say 0·01 Å. The forces are computed again for the new geometry and the nuclei are allowed to relax towards the equilibrium

geometry. The process is repeated until the norm of the forces becomes smaller than the preset threshold value, say 0·001. On minimizing the energy the norm of the forces keeps decreasing and it is found that when the norm is less than 0·001 further iterations do not change the geometry and the energy to any considerable extent.

The cartesian forces are then calculated for all possible configurations representing the planar vibrations by deforming the molecule by an amount of $\pm\frac{1}{2}\triangle S_i$ from the optimum geometry calculated, where $\triangle S_i$ is the displacement in ith symmetry coordinate. The displacements given for stretching and bending internal coordinates are confined to $\pm 0{\cdot}02$ Å and $\pm 1{\cdot}5°$ respectively. For each deformed configuration the symmetry forces (ϕ_i) are calculated by using suitable transformations. The symmetry force constants are then obtained by the relations

$$F_{ij} = \frac{\triangle \phi_i}{\triangle S_j} \text{ and } F_{ji} = \frac{\triangle \phi_j}{\triangle S_i}.$$

The values calculated for F_{ij} and F_{ji} are close to each other.

The optimum geometry for urea as obtained from CNDO/Force calculations is given in table 2. Of course, this geometry corresponds to the isolated urea molecule. No experimental geometry for the isolated urea molecule is available in the literature. However, for the sake of comparison the geometry in the crystalline state, determined by neutron diffraction studies (Worsham *et al* 1957) is included in table 2. The symmetry force constants calculated by the CNDO/Force method are presented in table 3. As pointed out by Kanakavel *et al* (1976), it has been found that the order of magnitude of the bending and the interaction force constants are quite reasonable and the signs of the stretch-bend interaction force constants are in accordance with the signs predicted by the orbital following arguments discussed by Mills (1963). The magnitude of stretching force constants are, however, high.

2.2. *Observed frequency data*

Recently, Hadzi *et al* (1976) measured the vibrational frequencies of urea, urea-D_4, urea-$^{15}N_2$, urea-$^{15}N_2D_4$ and urea-^{18}O in the solid and in acetonitrile solutions. We have employed Hadzi's data in our calculations. Stewart (1957) and Arenas and

Table 2. Experimental and calculated geometries of urea.

Bond length	Exp.*	Calc. CNDO/Force method	Bond angle	Exp.*	Calc. CNDO/Force method
r_1 (CO)	1·243 Å	1·2825 Å	α (NCN)	117·0°	116·48°
$r_2=r_3$ (CN)	1·351 Å	1·3698 Å	$\beta_1=\beta_2$ (NCO)	121·5°	121·76°
$r_4=r_5$ (NH)	0·995 Å	1·0604 Å	$\gamma_1=\gamma_2$ (HNH)	122·1°	114·90°
$r_6=r_7$ (NH)	0·995 Å	1.0614 Å	$\delta_1=\delta_2$ (HNC)	119·8°	121·24°
			$\delta_3=\delta_4$ (HNC)	118·1°	123·86°

*Ref. Worsham *et al* (1957)

Table 3. Symmetry force constants (in mdyn Å^{-1}) of urea.

Force constant	CNDO/ Force	Solid phase	Solutio	Force constant	CNDO/ Force	Solid phase	Solution
			A_1 Species				
$F_{1,1}$	26·894	10·774	12·102	$F_{3,4}$	0·054	0·086	0.056
1,2	3·171	3·061	3·154	3,5	0·040	0·005	0·026
1,3	−0·038	−0·133	−0·076	3,6	0·147	0·006	0·001
1,4	−0·002	−0·048	−0·012	3,7	0·000	0·000	0·000
1,5	−0·488	−0·226	−0·384	4,4	14·648	6·328	6·617
1,6	−0·052	−0·052	−0·004	4,5	0·104	0·014	0·019
1,7	−0·035	−0·004	−0·037	4,6	−0·005	−0·042	−0·001
2,2	21·602	7·795	7·311	4,7	0·292	0·025	0·022
2,3	0·657	0·358	0·493	5,5	0·957	1·469	1·261
2,4	−0·009	−0·005	−0·001	5,6	−0·046	−0·014	−0·113
2,5	0·356	0·567	0·269	5,7	0·115	0·014	0·005
2,6	−0·355	−0·271	−0·258	6,6	0·552	0·480	0·531
2,7	−0·002	−0·002	−0·046	6,7	0·006	0·035	0·006
3,3	14·968	6·490	6·614	7,7	0·546	0·624	0·670
			B_2 species				
10,10	19·079	6·797	6·332	12,12	14·647	6·359	6·626
10,11	0·584	0·474	0·446	12,13	−0·067	−0·002	−0·006
10,12	−0·013	−0·029	−0·015	12,14	−0·006	−0·025	−0·007
10,13	0·588	0·723	0·625	12,15	0·267	0·018	0·009
10,14	−0·263	−0·307	−0·175	13,13	0·955	1·320	1·305
10,15	−0·069	−0·108	−0·111	13,14	−0·025	−0·002	−0·003
11,11	14·976	6·491	6·614	13,15	−0·076	−0·184	−0·108
11,12	0·049	0·032	0.033	14,14	0·540	0·439	0·521
11,13	0·056	0·072	0.076	14,15	0·014	0·152	0·044
11,14	0·158	0·002	0.011	15,15	0·520	0·590	0·595
11,15	0·006	0·001	0.001				

Paralleda (1971) assigned the band at ~1055 cm^{-1} to B_2 species of NH_2 rocking mode and the band at ~1155 cm^{-1} to the corresponding A_1 type vibration. On the basis of the polarized infrared spectra, Yamaguchi *et al* (1957) preferred to assign the higher frequency band to both A_1 and B_2 NH_2 rocking modes. The bands at ~1001 cm^{-1} and at ~887 cm^{-1} in the case of urea-D_4 were assigned to A_1 and B_2 species of ND_2 rockings respectively. Considering the product rule, Duncan (1971) supported the original assignments of Stewart (1957) to NH_2 rocking modes and placed the B_2 ND_2 rocking of urea-D_4 at 850 cm^{-1}. Hadzi *et al* (1976) pointed out that in their calculations, out of the two frequency assignments to B_2 NH_2 rocking modes 1055 cm^{-1} and 1156 cm^{-1}, the lower frequency yielded no satisfactory agreement between the observed and the calculated frequencies. Besides this, as the lower frequency band was missing in the spectrum of dissolved urea, these authors pointed out that the frequency shift of ~100 cm^{-1} on going to solution phase would be unusually large for this mode. Therefore they supported the assignments of Yamaguchi *et al* (1957) to NH_2 and ND_2 rocking vibrations. However, they preferred to assign the band at ~850 cm^{-1} in the case of urea-D_4 to A_1 type CN stretching which was also originally assigned to the 887 cm^{-1} band by Yamaguchi *et al* (1957). In our calcu-

lations, we have followed Hadzi's assignments in the case of urea-D_4; but in the case of urea we consider the $\sim$1055 cm^{-1} band as belonging to B_2 NH_2 rocking mode assuming that this band might be very weak in the solution phase. It should not be ignored that the solvent accetonitrile is not completely transparent in this region and hence such an assumption is not out of place. Since this band was not reported by Hadzi *et al* (1976), we have adopted it from Arenas and Paralleda (1971) for the solid phase. A frequency shift similar to that of $\sim$1155 cm^{-1} band (A_1 species of NH_2 rocking mode) has been considered for this band in solution phase.

2.3. *Refinement procedure*

Refinements are performed on the symmetry force field for the planar vibrations both in the solid and the solution phases. Since the stretching force constants obtained from CNDO/Force method are very high, as Kanakavel (1976) suggested the initial force field is set up by taking the interaction and bending force constants obtained from the CNDO/Force calculations and the stretching force constants from the force field obtained by Duncan (1971) for urea. The experimental and calculated geometries shown in table 2 are employed to calculate the G matrices of urea and its isotopic analogues in the solid and solution phases respectively. The FPERT program of Schachtschneider (1964) is used to refine the force constants. The damped least square procedure, suggested by Adams and Churchill (1970) is employed to overcome the singularity of $J'WJ$ matrix which we often come across in the refinement calculations because of the strong correlations among several force constants.

The refinements of symmetry force fields belonging to A_1 and B_2 species are treated separately. Firstly, the diagonal force constants are refined and when the convergence is achieved, iterations are carried out over all the force constants until a best fit between the observed and the calculated frequencies is obtained. During the iterations the signs of the interaction force constants were kept unchanged, since in several cases the comparison with the experimental force fields proved that the signs

Table 4. Redundancy free internal valence force constants (in mdyn Å^{-1}) for urea*

Force constant	Solid phase	Solution	Force constant	Solid phase	Solution
$f_{1,1}$	10·774	12·102	$f_{3,9}$	−0·511	−0·442
$f_{1,2}$	2·165	2·230	$f_{4,4}$	6·475	6·662
$f_{1,4}$	−0·090	—	$f_{4,6}$	0·073	—
$f_{1,8}$	−0·226	−0·384	$f_{6,6}$	6·358	6·573
$f_{2,2}$	7·296	6·822	$f_{8,8}$	1·469	1·261
$f_{2,3}$	0·499	0·489	$f_{8,10}$	—	−0·080
$f_{2,4}$	0·282	0·326	$f_{9,9}$	1·320	1·305
$f_{2,6}$	0·306	0·338	$f_{9,12}$	−0·130	−0·076
$f_{2,8}$	0·401	0·190	$f_{9,13}$	0·130	0·076
$f_{2,9}$	0·511	0·442	$f_{10,10}$	0·459	0·526
$f_{2,10}$	−0·289	−0·216	$f_{10,12}$	0·093	—
$f_{2,12}$	−0·055	−0·079	$f_{10,13}$	−0·058	—
$f_{2,13}$	0·053	—	$f_{12,12}$	0·607	0·633

*The interaction force constants, not included in this table have insignificant values, usually below ± 0·05 mdyn Å^{-1}.

Table 5. Observed and calculated frequencies and potential energy distribution (PED) of (a) urea, (b) urea -D_4, (c) urea -$^{15}N_2$, (d) urea -$^{15}N_2D_4$ and (e) urea -^{18}O in the solid phase and in solution.

Obs. cm^{-1}	Calc. cm^{-1}	PED		Obs. cm^{-1}	Calc. cm^{-1}	PED	
(a)$(NH_2)_2CO$		Solid				Solution	
A_1 species:							
3449	3452·9	$f_{4,4}(75)$	$f_{6,6}(25)$	3503	3511·6	$f_{4,4}(62)$	$f_{6,6}(37)$
3347	3352·0	$f_{6,6}(75)$	$f_{4,4}(24)$	3390	3398·1	$f_{6,6}(63)$	$f_{4,4}(37)$
1687	1682·7	$f_{1,1}(43)$	$f_{1,10}(43)$	1695	1694·3	$f_{1,1}(97)$	
1606	1602·6	$f_{10,10}(54)$	$f_{1,1}(45)$	1614	1610·0	$f_{10,10}(99)$	
1157	1155·5	$f_{12,12}(61)$	$f_{1,1}(22)$	1167	1165·5	$f_{12,12}(59)$	$f_{1,1}(14)$
1005	991·1	$f_{2,2}(88)$	$f_{12,12}(13)$	969	966·4	$f_{2,2}(84)$	$f_{12,2}(18)$
560	558·7	$f_{8,8}(84)$		509	505·2	$f_{8,8}(87)$	
B_2 Species:							
3449	3454·4	$f_{4,4}(61)$	$f_{6,6}(39)$	3503	3512·6	$f_{4,4}(58)$	$f_{6,6}(41)$
3447	3353·9	$f_{6,6}(60)$	$f_{4,4}(39)$	3390	3398·8	$f_{6,6}(58)$	$f_{4,4}(42)$
1632	1629·7	$f_{10,10}(75)$	$f_{2,2}(18)$	1614	1614·1	$f_{10,10}(92)$	
1467	1467·6	$f_{2,2}(74)$	$f_{9,9}(19)$	1419	1420·7	$f_{2,2}(80)$	$f_{9,9}(21)$
1055	1059·3	$f_{12,12}(75)$	$f_{2,2}(26)$	1066 (assumed)	1067.3	$f_{12,12}(83)$	$f_{2,2}(16)$
574	575·1	$f_{9,9}(89)$	$f_{12,12}(29)$	576	577.4	$f_{9,9}(83)$	$f_{12,12}(15)$
(b) $(ND_2)_2CO$		Solid				Solution	
A_1 Species:							
2591	2580·9	$f_{4,4}(63)$	$f_{6,6}(36)$	2623	2615·6	$f_{4,4}(56)$	$f_{6,6}(43)$
2437	2425·8	$f_{6,6}(64)$	$f_{4,4}(35)$	2474	2464·5	$f_{6,6}(57)$	$f_{4,4}(43)$
1621	1622·2	$f_{1,1}(94)$		1678	1678·4	$f_{1,1}(102)$	
1249	1254·5	$f_{10,10}(81)$	$f_{2,2}(30)$	1239	1243·2	$f_{10,10}(74)$	$f_{2,2}(27)$
1002	1008·0	$f_{12,12}(27)$	$f_{2,2}(27)$	991	993·1	$f_{12,12}(29)$	$f_{10,10}(23)$
		$f_{1,1}(11)$	$f_{8,8}(11)$			$f_{2,2}(18)$	
853	859·8	$f_{2,2}(41)$	$f_{12,12}(40)$	833	837·9	$f_{2,2}(50)$	$f_{12,12}(38)$
474	788·2	$f_{8,8}(74)$	$f_{12,12}(23)$	429	434·0	$f_{8,8}(79)$	$f_{12,12}(18)$
B_2 Species:							
2591	2579·1	$f_{4,4}(56)$	$f_{6,6}(44)$	2623	2613·4	$f_{4,4}(55)$	$f_{6,6}(45)$
2437	2420.7	$f_{6,6}(56)$	$f_{4,4}(44)$	2474	2463·5	$f_{6,6}(55)$	$f_{4,4}(45)$
1485	1483·1	$f_{2,2}(97)$		1448	1444·0	$f_{2,2}(96)$	
1157	1153·7	$f_{10,10}(87)$		1152	1151·0	$f_{10,10}(90)$	
888	885.6	$f_{12,12}(59)$	$f_{2,2}(18)$	862	861·0	$f_{12,12}(70)$	$f_{2,2}(12)$
508	506·1	$f_{9,9}(76)$	$f_{12,12}(52)$	522	521·6	$f_{9,9}(73)$	$f_{12,12}(32)$
(c) $(^{15}NH_2)_2CO$		Solid				Solution	
A_1 Species:							
3442	3441·2	$f_{4,4}(77)$	$f_{6,6}(23)$	3496	3500·1	$f_{4,4}(63)$	$f_{6,6}(37)$
3343	3347·8	$f_{6,6}(77)$	$f_{4,4}(23)$	3387	3393·5	$f_{6,6}(64)$	$f_{4,4}(36)$
1679	1678·9	$f_{1,1}(45)$	$f_{10,10}(41)$	1692	1693·2	$f_{1,1}(97)$	
1604	1598·7	$f_{10,10}(56)$	$f_{1,1}(43)$	1604	1604·1	$f_{10,10}(99)$	
1151	1147·5	$f_{12,12}(63)$	$f_{1,1}(22)$	1160	1156·6	$f_{12,12}(61)$	$f_{1,1}(14)$
984	977·9	$f_{2,2}(89)$	$f_{12,12}(11)$	950	946·9	$f_{2,2}(85)$	$f_{12,12}(16)$
552	550·5	$f_{8,8}(84)$		501	497·3	$f_{8,8}(87)$	

(c) $(^{15}ND_2)_2CO$	Solid			Solution			
B_2 Species:							
3442	3442·4	$f_{4,4}(61)$	$f_{6,6}(39)$	3496	3501·2	$f_{4,4}(59)$	$f_{6,6}(41)$
3343	3350·4	$f_{6,6}(61)$	$f_{4,4}(39)$	3387	3394·3	$f_{6,6}(59)$	$f_{4,4}(41)$
1621	1621·4	$f_{10,10}(77)$	$f_{2,2}(14)$	1604	1605·6	$f_{10,10}(94)$	
1462	1462·1	$f_{2,2}(76)$	$f_{9,9}(20)$	1414	1414·1	$f_{2,2}(81)$	$f_{9,9}(21)$
1046	1045·9	$f_{12,12}(76)$	$f_{2,2}(26)$	1056 (assumed)	1056·6	$f_{12,12}(83)$	$f_{2,2}(16)$
568	570·3	$f_{9,9}(89)$	$f_{12,12}(28)$	571	571·6	$f_{9,9}(83)$	$f_{12,12}(15)$

(d) $(^{15}ND_2)_2CO$	Solid			Solution			
A_1 Species:							
2573	2563·3	$f_{4,4}(64)$	$f_{6,6}(35)$	2609	2599·0	$f_{4,4}(57)$	$f_{6,6}(42)$
2427	2419·4	$f_{6,6}(65)$	$f_{4,4}(34)$	2468	2457·2	$f_{6,6}(57)$	$f_{4,4}(43)$
1617	1621·3	$f_{1,1}(95)$		1679	1677·8	$f_{1,1}(102)$	
1237	1239·3	$f_{10,10}(84)$	$f_{2,2}(25)$	1227	1228·3	$f_{10,10}(78)$	$f_{2,2}(24)$
994	999·4	$f_{2,2}(29)$	$f_{12,12}(28)$	983	986·7	$f_{12,12}(30)$	$f_{10,10}(21)$
		$f_{8,8}(11)$	$f_{1,1}(10)$			$f_{2,2}(19)$	$f_{8,8}(11)$
843	847·3	$f_{2,2}(44)$	$f_{12,12}(40)$	822	824·2	$f_{2,2}(52)$	$f_{12,12}(39)$
471	474·3	$f_{8,8}(75)$	$f_{12,12}(21)$	426	430·2	$f_{8,8}(79)$	$f_{12,12}(17)$
B_2 Species:							
2573	2562·1	$f_{4,4}(56)$	$f_{6,6}(44)$	2609	2597·4	$f_{4,4}(55)$	$f_{6,6}(44)$
2427	2415·0	$f_{6,6}(56)$	$f_{4,4}(43)$	2468	2456·3	$f_{6,6}(55)$	$f_{4,4}(45)$
1472	1470·4	$f_{2,2}(97)$		1428	1430·5	$f_{2,2}(96)$	
1154	1152·1	$f_{10,10}(88)$		1150	1148·8	$f_{10,10}(91)$	
874	871·7	$f_{12,12}(59)$	$f_{2,2}(18)$	851	850·0	$f_{12,12}(71)$	$f_{2,2}(12)$
507	504·3	$f_{9,9}(76)$	$f_{12,12}(51)$	521	518·7	$f_{9,9}(73)$	$f_{12,12}(31)$

(e) $(NH_2)_2C^{18}O$	Solid			Solid			
A_1 Species:				B_2 Species:			
3442	3452·9	$f_{4,4}(75)$	$f_{6,6}(25)$	3442	3454·4	$f_{4,4}(61)$	$f_{6,6}(39)$
3348	3352·0	$f_{6,6}(75)$	$f_{4,4}(24)$	3348	3353·9	$f_{6,6}(60)$	$f_{4,4}(39)$
1673	1672·3	$f_{10,10}(57)$	$f_{1,1}(29)$	1624	1629·6	$f_{10,10}(75)$	$f_{2,2}(18)$
1587	1590·4	$f_{1,1}(54)$	$f_{10,10}(40)$	1464	1467·0	$f_{2,2}(75)$	$f_{9,9}(19)$
1140	1137·6	$f_{12,12}(61)$	$f_{1,1}(26)$	—	1057·6	$f_{12,12}(76)$	$f_{2,2}(25)$
—	996·3	$f_{2,2}(90)$	$f_{12,12}(10)$	—	562·0	$f_{9,9}(89)$	$f_{12,12}(28)$
558	552·9	$f_{8,8}(84)$					

of the interaction force constants obtained from CNDO/Force calculations were well predicted. The final* symmetry force fields for the solid phase and the solution phase are included in table 3.

*The CO stretching/CN_2 symmetric stretching interaction constant $F_{1,2}$ obtained from CNDO/Force method (3·171 mdyn Å^{-1}) is found to be higher than that reported by Duncan (1971) (2·507 mdyn Å^{-1}). We tried two initial force fields with $F_{1,2} = 3{\cdot}171$ mdyn Å^{-1} and 2·5 mdyn Å^{-1}. On carrying out the interactions the latter force field yielded a very low value (8·5 mdyn Å^{-1}) to the CO stretching force constant and the other force constants also changed abruptly. On the basis of these observations we decided to drop the latter force field for any further consideration.

A general force field is expressed (IUPAC 1977) in terms of $3N-6$ ($3N-5$ for linear molecules) basis coordinates which may be internal symmetry coordinates, local symmetry coordinates or any other most suitable to the problem, where N is the number of atoms in the molecule. The internal valence force constants cannot be obtained through simple transformation from the symmetry force constants, unless some assumptions are made on the symmetry force constants corresponding to the redundant symmetry coordinates. It is customary therefore, to transform the symmetry force field to the redundancy free internal valence force field. The redundancy free IVFF corresponding to the redundancy free internal valence coordinates of table 1 are summarized in table 4. The calculated and the observed frequencies for various isotopic species of urea and their PED in terms of redundancy free IVFF are shown in table 5.

2.4. *Discussion*

The symmetry force fields listed in table 3 can be considered as the first complete force fields for the in-plane vibrations of urea, since in all the previous works some interaction force constants or the others were constrained to zero. The CO stretching force constants obtained in our studies (table 4) are found to be less than those reported for formaldehyde (Duncan 1973) and carbonyl fluoride (Mallinson *et al* 1975) (~13·0 and ~14·8 mdyn Å^{-1} respectively). The CN stretching force constants are found to be higher than that in methylamine (~5·1 mdyn Å^{-1}) (Hirakawa *et al* 1972). These observations can be explained on the basis of the possible resonance forms of urea molecule leading to a decrease in the CO bond order and an increase in CN bond order. A higher value of CO stretch/CN stretch interaction constant $f_{1,2}$ (~2·2 mdyn Å^{-1}) can also be explained on the basis of resonance. A similar high value (2·267 mdyn Å^{-1}) has been reported for the corresponding interaction force constant in methylpropionamide by Usha Bai and Venkata Ramiah (1973). The CN_2 stretch/NH_2 stretch interaction force constants $F_{2,3}$ and $F_{10,11}$ are found to have significant values ranging between 0·36 to 0·47 mdyn Å^{-1}, which were originally constrained to zero by Duncan (1971). It is not surprising that these interaction constants should be non-zero as CN and NH bonds are quite close. This is also reflected in the redundancy free IVFF. The force constants $f_{2,4}$ and $f_{2,6}$ corresponding to neighbouring CN and NH interaction have values ranging between 0·28 to 0·34 mdyn Å^{-1}.

As can be noticed in table 5, in contrast to Hadzi *et al* (1976), with our final force field, we obtain an excellent reproduction of the frequencies by assuming 1055 cm^{-1} band in the place of B_2 NH_2 rocking mode. This band is found to have 75% contribution from NH_2 rocking in the solid phase, while, 83% contribution in the solution phase. Stewart (1957) assigned the band at ~1686 cm^{-1} of solid urea to CO stretching and the band at ~1602 cm^{-1} to A_1 NH_2 bending modes. The normal coordinate analysis of Yamaguchi *et al* (1957) and Duncan (1971) show that the 1602 cm^{-1} band has a greater contribution from CO stretching than the 1686 cm^{-1} band. On the basis of their calculations, Hadzi *et al* (1976) concluded that in the solid urea the CO stretching mode is spread over the 1687 cm^{-1} (37%) and 1606 cm^{-1} (20%) bands. In dissolved urea the CO stretching is located at the higher frequency with 72% contribution. Our calculations show that the bands at 1687 cm^{-1} and 1606 cm^{-1} of

urea in the solid phase have a very strong mixing between CO stretching and NH_2 bending modes. The bands at 1695 cm^{-1} and 1614 cm^{-1} of dissolved urea seem to represent pure CO stretching (96%) and NH_2 bending (99%) respectively. A similar trend is observed in the case of urea-$^{15}N_2$ and urea-^{18}O also.

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References

Adams D M and Churchill R G 1970 *J. Chem. Soc.* A 697
Arenas J and Paralleda R 1971 *J. Mol. Struct.* **10** 253
Duncan J L 1971 *Spectrochim. Acta* **A27** 1197
Duncan J L 1973 *Chem. Phys. Lett.* **23** 597
Hadzi D, Kidric J, Khezevic Z V and Barlic B 1976 *Spectrochim. Acta* **A32** 693
Hirakawa A Y, Tsuboi M and Shimanouchi T 1972 *J. Chem. Phys.* **57** 1236
IUPAC 1977 *Appl. Spectrosc.* **31** 569
Kanakavel M, Chandrasekhar J, Subramanian S and Singh S 1976 *Theoret. Chim. Acta* **43** 185
Kanakavel M 1976 *Vibrational analysis and evaluation of force fields of polyatomic molecules*, Ph.D. Thesis, Indian Institute of Technology, Madras
Laulicht I, Pinchas S, Petreanu E and Samuel D 1965 *Spectrochim. Acta* **21** 1487
Mallinson P D, McKean D C, Holloway J H and Oxton I A 1975 *Spectrochim. Acta* **A31** 143
Mills I M 1963 *Spectrochim. Acta* **19** 1585
Pople J A and Beveridge D L 1970 Approximate Molecular Orbital Theory, (New York: McGraw-Hill)
Pulay P and Torok F 1973 *Mol. Phys.* **25** 1153
Schactschneider J H 1964 Technical Reports No. 57-65, Shell Development Co., California.
Shteinberg B Ya, Mushkim Yu I and Finkelshtein A I 1972 *Opt. Spectrosc.* **33** 589
Stewart J E 1957 *J. Chem. Phys.* **26** 248
Usha Bai P and Venkata Ramiah K 1973 *Indian J. Pure. Appl. Phys.* **11** 171
Waldron R D and Badger R M 1957 *J. Chem. Phys.* **26** 255
Worsham J E, Levy H A and Peterson S W 1957 *Acta Crystallogr.* **10** 319
Yamaguchi A, Miyazawa T, Shimanouchi T and Mizushima S 1957 *Spectrochim. Acta* **10** 170