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Force field calculations for formamide, acetamide, and urea using the CNDO/force method^{a)}

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CNDO/force calculations are employed to evaluate theoretical force fields for formamide, acetamide, and urea. Since the stretching force constants are overestimated and other diagonal as well as off-diagonal force constants are predicted reasonably well by these calculations, the initial force fields are set up by transferring the stretching force constants from structurally related molecules and by including the other force constants from the CNDO force field. The experimental force fields are obtained for the condensed phases as well as monomeric species using vibrational frequencies by carrying out least squares refinement. Frequencies of HCONH₂, HCOND₂, DCONH₂, DCOND₂, HCONHD, and DCONHD for formamide, CH₃CONH₂, CH₃COND₂, CD₃CONH₂, CD₃COND₂, CH₃CONHD, CD₃CONHD, and CH₃CO ¹⁵NH₂ for acetamide, and NH₂CONH₂, ND₂COND₂, ¹⁵NH₂CO ¹⁵NH₂, ¹⁵ND₂CO ¹⁵ND₂, and NH₂C ¹⁸ONH₂ for urea are employed in refining the force fields. The force fields obtained are found to be reliable on the basis of the force constants for chemically related molecules, frequency fits, and potential energy distributions.

I. INTRODUCTION

Several authors have reported the vibrational spectra for the condensed phases and monomeric species of formamide,¹⁻¹⁰ acetamide,¹¹⁻¹⁷ and urea.¹⁷⁻²⁵ In the early normal coordinate analyses of formamide performed by Miyazawa²⁶ and Thomas,²⁷ point mass models were employed. Itoh and Shimanouchi¹ and Suzuki² evaluated the Urey-Bradley force fields (UBFF's). In the above calculations, vibrational frequencies of the condensed phases were used. Considering the frequencies of the isolated species, Tanaka and Machida⁸ recently evaluated a modified Urey-Bradley force field, whereas Gardiner *et al.*²⁸ reported a simple valence force field. For acetamide all of the force fields reported in the literature¹¹⁻¹⁴ were based on the solid phase frequencies. Lagrange¹¹ reported a valence force field (VFF) while other authors¹²⁻¹⁴ obtained Urey-Bradley force fields. Force field studies based on non-planar amide structure were also reported for formamide²⁹ and acetamide.³⁰ In the case of urea, the solid phase frequencies were employed by Yamaguchi *et al.*²⁰ and by Duncan³¹ in evaluating, respectively, Urey-Bradley and symmetry force fields. Considering the frequencies of the solid as well as solution phases, Hadzi *et al.*²⁵ recently obtained UBFF's of urea.

In the conventional least squares method of force field refinement using vibrational frequencies, the initial force field is set up generally by transferring the force constants from structurally related molecules. The final force fields resulting from these calculations are often found to depend on the initial force fields. The diagonal force constants may reasonably be transferred

among structurally related molecules but such a transfer is difficult in the case of off-diagonal force constants, since they depend greatly on the nature of molecules. The interaction force constants also play an important role in determining the total force field as well as the potential energy distributions (PED) of a molecule. Hence, it is essential to consider reliable values for these force constants while constructing the initial force field.

It was found in the previous studies³²⁻³⁷ that CNDO MO calculations employing the gradient method (also called CNDO/force method) predict in general the signs of interaction force constants correctly. The magnitudes of bending, stretch-bend, and bend-bend force constants obtained from these calculations are close to the experimental values whereas those of stretch-stretch interaction constants are about 50% higher than the experimental values. The stretching force constants are exaggerated by a factor of 2-3.5. *Ab initio* calculations are proved to yield good results³⁸ but require a lot of computation time, especially for large molecules. It is proposed that for large molecules reasonable force fields can be obtained using the following procedure: CNDO/force calculations are performed for the molecule under consideration and the CNDO force field is obtained. The stretch-stretch interaction force constants of the CNDO force field are scaled down using a scale factor. The initial force field is constructed by considering the scaled values of stretch-stretch interaction constants whereas the other interaction and bending force constants are taken from the CNDO force field. The stretching force constants are transferred from structurally related molecules. The initial force field thus constructed is refined further using the vibrational frequencies of normal and isotopic species. Reasonable constraints on the force fields are imposed when the number of force constants to be evaluated is greater than the number of frequencies used.

As indicated above, mostly UBFF's have been reported in the literature for amides and urea. Internal or symmetry force fields were seldom con-

^{a)}See AIP document No. PAPS JCPSA-15-860-17 for 17 pages of Tables (VI to XI). Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, N. Y. 10017. The price is \$1.50 for each microfiche (98 pages), or or \$5 for photocopies of up to 30 pages with \$0.15 for each additional page over 30 pages. Airmail is additional. Make checks payable to the American Institute of Physics.

sidered and most of the force fields reported were evaluated using the frequencies of the condensed phases. In the present study, a systematic evaluation of the redundancy-free internal valence force fields (RFIVFF's) is carried out for formamide, acetamide, and urea³⁹ using the procedure suggested above. The force fields are obtained for the monomers as well as for the condensed phases and the variations in the force fields are analyzed.

II. COMPUTATIONAL DETAILS AND RESULTS

A modified version³⁵ of the computer program CNINDO of Pople and Beveridge⁴⁰ is used for CNDO/force calculations. In the optimization of molecular geometry, Pulay's steepest descent method³² is employed. For each molecule, considering the CNDO/2 wave functions and an arbitrary geometry, the forces acting on all the atoms are computed by analytically differentiating the total energy with respect to the nuclear coordinates. Each atom is then shifted along the direction of the force acting on it by a small distance, viz., 0.01–0.001 Å. With this new configuration the forces are again calculated and the nuclei are allowed to relax towards the equilibrium geometry. This process is repeated until "consistency" in the molecular geometry is achieved. The Cartesian forces are then calculated for the configurations representing different modes of vibrations by distorting the molecule from the optimized reference geometry in the positive and negative directions of internal (or symmetry) coordinates by an amount of $\frac{1}{2}\Delta R_i$. The distortions used are 0.01 Å, 1°, and 2°, respectively, for stretching, bending, and torsional coordinates. The Cartesian forces are then transformed into internal forces (ϕ_i) using appropriate transformations.^{32,35} The force constants are derived using the numerical differentiation of the internal forces with respect to the internal coordinates given by

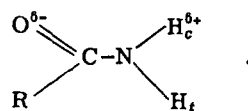
$$F_{ij} = -\Delta\phi_i/\Delta R_j \quad \text{and} \quad F_{ji} = -\Delta\phi_j/\Delta R_i. \quad (1)$$

The values obtained for F_{ij} and F_{ji} are very close to each other. Whenever a small, though insignificant, difference is found in these values, the average of these two values is taken as F_{ij} as well as F_{ji} in order to ensure a symmetric force constant matrix. In the present work the redundancy-free internal valence force fields are evaluated as per the recommendations of IUPAC,⁴¹ which pointed out that the force constants corresponding to the coordinates that are expressed by redundant conditions cannot be determined.

The initial force fields are set up according to the procedure given in Sec. I. The stretch-stretch interaction force constants of the CNDO force field are scaled by a factor of 0.65 while constructing the initial force fields. This optimum scale factor was obtained by comparing the stretch-stretch interaction force constants of CNDO force fields for H_2CO and F_2CO with those of most reliable experimental force fields.^{42,43} Pulay *et al.*^{33,44} expressed empirically the scale factor for the interaction force constant F_{ij} as the geometric mean of the scale factors for the diagonal force constants F_{ii} and F_{jj} . This requires that one calculate separate scale factors for all F_{ij} values. It is felt that a simple scale

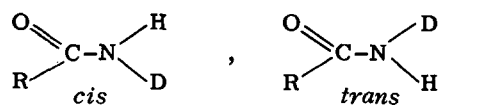
factor as given in the present work is satisfactory particularly when the force field is further refined using vibrational frequencies. Schachtschneider's FPERT program⁴⁴ which employs Wilson's GF matrix method⁴⁵ is used to carry out the force field refinements after including the damped least squares routines. The absolute weighting factors⁴⁶ are employed during refinement. Two types of force fields are evaluated in this work. In the first type termed FF1, the signs of interaction constants are kept unaltered during the iterations, since it is found that the signs predicted by CNDO/force calculations are generally reliable. However, while calculating the second type of force field called FF2, no such constraint is imposed on the signs of interaction constants in order that the frequency fit may be improved further. All the calculations have been performed using an IBM 370/155 computer.

A number of investigators concluded that the formamide molecule is planar, based on microwave spectroscopic^{47,48} electron diffraction⁴⁸ and *ab initio*⁴⁹ studies. Earlier reports by Costain and Dowling⁵⁰ suggested slight nonplanarity for this molecule. *Ab initio* calculations^{49,51} predict a planar structure for acetamide also. In the present calculations the planar structure is employed for the amide group. In Table I the optimized geometries obtained from CNDO/force calculations are compared with the other theoretical⁴⁹ and experimental^{48,52–56} geometries reported earlier. The results of the CNDO/force calculations show that the distance of the NH bond which is *cis* with respect to the C=O bonds is longer than that of the NH bond which is *trans*, and the bond angle CNH_{cis} is smaller than the angle CNH_{trans} . These findings are also in accordance with the *ab initio* results.⁴⁹ This may be attributed to the nonbonded electrostatic attraction between the carbonyl oxygen and amide hydrogen (H_c) atoms, since they have opposite polarities as shown below:



The redundancy-free internal coordinates considered are given in Table II in terms of the internal coordinates represented in Fig. 1. The CNDO force fields obtained are summarized in Tables III–V for formamide, acetamide, and urea.

For monomeric formamide, the vibrational frequencies of HCONH_2 , HCOND_2 , *cis*- HCONHD , *trans*- HCONHD , and their C-deuterated derivatives in CHCl_3 solutions reported by Tanaka and Machida⁸ are used. The ^{15}N -isotopic shifts quoted in Ref. 8 from the work of Parellada and Arenas⁷ are also considered in deriving the force constants after appropriately converting them into absolute frequencies. The *cis* and *trans* structures of amides are as represented below^{8,12}:



In the case of the condensed phase calculations of forma-

TABLE I. Calculated and experimental geometries (distances in Å and angles in deg).

Bond distance or bond angle	Formamide				Acetamide			
	Calc. ^a CNDO	Calc. ^b <i>ab initio</i>	Expt. ^{c,d}	Expt. ^{e,f}	Calc. ^a CNDO	Calc. ^b <i>ab initio</i>	Expt. ^{c,g}	Expt. ^{h,i}
r_{CO}	1.265	1.215	1.212	1.219	1.278	1.218	1.220	1.260
$r_{CH_{al}}$	1.120	1.083	1.125	1.098
r_{CN}	1.360	1.356	1.368	1.352	1.373	1.364	1.380	1.334
r_{CC}	1.453	1.519	1.519	1.505
r_{NH_c}	1.061	0.995	1.027	1.0016	1.062	0.994	1.022	...
r_{NH_t}	1.059	0.952	1.027	1.0015	1.061	0.992	1.022	...
$r_{CH_{me}}$	1.118	1.081	1.124	...
$\angle OCN$	123.3	125.1	125.0	124.7	117.8	122.6	122.0	123.2
$\angle NCH$	115.6	112.5	112.7	112.7
$\angle NCC$	118.3	113.8	115.1	...
$\angle CCO$	123.9	119.6
$\angle NCN$
$\angle CNH_c$	120.7	119.3	118.7	118.5	122.6	118.6	118.5	...
$\angle CNH_t$	123.8	...	119.7	120.0	123.8	122.0	120	...
$\angle HNH$	115.5	118.9	...	121.6	114.2
$\angle CCH_{me}$	111.3	109.7	109.8	...

Bond distance or bond angle	Urea		
	Calc. ^a CNDO	Expt. ^{j,k}	Expt. ^{h,l}
r_{CO}	1.283	1.243	1.276
$r_{CH_{al}}$
r_{CN}	1.370	1.351	1.326
r_{CC}
r_{NH_c}	1.061	0.995	0.88
r_{NH_t}	1.060	0.995	0.68
$r_{CH_{me}}$
$\angle CCN$	121.8	121.5	121
$\angle NCH$
$\angle NCC$
$\angle CCO$
$\angle NCN$	116.5	117.0	118
$\angle CNH_c$	121.2	119.8	119
$\angle CNH_t$	123.9	118.1	109
$\angle HNH$	114.9
$\angle CCH_{me}$

H_{al} —aldehydic hydrogen. H_c and H_t refer, respectively, to the amide hydrogen atoms which are *cis* and *trans* with respect to the carbonyl bond. H_{me} —methyl group hydrogen.

^aThis work.

^bReference 49.

^cElectron diffraction results.

^dReference 52.

^eMicrowave spectroscopic results.

^fReference 48.

^gReference 53.

^hX-ray diffraction results.

ⁱReference 54.

^jNeutron diffraction results.

^kReference 55.

^lReference 56.

mide, the IR frequencies reported by Suzuki² for liquid $HCONH_2$, $DONH_2$, and their ND_2 derivatives and those reported by Smith *et al.*³ for liquid $HCONHD$ and $DCONHD$ are used. Based on Raman depolarization studies, Bukowska⁵⁷ concluded recently that the bands at 3410 and 3330 cm^{-1} (and not 3330 and 3190 cm^{-1}) should be assigned to asymmetric and symmetric NH_2 stretching modes, respectively. According to him, the 3190 cm^{-1} band corresponds to the overtone of NH_2 symmetric bending mode. Bukowska's assignment is followed in this work.

For monomeric acetamide, the solution phase IR

data^{6,14,15} of CH_3CONH_2 , $CH_3CO^{15}NH_2$, and CH_3COND_2 are used in deriving the force constants of A' species. For A'' vibrations the argon matrix isolation IR frequencies of CH_3CONH_2 reported by King¹⁷ are employed. Uno *et al.*¹² measured the IR spectra of the orthorhombic crystal forms of CH_3CONH_2 , CH_3COND_2 , *cis*- CH_3CONHD , *trans*- CH_3CONHD , and their $-CD_3$ derivatives, and assigned the bands. Lagrange¹¹ reported the IR and Raman spectra of the same crystal modification of CH_3CONH_2 , CH_3COND_2 , CD_3CONH_2 , and CD_3COND_2 . The assignments of Lagrange are found to be different from those of Uno *et al.* Lagrange assigned the band at 832 cm^{-1} of CD_3CONH_2 to the NH_2 torsional mode

TABLE II. Redundancy-free internal coordinates.

Coordinate		Description
Formamide		
In plane:		
(1) $\nu_{\text{C=O}}$	$=R$	C=O stretch
(2) $\nu_{\text{C-H}}$	$=d$	C-H stretch
(3) $\nu_{\text{C-N}}$	$=L$	C-N stretch
(4) $\nu_s(\text{NH}_2)$	$=2^{-1/2} (r_1 + r_2)$	NH ₂ stretch
(5) $\nu_a(\text{NH}_2)$	$=2^{-1/2} (r_1 - r_2)$	NH ₂ stretch
(6) δ_{HCN}	$=6^{-1/2} (2\delta_1 - \delta_2 - \delta_3)$	HCN deformation
(7) ρ_{CO}	$=2^{-1/2} (\delta_2 - \delta_3)$	C=O rock
(8) $\delta(\text{NH}_2)$	$=6^{-1/2} (2\theta - \mu_1 - \mu_2)$	NH ₂ deformation
(9) $\rho(\text{NH}_2)$	$=2^{-1/2} (\mu_1 - \mu_2)$	NH ₂ rock
Out of plane:		
(10) γ_{CO}	$=\phi$	C=O wag
(11) $\tau(\text{NH}_2)$	$=\frac{1}{2}(\tau_1 + \tau_2 + \tau_3 + \tau_4)$	NH ₂ torsion
(12) $\omega(\text{NH}_2)$	$=\frac{1}{2}(\tau_1 - \tau_2 + \tau_3 - \tau_4)$	NH ₂ wag
Acetamide		
In plane:		
(1) $\nu_{\text{C=O}}$	$=R$	C=O stretch
(2) $\nu_{\text{C-C}}$	$=D$	C-C stretch
(3) $\nu_s(\text{CH}_3)$	$=3^{-1/2} (r_1 + r_2 + r_3)$	CH ₃ stretch
(4) $\nu_a(\text{CH}_3)$	$=6^{-1/2} (2r_1 - r_2 - r_3)$	CH ₃ stretch
(5) $\nu_{\text{C-N}}$	$=L$	C-N stretch
(6) $\nu_s(\text{NH}_2)$	$=2^{-1/2} (d_1 + d_2)$	NH ₂ stretch
(7) $\nu_a(\text{NH}_2)$	$=2^{-1/2} (d_1 - d_2)$	NH ₂ stretch
(8) δ_{CCN}	$=6^{-1/2} (2\delta_1 - \delta_2 - \delta_3)$	CCN deformation
(9) ρ_{CO}	$=2^{-1/2} (\delta_2 - \delta_3)$	C=O rock
(10) $\delta_s(\text{CH}_3)^a$	$=[3(1+b^2)]^{-1/2} [b(\alpha_1 + \alpha_2 + \alpha_3) - (\beta_1 + \beta_2 + \beta_3)]$	
(11) $\delta_s'(\text{CH}_3)$	$=6^{-1/2} (2\alpha_1 - \alpha_2 - \alpha_3)$	CH ₃ deformation
(12) ρ_{CH_3}	$=6^{-1/2} (2\beta_1 - \beta_2 - \beta_3)$	CH ₃ rock
(13) $\delta(\text{NH}_2)$	$=6^{-1/2} (2\theta - \mu_1 - \mu_2)$	NH ₂ deformation
(14) $\rho(\text{NH}_2)$	$=2^{-1/2} (\mu_1 - \mu_2)$	NH ₂ rock
Out of plane:		
(15) $\delta_a(\text{CH}_3)$	$=2^{-1/2} (\alpha_2 - \alpha_3)$	CH ₃ deformation
(16) ρ_{CH_3}	$=2^{-1/2} (\beta_2 - \beta_3)$	CH ₃ rock
(17) γ_{CO}	$=\phi$	C=O wag
(18) $\tau(\text{NH}_2)$	$=(\tau_1 + \tau_2 + \tau_3 + \tau_4)$	NH ₂ torsion
(19) $\omega(\text{NH}_2)$	$=(\tau_1 - \tau_2 + \tau_3 - \tau_4)$	NH ₂ wag
Urea		
In plane:		
(1) $\nu_{\text{C=O}}$	$=R$	C=O stretch
(2) $\nu_{\text{C-N}}$	$=L_1$	C-N stretch
(3) $\nu_{\text{C-N}}$	$=L_2$	C-N stretch
(4) $\nu_s(\text{NH}_2)$	$=2^{-1/2} (r_1 + r_2)$	NH ₂ stretch
(5) $\nu_s(\text{NH}_2)$	$=2^{-1/2} (r_3 + r_4)$	NH ₂ stretch
(6) $\nu_a(\text{NH}_2)$	$=2^{-1/2} (r_1 - r_2)$	NH ₂ stretch
(7) $\nu_a(\text{NH}_2)$	$=2^{-1/2} (r_3 - r_4)$	NH ₂ stretch
(8) δ_{NCN}	$=6^{-1/2} (2\delta_1 - \delta_2 - \delta_3)$	NCN deformation
(9) ρ_{CO}	$=2^{-1/2} (\delta_2 - \delta_3)$	C=O rock
(10) $\delta(\text{NH}_2)$	$=6^{-1/2} (2\theta_1 - \mu_1 - \mu_2)$	NH ₂ deformation
(11) $\delta(\text{NH}_2)$	$=6^{-1/2} (2\theta_2 - \mu_3 - \mu_4)$	NH ₂ deformation
(12) $\rho(\text{NH}_2)$	$=2^{-1/2} (\mu_1 - \mu_2)$	NH ₂ rock
(13) $\rho(\text{NH}_2)$	$=2^{-1/2} (\mu_3 - \mu_4)$	NH ₂ rock
Out of plane (B_1 species):		
(14) γ_{CO}	$=\phi$	C=O wag
(15) $\tau(\text{NH}_2)$	$=8^{-1/2} (\tau_1 + \tau_2 - \tau_3 - \tau_4 + \tau_1' + \tau_2' - \tau_3' - \tau_4')$	NH ₂ torsion
(16) $\omega(\text{NH}_2)$	$=8^{-1/2} (\tau_1 - \tau_2 - \tau_3 + \tau_4 + \tau_1' - \tau_2' - \tau_3' + \tau_4')$	NH ₂ wag

$$^a b = -3 \sin \beta \cos \beta / \sin \alpha.$$

TABLE III. Force fields of formamide.^a

Force constant	Theor. CNDO	Expt. (for monomer)		Expt. (for liquid)	
		FF1	FF2	FF1	FF2
F1, 1,	30.142	12.301	12.269	11.736	11.699
F1, 2	0.658	0.476	0.518	0.416	0.509
F1, 3	2.696	1.851	1.977	1.828	1.835
F1, 4	-0.057
F1, 6	-0.450	-0.564	-0.499	-0.567	-0.561
F1, 7	-0.180	-0.083	-0.148	-0.002	-0.044
F1, 8	-0.031
F1, 9	-0.029
F2, 2	11.448	4.562	4.578	4.561	4.507
F2, 3	0.551	0.411	0.460	0.142	0.306
F2, 6	0.174	0.007	0.036	0.010	0.021
F2, 7	0.279	0.073	0.205	0.000	-0.230
F2, 8	-0.020
F2, 9	0.043	0.018	-0.096	0.008	-0.109
F3, 3	20.786	7.166	6.939	7.235	7.247
F3, 4	0.674	0.403	0.555	0.412	0.482
F3, 5	0.037	0.039	0.051	0.014	0.020
F3, 7	-0.451	-0.241	-0.351	-0.323	-0.323
F3, 8	-0.329	-0.180	0.272	-0.173	-0.179
F3, 9	-0.046	-0.011	0.081	-0.004	0.084
F4, 4	15.028	6.716	6.718	6.378	6.385
F4, 8	0.150	0.010	-0.043	0.011	0.006
F4, 9	0.025
F5, 5	14.704	6.648	6.605	6.045	6.045
F5, 6	0.066	0.010	-0.101	0.008	-0.103
F5, 7	0.050	0.002	-0.034	0.005	-0.003
F5, 9	0.281	0.019	-0.012	0.010	0.023
F6, 6	0.771	0.907	0.818	0.967	0.953
F6, 7	0.072	0.294	0.238	0.406	0.395
F6, 8	-0.019	-0.019	0.035	-0.000	0.004
F6, 9	0.081	0.048	0.101	0.027	0.027
F7, 7	0.892	0.770	0.871	1.005	1.028
F7, 8	0.020	0.003	0.085	0.004	0.016
F7, 9	0.064	0.118	0.135	0.144	0.143
F8, 8	0.538	0.450	0.469	0.473	0.474
F9, 9	0.513	0.544	0.557	0.627	0.630
F10, 10	0.583	0.565			
F10, 11	-0.035	-0.038			
F11, 11	0.057	0.0659			
F12, 12	0.096	0.0150			

^aUnits for force constants: stretch-stretch in $\text{mdyn } \text{\AA}^{-1}$, stretch-bend in mdyn rad^{-1} , and bend-bend in $\text{mdyn } \text{\AA} \text{ rad}^{-2}$.

(A''), whereas this band was assigned by Uno *et al.* to a mixed mode of CC stretching and CD_3 in-plane rocking vibrations (A'). The bands at about 1040 cm^{-1} in the spectra of CD_3CONH_2 and CD_3COND_2 were assigned to $A'\delta_s(\text{CD}_3)$ and $A''\delta_a(\text{CD}_3)$ modes by Uno *et al.* and Lagrange, respectively. A satisfactory fit is obtained in this work by considering the frequencies and assignments reported by Uno *et al.*¹²

Hadzi *et al.*²⁵ reported the IR spectra for the solid phase and acetonitrile solutions of NH_2CONH_2 , ND_2COND_2 , and their (^{15}N)₂ derivatives. The spectra of NH_2CONH_2 , ND_2COND_2 , and $^{15}\text{NH}_2\text{CO } ^{15}\text{NH}_2$ were reported earlier by other authors¹⁸⁻²¹ also. There are some controversies in assigning the bands of urea. Stewart¹⁸ and Arenas and Parellada²¹ assigned the band at 1055 cm^{-1} in NH_2CONH_2 to the B_2 NH_2 rocking mode and the band at 1155 cm^{-1} to the corresponding A_1 type vibra-

tion. Based on polarized IR spectra, Yamaguchi *et al.*²⁰ preferred to assign the latter band to both the A_1 and B_2 NH_2 rocking modes. The bands at 1001 and 997 cm^{-1} in ND_2COND_2 were assigned by Yamaguchi *et al.* to ND_2 rocking modes of A_1 and B_2 species, respectively. Considering the product rule, Duncan³¹ supported the original assignment of Steward to NH_2 rocking modes, and assigned the B_2 type ND_2 rocking mode of ND_2COND_2 to the band around 850 cm^{-1} . Hadzi *et al.*²⁵ pointed out, however, that the 1055 cm^{-1} band was missing in the acetonitrile solution spectrum of urea and also that they could not obtain a satisfactory fit with the assignment of this band to the B_2 NH_2 rocking mode. As a result of this, these authors supported Yamaguchi's²⁰ assignments for NH_2CONH_2 . However, a different assignment was proposed for ND_2COND_2 . Yamaguchi *et al.*²⁰ assigned the 887 cm^{-1} band in ND_2COND_2 to the A_1 CN stretching mode, apart from its assignment to the B_2

TABLE IV. Force fields of acetamide.^a

Force constant	Theor. CNDO	Expt. (for monomer) FF1	Expt. (for solid)	
			FF1	FF2
F1, 1	28.729	12.023	10.779	10.785
F1, 2	1.266	0.9 ^b	0.909	0.900
F1, 5	2.623	1.8 ^b	1.775	1.788
F1, 8	-0.505	-0.658	-0.514	-0.516
F1, 9	-0.092	-0.074	-0.091	-0.081
F1, 10	-0.058	-0.09 ^b	-0.051	-0.013
F1, 12	-0.084	-0.212	-0.033	-0.040
F1, 13	-0.038
F1, 14	-0.031
F2, 2	15.940	4.431	4.503	4.508
F2, 3	0.572	0.4 ^b	0.458	0.490
F2, 5	0.898	0.6 ^b	0.437	0.468
F2, 8	0.221	0.264	0.190	0.252
F2, 9	0.400	0.5 ^b	0.411	0.386
F2, 10	-0.415	-0.3 ^b	-0.295	-0.286
F2, 12	0.086	0.08 ^b	0.002	0.013
F2, 13	-0.036
F2, 14	0.040
F3, 3	12.247	5.161	5.016	4.987
F3, 9	0.039
F3, 10	0.196	0.091	0.012	-0.085
F4, 4	11.765	4.906	4.785	4.758
F4, 8	0.060	0.047	0.041	0.037
F4, 9	-0.028
F4, 11	-0.259	-0.05 ^b	-0.002	-0.034
F4, 12	0.281	0.05 ^b	0.030	0.025
F5, 5	20.030	6.812	7.054	7.072
F5, 6	0.656	0.45 ^b	0.564	0.604
F5, 8	0.140	0.201	0.147	0.124
F5, 9	-0.452	-0.353	-0.209	-0.216
F5, 10	-0.059	-0.05 ^b	-0.037	-0.030
F5, 11	0.021
F5, 12	0.040
F5, 13	-0.319	-0.18 ^b	-0.151	-0.156
F5, 14	-0.046
F6, 6	14.926	6.714	5.832	5.887
F6, 8	0.028
F6, 13	0.162
F7, 7	14.598	6.663	6.059	6.059
F7, 8	0.082
F7, 9	0.065
F7, 14	0.275
F8, 8	0.814	1.273	1.251	1.231
F8, 9	0.096	0.113	0.074	0.045
F8, 10	-0.023
F8, 11	0.027
F8, 12	0.103	0.150	0.073	0.084
F8, 13	-0.023
F8, 14	0.082	0.071	0.047	0.050
F9, 9	0.996	1.147	1.283	1.300
F9, 10	-0.041	-0.052	-0.016	0.001
F9, 11	-0.012
F9, 12	-0.054	-0.071	-0.172	-0.141
F9, 13	0.019
F9, 14	0.068	0.155	0.028	0.036
F10, 10	0.726	0.598	0.542	0.544
F10, 11	-0.018
F10, 12	-0.033	-0.03 ^b	-0.010	0.035
F11, 11	0.749	0.541	0.520	0.505
F11, 12	-0.065	-0.02 ^b	-0.012	0.020
F12, 12	0.775	0.648	0.649	0.668
F12, 14	0.017
F13, 13	0.554	0.478	0.490	0.491
F14, 14	0.545	0.553	0.661	0.656
F15, 15		0.555		

TABLE IV (Continued)

Force constant	Theor. CNDO	Expt. (for monomer) FF1	Expt. (for solid)	
			FF1	FF2
F16, 16		0.525		
F16, 17		-0.1 ^b		
F17, 17		0.713		
F18, 18		0.059		
F19, 19		0.0139		

^aAs in Table III.^bConstrained force constant values.

ND₂ rocking mode, whereas Hadzi *et al.*²⁵ assigned the band at 850 cm⁻¹ to the A₁ CN stretching mode. In this work the assignments of Stewart¹⁸ and Hadzi *et al.*,²⁵ respectively, for NH₂CONH₂ and ND₂COND₂ are considered. The frequencies for NH₂CONH₂, ¹⁵NH₂CO¹⁵NH₂, and their fully deuterated analogs in the solid phase and in the acetonitrile solutions are taken from the work of Hadzi *et al.*²⁵ The frequencies of solid NH₂C¹⁸ONH₂ are considered from Ref. 22. Contrary to Hadzi *et al.*, a satisfactory fit is obtained in this work by considering the band around 1055 cm⁻¹ for the B₂ NH₂ rocking mode. A frequency shift similar to that of the band at 1155 cm⁻¹ (A₁ NH₂ rocking mode) on going from the solid phase to the solution phase is assumed for the 1055 cm⁻¹ band (B₂ NH₂ rocking mode) while performing the calculations for the monomers. For B₁ vibrations of urea, the fre-

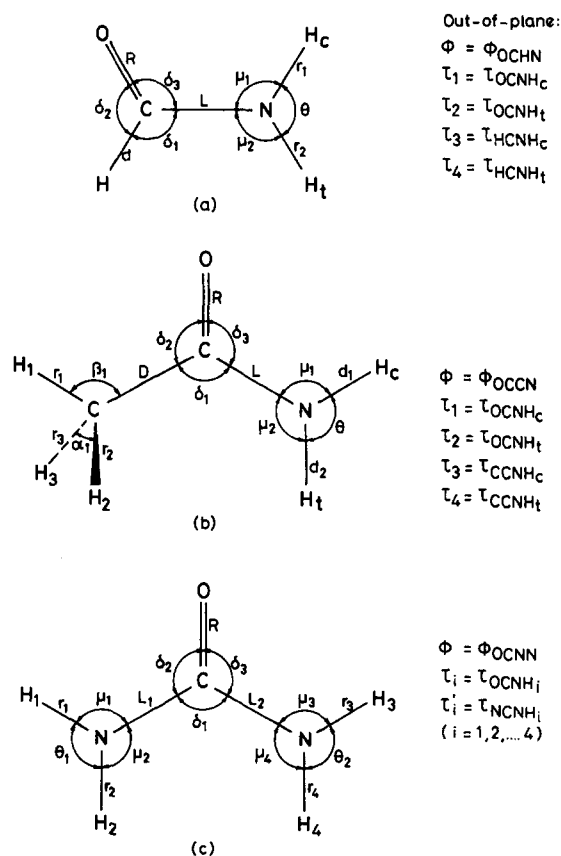


FIG. 1. Internal coordinates for (a) formamide, (b) acetamide, and (c) urea.

TABLE V. Force fields of urea.^a

Force constant	Theor. CNDO	Expt. (for monomer)		Expt. (for solid)	
		FF1	FF2	FF1	FF2
F1, 1	26.880	11.667	11.637	10.333	10.298
F1, 2	2.232	1.823	1.743	1.714	1.688
F1, 8	-0.486	-0.643	-0.586	-0.525	-0.506
F1, 10	-0.037	-0.018	0.000	-0.001	0.026
F1, 12	-0.024
F2, 2	20.333	6.744	6.846	6.982	7.078
F2, 3	1.268	0.847	0.916	0.914	0.903
F2, 4	0.623	0.169	0.281	0.330	0.388
F2, 8	0.248	0.242	0.318	0.294	0.272
F2, 9	0.416	0.356	0.423	0.393	0.434
F2, 10	-0.309	-0.212	-0.196	-0.218	-0.256
F2, 11	-0.045	-0.022	-0.030	-0.003	0.041
F2, 12	-0.035	-0.103	-0.092	-0.006	-0.024
F2, 13	0.034	0.014	-0.082	0.015	-0.049
F4, 4	14.957	6.635	6.571	6.475	6.493
F4, 6	0.049
F4, 8	0.028
F4, 9	0.041	0.080	0.043	0.043	0.040
F4, 10	0.152	0.002	-0.177	0.011	0.049
F6, 6	14.634	6.563	6.570	6.337	6.400
F6, 8	0.075	0.030	-0.003	0.011	0.019
F6, 9	-0.049	-0.001	0.041	-0.006	-0.007
F6, 12	0.279	0.008	0.049	0.012	0.145
F6, 13	0.013
F8, 8	0.958	1.315	1.208	1.623	1.512
F8, 10	-0.032	-0.046	-0.038	-0.039	-0.018
F8, 12	0.081	0.085	0.040	0.079	0.039
F9, 9	0.960	1.301	1.232	1.332	1.267
F9, 10	-0.015	-0.054	-0.048	-0.005	-0.036
F9, 12	-0.050	-0.105	-0.100	-0.152	-0.143
F10, 10	0.546	0.459	0.467	0.458	0.461
F10, 12	0.010
F12, 12	0.533	0.552	0.586	0.598	0.619
F12, 13	0.013
F14, 14		0.691			
F15, 15		0.059			
F16, 16		0.0101			

^aAs in Table III.

quencies are taken from Refs. 17 and 18. The band at 227 cm^{-1} in the argon matrix isolation spectrum¹⁷ of NH_2CONH_2 is assigned to the NH_2 wagging mode of the monomer in comparison with the spectrum of formamide monomer.⁸

The G matrices are constructed using the experimental geometries given in Table I. For formamide and acetamide monomers, the geometries derived from microwave spectroscopic⁴⁸ and electron diffraction⁵³ studies, respectively, are employed. For the condensed phase calculations, the structural parameters reported by Hamilton⁵⁴ and Ladell⁵⁸ are used for acetamide and formamide, respectively; the NH and CH bond distances are assumed to be 1.02 and 1.08 Å, respectively, and tetrahedral angles are considered around the methyl C atom whereas the angles around the N atom are assumed to be 120° . The structural parameters derived by Worsham *et al.*⁵⁵ from neutron diffraction analysis are employed for the geometries of the condensed phase and the monomer of urea.

Formamide belongs to C_s symmetry and the 12 normal

modes can be divided into $9A' + 3A''$ vibrations. In the case of A' species, 31 significant force constants considered are refined using 61 vibrational frequencies for the monomer and 63 frequencies for the liquid phase. For A'' species four force constants considered are refined using six frequencies of the monomer. Considering the C_s symmetry of acetamide, the 21 normal vibrations are grouped as $14A' + 7A''$. For the A' species of acetamide a 43 parameter experimental force field is considered. In the case of the monomer, 28 parameters are adjusted using 32 frequencies. The mathematical constraints imposed on this force field are based on the results obtained for the other molecules considered in the earlier⁵⁹ and present studies. For the A'' species a six parameter force field is considered. Using five out-of-plane frequencies for matrix isolated CH_3CONH_2 , five force constants are adjusted. The only off-diagonal force constant considered $F16, 17$, corresponding to the interaction $\gamma_{\text{CO}}/\rho_1(\text{CH}_3)$, is kept fixed at $-0.1\text{ mdyn Å rad}^{-2}$ because similar values were obtained for the corresponding force constants in acetaldehyde and acetone.⁵⁹ Based on the C_{2v} symmetry of urea, the 18

normal modes are grouped as $7A_1 + 6B_2 + 2A_2 + 3B_1$. Force fields containing 28 parameters are evaluated for the in-plane vibrations considering all 13 modes ($7A_1 + 6B_2$) together. For the monomer 52 frequencies are used in the refinement whereas 62 frequencies are considered for the solid phase. Of the five out-of-plane vibrations ($2A_2 + 3B_1$), the two modes belonging to A_2 species are infrared inactive. Considering the three frequencies of B_1 species of NH_2CONH_2 , a symmetry force field having only the diagonal force constants is obtained. The force fields for formamide, acetamide, and urea are given in Tables III, IV, and V, respectively. For acetamide monomer, the force fields FF1 and FF2 are found to be essentially the same and hence the FF2 is not listed in Table IV. The calculated and observed frequencies for the three molecules and their isotopic substituted species are summarized in Tables VI–XI along with PED, which have been deposited with PAPS.

III. DISCUSSION

Between the force fields FF1 and FF2 only few force constants differ in sign and these force constants are found to have in general very small magnitudes. For formamide a few force constants evaluated using *ab initio* calculations were reported by Fogarasi *et al.*⁴⁹ and Ottersen and Jensen.⁶⁰ In the present work, the force constants for CO stretching (F_{CO}) and CN stretching (F_{CN}) modes of formamide monomer are estimated to be on the order of 12.3 and 7 mdyn \AA^{-1} , respectively. These values are comparable to the corresponding *ab initio* estimates⁶⁰ (13.3 and 8 mdyn \AA^{-1} , respectively). *Ab initio* calculations are known to overestimate the stretching force constants slightly.³⁸ On this ground, the values obtained in this work are reasonable. The experimental value obtained presently for $-\text{NH}_2$ torsional force constant ($F_{11, 11} = 0.066$ mdyn $\text{\AA} \text{rad}^{-2}$) is also close to the *ab initio* value⁴⁹ of 0.076 mdyn $\text{\AA} \text{rad}^{-2}$.

The carbonyl stretching force constants in all the three molecules (formamide, acetamide, and urea) are less than that in formaldehyde (12.9 mdyn \AA^{-1})⁴³ whereas the CN stretching force constants are higher than that in methylamine (5.1 mdyn \AA^{-1}).⁶¹ This can be explained on the basis of the strong π -electron delocalization present in amides leading to a decrease in the CO bond order and an increase in the CN bond order. The inductive effect of the $-\text{NH}_2$ group would increase the force constant value of F_{CO} . However, the net decrease in the F_{CO} value due to $-\text{NH}_2$ substitution suggests that the influence of the resonance effect on F_{CO} outweighs that of the inductive effect. The substituent $-\text{CH}_3$ is also known to decrease the value of F_{CO} because of its inductive and hyperconjugative effects.⁵⁹ The lower force constant value for F_{CO} in urea in comparison to that in formamide is accounted for by the presence of two $-\text{NH}_2$ groups in the former. The force constant F_{CN} in urea is also found to be smaller than that in formamide. Probably, the two $-\text{NH}_2$ groups in urea compete with each other in making their lone pair of electrons available for the delocalization with the carbonyl π bond, thereby mutually decreasing the CN bond order slightly.

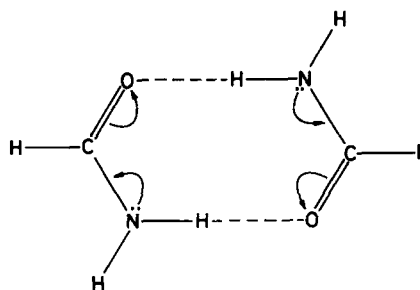


FIG. 2. Structure of formamide dimer.

The presence of a considerable amount of π -electron delocalization in amides is also reflected in the CO/CN interaction force constants. These force constants have very high positive values, which is similar to the conclusion drawn by Duncan³¹ for urea. The CO/CC interaction force constant in acetamide is also found to be a significant positive quantity but it is smaller than the CO/CN interaction constants. A similar trend is noticed in the force constants for the CN/CC interaction force constant of acetamide and CN/CN interaction force constants of urea. In all three molecules under consideration, the force constants corresponding to $-\text{NH}_2$ group vibrations do not differ considerably. The force constants of methyl group vibrations in acetamide are comparable to those in acetaldehyde and acetone.⁵⁹ The interaction force constants between the CN stretching and NH_2 symmetric stretching modes of amides are found to have significant values. A similar high value (0.474 mdyn \AA^{-1}) was noticed for the corresponding force constant in methylamide.⁶¹ In the previous studies, for acetamide¹¹ and urea³¹ these interaction force constants were assumed to be zero.

The changes in the force fields on going from the monomers to the condensed phase are similar in all three molecules considered. The significant decrease in CO and NH_2 stretching force constants is due to the strong intermolecular hydrogen bonding interactions, between the carbonyl oxygen and amide hydrogen atoms, which are present in the condensed phase. The force constant values for F_{CN} are slightly higher in the case of the condensed phase than those in the case of monomers. A parallel result was obtained by *ab initio* calculations also.⁶⁰ A value of 8.7 mdyn \AA^{-1} was obtained for formamide dimer while a value of 8.0 mdyn \AA^{-1} was reported for the monomer. Because of the hydrogen bonding arising due to the electrostatic attraction between the carbonyl oxygen of one molecule with the amide hydrogen of the other molecule, the resonance delocalization of the lone pair of electrons from the N atom is much more pronounced in the dimer or in the condensed phase, thus strengthening the CN bond which is reflected in the force constant F_{CN} . This is illustrated in Fig. 2. The NH_2 rocking force constant increases on going from the monomer to the condensed phase; however, the NH_2 symmetric bending force constant is not affected significantly. It is also found that in general the force constants corresponding to the skeletal deformation modes have higher values in the

condensed phase compared to those in the monomeric species.

The vibrational frequencies are reproduced equally well by FF1 and FF2 in all the cases. In general, the PED's are in agreement with the proposed assignments. Tentative band assignments for HCONHD and DCONHD in the liquid phase were proposed by Smith and Thompson.³ On the basis of the PED obtained in the present studies, the assignments for these species should be slightly revised which are, however, consistent with the related species of formamide and acetamide. In all isotopic species of monomeric formamide the CN stretching and skeletal deformation modes also contribute reasonably to the CO stretching frequencies. A similar observation is also made for the monomers of N-deuterated derivatives of acetamide and urea. In the parent species of urea and acetamide monomers, the carbonyl stretching frequencies have little contributions from other modes. In the case of solid urea, the CO stretching and NH₂ bending modes couple with each other strongly for the amide I and amide II bands at 1687 and 1606 cm⁻¹, respectively. The larger contribution for the 1687 cm⁻¹ band is, however, from the CO stretching mode whereas for the 1600 cm⁻¹ band it is from the NH₂ symmetric bending mode. The CN stretching mode also contributes slightly to both the bands mentioned above. In the condensed phase of formamide and acetamide, though such couplings are present, they are less pronounced. In the monomers of all three molecules, the bands around 1600 cm⁻¹ represent almost pure NH₂ symmetric bending modes.

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