Force Field and Mean Amplitudes of Vibration of $(NH_2)_2CX$ Compounds (X = O, S, Se)

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Normal coordinate analysis of urea, thiourea and selenourea was performed on the basis of the general valence force field; Wilson's FG matrix method has been used. The final force fields were obtained through an iterative selfconsistent method. The vibrational assignment for these molecules is discussed. Calculated mean amplitudes of vibration for the urea series and their deuterated derivatives are reported.

Introduction

The urea, thiourea and selenourea are of some considerable interest in organic chemistry as the simplest diamides. These molecules are also interesting in inorganic chemistry because they are capable of forming transition metal complexes.

Recently the IR spectra of solid and in CH_3CN dissolved normal urea and thiourea, thier ^{15}N and ^{2}H isotopic species, and of solid selenourea and selenourea-D_4 have been reported by Hadži et al. [1]. These authors have also calculated the Urey-Bradley force fields for the planar vibrations of the urea series. However, a number of points about the assignments of characteristic frequencies are still controversial [2]. Hence a reinvestigation of the force fields of urea, thiourea and selenourea, free from the limitations of the Urey-Bradley method used in the previous study, was considered necessary. For this purpose the iterative selfconsistent method [3] was used. The reliability of the force constant results given by this method has been tested in series of simple polyatomic molecules [4].

Calculations

The diagonal values of the $F^{(0)}$ matrix for urea, which are necessary to initiate the iterative calculation are obtained from the following equation:

$$F_{ii}^{(0)} = \lambda_i / G_{ii}\,, \qquad (1)$$

where $\lambda_i = (\omega_i/1303.16)^2$ and ω_i is the i^{th} experimental vibration frequency (1). The G matrix was constructed through the formulation given by Steele [8]. The geometrical parameters were taken from the literature [5–7].

The final F matrix for Urea was obtained after 17 iterative steps. The compliance matrix, F^{-1} [9, 10], was transferred to thiourea and selenourea to start the calculation of their force field. The modification of $F^{(0)}$ for these molecules appears only in the coordinate which involve the S and Se atoms. The diagonal terms of the final F and F^{-1} matrices of the urea series are shown in Table 1. The assignment of theoretical frequencies made using the L and PED [11] matrices is given in Tables 2 and 3.

The force fields developed were used to calculate the mean amplitudes of vibration (l) for different

Table 1. Force constants (mdyn/Å) and compliance constants (Å/mdyn).

	Urea		Thiourea		Selenourea	
f_{CX} [a]	10.74 [b]	0.10 [c]	4.73 [b]	0.23 [c]	4.87 [b]	0.23 [c]
f_{CN}	8.03	0.14	9.09	0.12	9.25	0.12
f_{NH}	6.32	0.16	5.83	0.17	5.96	0.17
f_{HnH}	0.83	1.53	0.76	1.68	0.73	1.77
f_{CNH}	1.35	0.95	1.36	0.95	1.32	1.00
f_{NCX} [a]	2.73	0.65	1.99	0.59	2.99	0.52

[a] X = O, S, Se.
[b] Principal internal force constants calculated in this work.
[c] Diagonal compliance constants.

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Table 2. In-plane fundamental frequencies (cm^{-1}) and assigments of hydrogenated molecules.

Urea	Exp.[a]	Calcd.[b]	Assign		
A_1	3449	3461	asym.	str.	NH
	3347	3349	sym.	str.	NH
	1687	1683		bend.	NH_2
	1632	1630		str.	CO
	1157	1152		rock.	NH_2
	1005	1001		str.	CN
	574	569		skel.	def.
B_2	3449	3462	asym.	str.	NH
	3347	3349	sym.	str.	NH
	1606	1603		bend.	NH_2
	1467	1464		str.	CN
	1157	1152		rock.	NH_2
	560	550		skel.	def.
Thiourea					
A_1	3365	3389	asym.	str.	NH
	3200	3209	sym.	str.	NH
	1615	1617		bend.	NH_2
	1414	1414		str.	CN
	1114	1119		rock.	NH_2
	729	732		str.	CS
	409	416		skel.	def.
B_2	3365	3391	asym.	str.	NH
	3200	3218	sym.	str.	NH
	1615	1618		bend.	NH_2
	1473	1475		str.	CN
	1084	1088		rock.	NH_2
	487	478		skel.	def.
Selenourea					
A_1	3320	3344	asym.	str.	NH
	3250	3238	sym.	str.	NH
	1605	1614		bend.	NH_2
	1393	1390		str.	CN
	1117	1114		rock.	NH_2
	640	639		str.	CSe
	382	384		skel.	def.
B_2	3320	3348	asym.	str..	NH
	3250	3245	sym.	str.	NH
	1595	1589		bend.	NH_2
	1576	1471		str.	CN
	1082	1082		rock.	NH_2
	475	469		skel.	def.

[a] From [1].
[b] Frequencies calculated in this work.

Table. 3. In-plane fundamental frequencies (cm^{-1}) and assignments of deuterated molecules.

Urea	Exp.[a]	Calcd.[b]	Assign.		
A_1	2591	2582	asym.	str.	ND
	2437	2435	sym.	str.	ND
	1621	1621		str.	CO
	1249	1252		bend.	ND_2
	1002	1005		str.	CN
	888	885		rock.	ND_2
	474	478		skel.	del.
B_2	2591	2581	asym.	str.	ND
	2437	2435	sym.	str.	ND
	1485	1487		str.	CN
	1157	1159		bend.	ND_2
	853	864		rock.	ND_2
	508	516		skel.	def.
Thiourea					
A_1	2540	2522	asym.	str.	ND
	2360	2353	sym.	str.	ND
	1381	1381		str.	CN
	1141	1147		bend.	ND_2
	916	911		rock.	ND_2
	669	665		str.	CS
	390	387		skel.	def.
B_2	2540	2520	asym.	str.	ND
	2360	2346	sym.	str.	ND
	1504	1499		str.	CN
	1189	1180		bend.	ND_2
	834	830		rock.	ND_2
	420	427		skel.	def.
Selenourea					
A_1	2520	2500	asym.	str.	ND
	2350	2359	sym.	str.	ND
	1358	1360		str.	CN
	1182	1175		bend.	ND_2
	910	911		rock.	ND_2
	550	551		str.	CSe
	358	357		skel.	def.
B_2	2520	2500	asym.	str.	ND
	2350	2353	sym.	str.	ND
	1520	1525		str.	CN
	1130	1134		bend.	ND_2
	818	818		rock.	ND_2
	415	419		skel.	def.

[a] From [1].
[b] Frequencies calculated in this work.

types of bonded and nonbonded interatomic distances of the molecules here considered. These values were carried out through the formulation given by Morino et al. [12]. The results obtained for the urea series and their deuterated derivatives at 298 K are collected in Table 4.

Table 4. Mean amplitudes of vibration (in Å) at 298 K for H_4 and D_4 urea series ([a] X = O, S, Se).

	Urea		*Thiourea*		*Selenourea*	
	H_4	D_4	H_4	D_4	H_4	D_4
[a] C—X	0.039	0.039	0.045	0.045	0.044	0.044
C—N	0.043	0.043	0.042	0.042	0.042	0.042
N—H	0.073	0.062	0.074	0.062	0.074	0.063
[a] X...N	0.052	0.052	0.062	0.062	0.059	0.059
N...N	0.055	0.055	0.055	0.055	0.055	0.055
C...H	0.094	0.082	0.094	0.083	0.093	0.082

Discussion

The correlation proposed in the present study for the force constant of the CN stretching in the urea series, is similar to that reported by Duncan and Aitken [13, 14] and also confirmed by a molecular orbital study of Ažman [15]. The large difference for F_{CN} between urea and the other molecules could be explained by the great number of S and Se electrons in comparison to oxigen.

The present assignment of the NH and ND stretching modes in the urea series, is in agrement with that proposed in the literature [1, 2, 13, 14, 16 – 19]. Concerning the controversy about the assignment of the A_1 and B_2, NH_2 rocking modes for urea-H_4, we have placed the band at 1157 cm^{-1} to both these vibrations, supporting the assignment reported by Yamaguchi et al. [19] and Hadži et al. [1]. For urea-D_4 we have assigned the B_2 species of the ND_2 rocking mode at 853 cm^{-1}. A similar assignment has been made by Duncan [13]. Hadži et al. [1] preferred to assign this band to A_1 type CN stretching, which was also originally assigned to the 887 cm^{-1} band by Yamaguchi et al. [19].

Another controversial point is in the assignment of the bands at 1686 cm^{-1} to CO stretching and A_1 NH_2 bending modes. Our calculations show that the lower frequency has a greater contribution from CO stretching than the higher one, supporting the assignment of Duncan [13] and Yamaguchi et al. [19].

In the case of thiourea-H_4, we have assigned the band at 1414 cm^{-1} to A_1 CN stretching and the band at 1084 cm^{-1} to A_1 NH_2 rocking mode.

For selenourea-H_4 we have ascribed the band at 640 cm^{-1} to CSe stretching mode. Additionally, the bands at 1393 cm^{-1} and 1082 cm^{-1} have been assigned in this work to A_1 CN stretching and A_1 NH_2 rocking modes, respectively. These results, as well as those pointed out for thiourea, are different from the corresponding assignments reported by Hadži et al. [1], but they are in accordance with the expected correlation for the series.

The calculated mean amplitudes of vibration for the CN and CX distances (X = 0, S and Se), do not change with isotopic substitution. The calculated shifts for the rest of the distances are consistent with the IR spectra variation of the deuterated forms.

Although no experimental data is available for comparison, the present computation confirms the characteristic values for the C = 0 mean amplitude in a carboxyl group, as Cyvin et al. [20] pointed out. The C – N mean amplitude calculated in this work is in concordance with that reported by Puranik et al. [16]. On the other hand, the l (N – H) value, is in well correspondence with that observed in gaseous NH_3 [21].

Conclusions

The urea, thiourea and selenourea molecules with their tetradeuterated forms have been restudied through a general valence force field determined by an iterative selfconsistent method. The vibration frequencies were assigned to the distinct normal modes using the normal vibration mode form matrix (L) and the potential energy distribution (PED).

The calculated mean amplitudes are correlative in the series and practically do not alter in spite of considerable changes in the force fields.

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