Vibrational Spectra and Assignments for the Fundamental Vibrations of Imidazolidine-2-thione and -2-selenone

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Infrared spectra of imidazolidine-2-thione (*N,N'*-ethylenethiourea, ETU) and its *N,N'*-deuterated (ETU-d_2) and *S*-methylthiouronium iodides have been recorded from 4000 to 30 cm^{-1}. Normal coordinate analyses of ETU and ETU-d_2 have been made for all the fundamental frequencies, employing a Urey-Bradley potential function supplemented with valence type constants for the out of plane modes of the planar skeleton. Raman frequencies of ETU from literature have been utilised. The results of the vibrational analyses are discussed in relation to the group frequencies in structurally related molecules and frequency shifts on deuteration and *S*-methylation. The normal coordinate treatment is also performed for the planar vibrations of imidazolidine-2-selenone (*N,N'*-ethyleneselenourea, ESU) to propose assignments for ESU and so also to support the assignments of ETU.

Imidazolidine-2-thione, commonly referred to as *N,N'*-ethylenethiourea (ETU), is of considerable importance as a ligand in transition metal chemistry. ETU is an interesting molecule as a simple symmetrically disubstituted cyclic thiourea, $\overline{\text{NH–CH}_2\text{–CH}_2\text{–NH–C=S}}$, which has a –NHCSNH– group constrained in a *cis-cis* position. It may be expected to exhibit vibrations characteristic of this grouping and a comparison of the vibrations of ETU with those of sym. *N,N'*-dimethylthiourea[1] may be of interest. Very recently, the normal coordinate calculations on *N,N'*-ethyleneurea (imidazolidin-2-one) have been published[2] and its extension to the analogous sulfur and selenium compounds is desirable. On these accounts, a knowledge of the normal coordinates of ETU and its seleno analogue would be valuable.

Previous assignments of the principal bands of ETU were based upon empirical criteria.[3–5] An approximate normal coordinate analysis of only the in-plane vibrations of ETU treating methylene groups as point masses has also been reported.[6] However, the vibrational assignments are not complete and many of the fundamentals are uncertain or unassigned. In order to obtain as complete a vibrational assignment of the fundamentals as possible, the infrared spectra of ETU as well as its *N,N'*-deuterated (ETU-d_2) and the *S*-methyl derivatives are studied. The Raman data from literature[4,7] are also made use of. The assignments are supported by accomplishing normal coordinate analyses of ETU and ETU-d_2 for all the fundamental vibrations. The coordinate treatment is also extended to the in-plane vibrations of imidazolidine-2-selenone (*N,N'*-ethyleneselenourea, ESU) with which it can profitably be compared since only the sulfur-involving frequencies of ETU are expected to vary principally in ESU.

Experimental

ETU was prepared and purified according to Allen *et al.*[8] mp 197—198 °C. The *N,N'*-deuterated compound (ETU-d_2) was obtained by repeated exchange reaction with heavy water. The *S*-methyl derivative of ETU was prepared by a standard procedure.[9]

Spectra. Infrared spectra of the solid samples were measured on a Carl-Zeiss UR10 spectrophotometer from 4000 to 400 cm^{-1} in Nujol mull and KBr pellet. The observed frequencies were calibrated with standard frequencies of polystyrene. Infrared spectra between 400 to 30 cm^{-1} were recorded on a Polytec FIR 30 Fourier transform spectrometer. The instrument was calibrated by means of water vapor frequencies. The Raman frequencies[7] of ETU and the infrared bands[5] of ESU are quoted from published spectra. The infrared spectra of ETU-d_0 and ETU-d_2 between 300 to 50 cm^{-1} are given in Fig. 1.

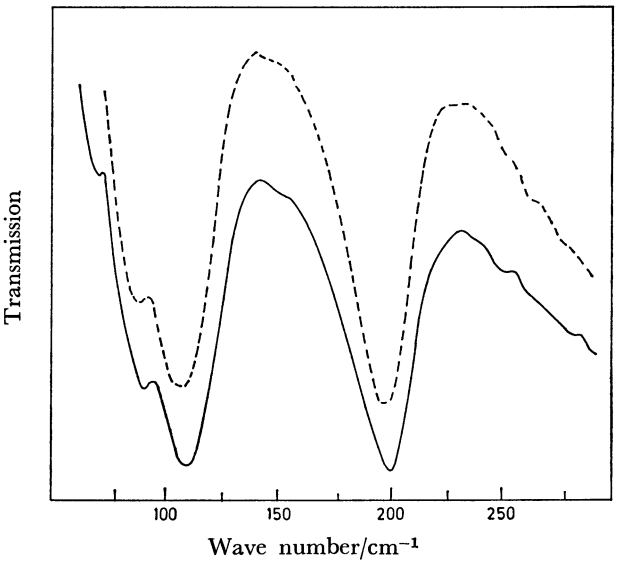

Fig. 1. Infrared spectra of ETU-d_0 (—) and ETU-d_2 (----).

Normal Coordinate Analysis

It is known by the X-ray crystal structure determination[10] that ETU has a C_{2v} symmetry. The 30 normal vibrations of ETU and ESU in the C_{2v} symmetry are classified into 19 in-plane ($10A_1$ and $9B_2$) and 11 out-of-plane ($5A_2$ and $6B_1$) modes of which the vibrations belonging to A_1, B_1, and B_2 species are infrared active and all are Raman active. The internal coordinates are depicted in Fig. 2. The out of plane vibrations of the planar ring are described in terms of the out of plane bending of the C–S and N–H groups and the torsional coordinates of the CN and C'N bonds.

TABLE 1. FORCE CONSTANTS OF IMIDAZOLIDINE-2-THIONE AND -2-SELENONE

Urey-Bradley constants[a] (mdyn/Å)								
	ETU	ESU		ETU	ESU		ETU	ESU
K(CX)	3.40	2.80	H(XCN)	0.09	0.08	F(XCN)	1.10	0.80
K(CN)	5.90	6.05	H(CNC)	0.40	0.36	F(CNC)	0.30	0.30
K(CN′)	3.10	3.00	H(NCN)	0.48	0.25	F(NCN)	0.68	0.72
K(CC)	2.95	2.95	H(NCC)	0.28	0.32	F(NCC)	0.45	0.45
K(CH)	4.40	4.40	H(HCH)	0.41	0.41	F(HCH)	0.06	0.06
K(NH)	5.30	5.30	H(HCC)	0.15	0.15	F(HCC)	0.50	0.50
			H(NC′H)	0.26	0.26	F(NC′H)	0.55	0.55
k(CH_2)	−0.016	−0.016	H(CNH)	0.28	0.27	F(CNH)	0.45	0.40
(mdyn·Å/rad²)			H(C′NH)	0.12	0.12	F(C′NH)	0.55	0.55
Valence constants (mdyn·Å/rad²)								
B_1	$f(\pi CS)$		0.080		A_2	$f(\pi NH)$		0.192
Species	$f(\pi NH)$		0.145		Species	$f(\tau$ ring)		0.144
	$f(\tau$ ring)		0.062					
	$f(\pi CS, \pi NH)$		−0.030					
	$f(\pi CS, \tau$ ring)		−0.020					

a) X=S or Se.

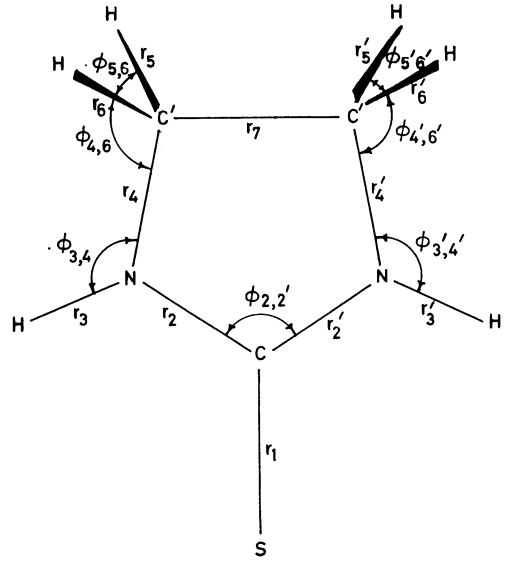

Fig. 2. Structure and internal coordinates of *N,N′*-ethylenethiourea.
Torsional coordinates are formed from the bond numbers.

The molecular parameters were taken from the X-ray structure data[10]—r(N–H) 0.99, r(C–H) 0.90, r(C–C) 1.536, r(C–N) 1.322, r(C′–N) 1.471 and r(C–S) 1.708 Å; ∠SCN 125.0°, ∠CNC 112.6°, ∠NCC 102.4°, ∠CNH 123.7°, ∠NC′H 104.07°, ∠CCH 109.6°, and ∠HCH 126.5°. For ESU, C=Se distance was assumed to be 1.86 Å and the rest of the structural parameters were the same as those of ETU. The symmetry coordinates used were constructed by standard procedures[11,12] and are not reported here for the sake of briefness.

The Wilson's GF matrix method[13] was employed. The numerical computations were performed with an IBM 360/44 Computer using programs similar to those of Shimanouchi.[14] Infrared frequencies were used for the calculations. Since the Urey-Bradley force (UBF) function has been successful in satisfactorily explaining the vibrational spectra of thioamides[15–18] and thioureas,[19,20] it was employed presently. For the out of plane A_2 and B_1 fundamentals, the Urey-Bradley force constants for the CH_2 groups, and the valence force constants for the out of plane deformations and torsional modes were used. The initial UBF constants were taken from succinonitrile[21] for the $-CH_2-CH_2-$ part and from *N*-methyl thioacetamide[15,16] (NMTA) for the –NHCSNH– part. The zeroth order calculated frequencies were close to the observed ones lending confidence to the assignments obtained. For the out-of-plane vibrations of the molecular skeleton, valence force constants were used and the initial values were taken from *N*-methylthiourea.[22] The force constants were refined by an iterative procedure and the final values of the force constants of ETU are presented in Table 1. The force constants of ETU were then transferred to ESU. In accord with the concept of selenation,[23] minimum modifications were effected in the force constants of ETU, particularly for those connected with the thioureide group to obtain a desired agreement between the calculated and observed frequencies for the in-plane fundamentals of ESU. The final values of the force constants of ESU are also given in Table 1.

Results and Discussion

Force Field. The agreement between the observed and calculated frequencies for both ETU and ETU-d_2 is good. The final values of the force constants of ETU seem appropriate and they are comparable with the corresponding ones in NMTA[15,16] and thioacetamide[15,17] (TAM) for the –NHCSNH– part and those from succinonitrile[21] for the $-CH_2-CH_2-$ part. These demonstrate the transferability of the UBF constants. For example, the C=S stretching constant of ETU (3.40 mdyn/Å) is similar to that of TAM[17] and NMTA[16] (3.40 and 3.45 mdyn/Å, respectively). Similarly, the C–N stretching constant of ETU (5.90

mdyn/Å) is also comparable with that of TAM and NMTA (5.70 mdyn/Å).

The agreement between the calculated and observed frequencies of ESU is good and the final values of the force constants of ESU differ very little from the transferred force constants of ETU. The C=Se stretching constant (2.80 mdyn/Å) is lower than the C=S stretching force constant of ETU (3.40 mdyn/Å), and the C–N constant of ESU (6.05 mdyn/Å) is slightly higher than that of ETU (5.90 mdyn/Å). A similar trend is noticed in the C–S and C–N force constants for thiourea and selenourea.[19] This indicates the increased contribution of the cannonical form $S^{-}-\overset{|}{C}=N^{+}<$ over the other structure, $S=\overset{|}{C}-N<$ in the selenium compound compared to the analogous sulfur compound.

Vibrational Assignments. Imidazolidine-2-thione: The observed and calculated fundamentals of ETU and ETU-d_2 are presented in Table 2 along with the assignments as derived from the potential energy distributions among the symmetry coordinates.

In-plane Vibrations: *Vibrations of the Methylene Groups*: *CH_2 Stretching and Bending.* There are two CH_2 stretching vibrations of ETU one each belonging to A_1 and B_2 species. A medium broad band at 2900 cm^{-1} has been attributed to both these modes. The CH_2 bending modes (ν_4 and ν_{14}) are assigned to the bands at 1470 and 1480 cm^{-1} (respectively). These are compatible with those of *N,N'*-ethyleneurea.[2]

CH_2 Wagging. The symmetric CH_2 wagging (A_1) is found as a mixed vibration contributing almost equally to the bands at 1286 and 1212 cm^{-1} whereas the asymmetric CH_2 wagging (B_2) may be assigned at 1312 cm^{-1}. The assignment of CH_2 wagging vibrations is similar to the corresponding modes in *N,N'*-ethyleneurea[2] at 1274 and 1207 cm^{-1}, in ethylene trithiocarbonate[24] at 1279 and 1248 cm^{-1}, and in thiazolidine[25] around 1320 and 1260 cm^{-1}.

Vibrations of the Thioureide Group: *NH Group Vibrations.* The symmetric and antisymmetric NH stretching modes (ν_1 and ν_{11}) are easily assigned to the broad bands centered at 3275 and 3250 cm^{-1}, which on deuteration are replaced by new bands at 2435 and 2400 cm^{-1}, respectively. In *N,N'*-ethyleneurea[2] both NH stretching vibrations are observed as a single strong band at 3285 cm^{-1}.

The symmetric NH bending (A_1) is found to be a mixed vibration contributing equally to the bands at 1528 and 1212 cm^{-1}. This assignment qualitatively agrees with the earlier ones of Klaboe,[4] and Mecke *et al.*[3] However, in *N,N'*-ethyleneurea, the corresponding mode is observed as a pure vibration at 1385 cm^{-1}. The asymmetric NH bending (B_2) is however found as a pure vibration at 1376 cm^{-1} and this assignment is similar to that of *N,N'*-ethyleneurea for a medium band at 1423 cm^{-1}. In ETU-d_2, the ND bending contributes to the bands at 860 and 892 cm^{-1} in the A_1 symmetry species whereas in the B_1 type the 927 cm^{-1} band originates from ND bending.

C–N and C=S Group Vibrations. The symmetric C–N stretching (A_1) coupled with NH bending is associated with the 1528 cm^{-1} band, whereas the asymmetric C–N stretching (B_2) is pure and is assigned at 1508 cm^{-1}. The CN stretching frequency (B_2) of ETU is about 50 cm^{-1} higher than the corresponding mode in *N,N'*-ethyleneurea as expected due to the increased C–N bond order. The infrared bands at 1508 and 1528 cm^{-1} show a pronounced shift towards higher frequencies and are observed at 1557 and 1570 cm^{-1} in the *S*-methylated ETU, the shift being explained by the increased double bond character of the CN bond following the methylation of the sulfur atom.

The nature of the C=S stretching mode of ETU is interesting. The C=S stretching coordinate is distributed principally among two vibrations giving rise to the strong bands in the infrared at 516 and 925 cm^{-1}, a major proportion of 42% for the 516 cm^{-1} and a lesser proportion of 26% for the 925 cm^{-1} band. In support of this assignment, very strong bands are observed in the Raman[4,7] at 927 and 513 cm^{-1}. The assignment of the 516 cm^{-1} band qualitatively agrees with the recent one of Verani[5] but differs from that of Klaboe,[4] and Mecke *et al.*,[7] who have assigned the C=S stretching frequency around 1200 cm^{-1}.

The attribution of the 516 cm^{-1} band to the C=S stretching mode is further supported from the infrared spectra of ESU and the *S*-methyl derivative of ETU. On *S*-methylation, which diminishes the double bond character of the C=S bond, the 516 cm^{-1} band of ETU shows a pronounced red shift and is found in the spectrum of the *S*-methyl derivative at 477 cm^{-1}. The 516 cm^{-1} band of ETU is replaced in the spectrum of ESU by a band at a much lower wave number, 357 cm^{-1}, thus confirming its assignment. In the metal complexes of ETU, increase in the C–N stretching band and decrease in the C–S stretching band (at 516 cm^{-1}), similar to that on *S*-methylation but of smaller magnitude, are observed.[25,26]

The C=S bending may be assigned at 343 cm^{-1}. This frequency is in between the corresponding frequency in NMTA[15,16] at 370 cm^{-1} and in thiazolidine-2-thione[28] at 292 cm^{-1}. In support of this assignment, the 345 cm^{-1} band of ETU is replaced in ESU by a new band at a lower frequency, 280 cm^{-1}.

Ring Vibrations. There are two ring deformation vibrations. The ring deformation belonging to the A_1 species is coupled and contributes chiefly to the bands at 925 and 516 cm^{-1}. The ring deformation belonging to the B_2 representation, on the other hand, is associated with the 678 cm^{-1} band. The latter assignment differs from that of Klaboe,[4] and Devillanova and Verani[5] who have assigned it to an NH out-of-plane bending. The assignment of the 678 cm^{-1} band to a ring deformation mode is comparable with the 703 cm^{-1} band of *N,N'*-ethyleneurea[2] and with similar assignments made for other five membered heterocyclic compounds. For instance, a ring deformation mode has been assigned in 2,5-pyrrolidinedithione[29] at 649 cm^{-1} and in thiazolidines[25,28] near 675 cm^{-1}. It is interesting to note that the 678 cm^{-1} band of ETU almost completely vanishes on *N*-deuteration. However, there is a new weak band at 645 cm^{-1} in the infrared spectrum of ETU-d_2 corresponding to the 678 cm^{-1} absorption of ETU as expected from the computed frequencies of ETU-d_2 and confirming its assignment to a ring deformation mode.

TABLE 2. OBSERVED AND CALCULATED FUNDAMENTALS (in cm^{-1}) AND ASSIGNMENTS FOR IMIDAZOLIDINE-2-THIONE

ETU-d_2		ETU-d_0			
		Obsd		Calcd	Assignment[a] (PED[b])/%)
Obsd	Calcd	Raman	IR		
A_1 species					
2435	2390	3293	3275	3268	νNH(100)
2880	2896	2900	2900	2896	νCH_2(99)
1465	1476	1520	1528	1528	νCN(37), δNH(36)
1445	1458	1473	1470	1463	δCH_2(89)
1280	1274	1286	1286	1282	$w CH_2$(40), νCC(20)
860	861	1213	1212	1225	$w CH_2$(49), δNH(35)
1200	1146	1106	1120	1118	νCC(42), νCN(17)
1022	1031	1000	1008	1008	νC'N(66), νCC(18)
1004		973			
892	894	927	925	899	ring def(37), νCS(26), νCN(20)
507	506	513	516	512	νCS(42), ring def(37)
B_2 species					
2400	2384	3250	3250	3266	νNH(100)
2925	2909	2900	2900	2911	νCH_2(99)
1492	1500	1520	1508	1509	νCN(75)
1445	1434	1480	1480	1475	δCH_2(81)
927	931	1380	1376	1379	δNH(79)
1315	1339	1310	1312	1313	$w CH_2$(59), νC'N(16)
1140	1144	1045	1050	1057	νC'N(72)
645	662	660	678	670	ring def(89)
326	333	333	343	344	δCS(91)
B_1 species					
2965	2996	2986	2986	2996	νCH_2(100)
1298	1300	1310	1312	1300	$t CH_2$(94)
920	904	927	925	905	$r CH_2$(85)
450	465	592	598	579	πNH(97)
200	200	205	200	205	πCS(70), τ ring(28)
107	90	80	109	99	τ ring(83)
			90		
A_2 species					
2930	2984	2936		2984	νCH_2(100)
1286	1277	1286	1286	1277	$t CH_2$(96)
	1080	1106	1108	1081	$r CH_2$(88)
512	532	660	678	666	πNH(97)
87	86	80	90	91	τ ring(99)

a) The frequencies of ETU-d_2 are so arranged as to approximately correspond to the assignments and the PEDs given for ETU-d_0; ν=stretching, δ=bending, r=rocking, w=wagging, t=twisting, π=out-of-plane bending and τ=torsion. b) PED=Potential energy distributions ($100 L_{ik}^2 F_{ii}/\lambda_k$); those less than 15% are omitted.

Out-of-plane Vibrations: B_1 *Vibrations.* The out-of-plane CH_2 stretching is assigned to a weak band at 2967 cm^{-1} comparable with the very weak Raman band of *N,N'*-ethyleneurea[2] at 2980 cm^{-1}. The CH_2 twisting of ETU at 1312 cm^{-1} is slightly higher than that in thiazolidines[25,28] and succinimides[30] assigned around 1230 to 1270 cm^{-1}. According to the normal coordinate treatment, the band at 925 cm^{-1} could also be assigned to CH_2 rocking and this is compatible with CH_2 rocking in ethylene trithiocarbonate[24] and thiazolidines[25,28] assigned between 935 to 950 cm^{-1}.

There are three skeletal modes belonging to B_1 species. The NH out-of-plane bending is assigned at 598 cm^{-1} and its origin from an NH group is confirmed by deuteration studies. On deuteration a new strong broad band at 450 cm^{-1} is observed in agreement with the calculated frequency at 465 cm^{-1}. If, on the other hand, the 678 cm^{-1} band is assigned to NH out-of-plane bending and the 598 cm^{-1} band to ring deformation, then the calculated frequencies for ETU-d_2 are not consistent with observed ones. The strong 598 cm^{-1} absorption of ETU is rather broad and typical of NH bands due to out-of-plane bending. The 678 cm^{-1} band may however be assigned to an NH bending of A_2 symmetry overlapping with the B_2 fundamental due to ring deformation.

The infrared and Raman spectra of ETU exhibit a strong band near 110 cm^{-1} (which is rather broad

Table 3. Observed and calculated fundamentals and assignments for imidazolidine-2-selenone

Frequency/cm^{-1} Obsd	Calcd	Assignment[a] (PED[b]/%)
A_1 species		
3520	3268	νNH(100)
n. a.	2896	νCH_2(99)
1500	1492	νCN(41), δNH(36)
1450	1461	δCH_2(87)
1275	1262	$w CH_2$(61)
1190	1211	δNH(45), $w CH_2$(20)
1080	1098	νCC(43), νCN(17)
988	981	νC'N(67), νCC(22)
		νCSe(58), ring def(47)
357	371	νCSe(58), ring def(28)
B_2 species		
3250	3266	νNH(100)
n. a.	2911	νCH_2(99)
1515	1514	νCN(79)
1475	1476	δCH_2(83)
1350	1357	δNH(58), $w CH_2$(31)
1300	1300	$w CH_2$(45), δNH(32)
1026	1038	νC'N(74)
664	660	ring def(89)
276	280	δCSe(92)

n. a. = not available. a), b): as in Table 2.

in the infrared with a shoulder band at 90 cm^{-1}). This band has been assigned to ring torsion of species B_1. Such features have been observed in related five-membered ring systems,[24,31-34] such as ethylene trithio-[24] and -triselenocarbonate[34] (at ≈90 and 70 cm^{-1}, respectively) and other cyclic carbonates[33] (≈95 cm^{-1}), *etc.* Lattice modes are assigned at still lower frequencies. The calculations for ETU indicate that the other ring puckering mode (of A_2 species) could be assigned in the same region. Since it was not possible to record the far infrared spectra of ETU in solution a doubt can arise that the band around 110 cm^{-1} could be due to lattice modes. An alternate choice for ring torsions may then be the strong band at 200 cm^{-1}, compatible with the assignment in ethylene carbonate[35] (at 215, 230 cm^{-1}) and *N,N'*-ethyleneurea[2] (near 250 cm^{-1}). In such a case, the assignment of C=S out of plane bending presents a difficulty. The former assignment is therefore preferred. Since the out of plane vibrations are fairly independent of each other, even if the latter assignment is preferred, it does not affect the overall results.

A_2 Vibrations. The vibrations belonging to A_2 species, according to the selection rules, are infrared inactive but Raman active for the molecular symmetry C_{2v}. These modes may be observed in the infrared if the molecule is not exactly of C_{2v} symmetry or if the site symmetry is lower. The X-ray structure data[10] of ETU indicate some deviations from C_{2v} symmetry.

The infrared and Raman bands observed corresponding to the calculated vibrations of the A_2 species of ETU and ETU-d_2 are also shown in Table 2. This seems to indicate the overlapping of the fundamentals. No new Raman band without a corresponding infrared band was observed. This shows that the effective molecular symmetry of ETU in the solid state may be slightly lower than C_{2v}.

Imidazolidine-2-selenone: The normal coordinate calculations for ETU is extended to the in-plane vibrations of ESU in an attempt to assign the planar frequencies of ESU and also to confirm some of the assignments made for ETU themselves. The frequency data together with their potential energy distributions derived from the calculations are shown in Table 3. The experimental frequencies are quoted from a published spectrum.[5]

As observed from Tables 2 and 3, the nature of the bands of ESU are very similar to the corresponding ones of ETU and only the bands at 925 and 516 cm^{-1} in the A_1 symmetry species and 343 cm^{-1} in the B_2 species of ETU are significantly shifted to lower frequencies suggesting the higher contribution from the C–S group vibrations to these bands. The assignments of ESU are thus straightforward.

Of particular interest in the spectrum of ESU are the C=Se stretching and bending vibrations. Notably, the potential energy distributions indicate that the observed band at 357 cm^{-1} may be assigned to C=Se stretching and it has considerable contribution from ring deformations. The C=Se stretching also contributes significantly (27%) to the (calculated) higher frequency band at 828 cm^{-1}. The present assignment of the 357 cm^{-1} band qualitatively agrees with Devillanova and Verani[5] who have attributed it to a coupled mode consisting of C=Se stretching, NCSe and NCN bending. The 357 and 828 cm^{-1} bands of ESU correspond approximately to the 516 and 925 cm^{-1} bands of ETU and thus represent a large decrease of over 100 to 140 cm^{-1} from sulfur to the corresponding selenium-involving vibration. The C=Se bending mode is found at 280 cm^{-1} thus producing a decrease of over 60 cm^{-1} from the C=S bending of ETU at 343 cm^{-1}.

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