

Heterocyclic Five-Membered Ring Molecules

II. Mean Amplitudes of Vibration and Related Quantities

S. J. CYVIN, B. N. CYVIN and G. HAGEN

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

and

P. MARKOV

Department of Organic Chemistry, University of Sofia, Bulgaria

Spectroscopic calculations were performed with the previously developed harmonic force fields for: 1,2,5-thiadiazole, 1,2,5-oxadiazole, 1,2,5-selenadiazole, 1,3,4-thiadiazole, 1,3,4-oxadiazole, thiophene, thiophene- d_4 , furan, and furan- d_4 . Calculated results for the following quantities are given: (a) mean amplitudes of vibration, (b) perpendicular amplitude correction coefficients, and (c) atomic vibration mean-square amplitudes. For the two thiadiazoles and for thiophene the calculated mean amplitudes are compared with electron diffraction results.

Recently an extensive analysis was made to develop harmonic force fields for a number of heterocyclic five-membered ring molecules.¹ In the present paper some spectroscopic calculations based on these force fields are reported.

MEAN AMPLITUDES OF VIBRATION

General

The theory of mean amplitudes of vibration is fully described elsewhere.² Here we only point out that the mean amplitudes (l -values) are thermal quantities associated with every bonded or nonbonded atom pair in a molecule, and

$$l^2 = \langle Az^2 \rangle \quad (1)$$

where $\langle Az^2 \rangle$ is the mean-square parallel amplitude. The equality (1) holds within the usually assumed approximation of small harmonic vibrations.

Table 1. Mean amplitudes of vibration (l) and perpendicular amplitude correction coefficients (K) for 1,2,5-thiadiazole; Å units.

SN ₂ (CH) ₂	$i-j$	(Equil. dist.)	l		K	
			0°K	298°K	0°K	298°K
C-H	4-6	(1.080)	0.0768	0.0768	0.0179	0.0187
S-N	1-2	(1.632)	0.0431	0.0438	0.0011	0.0012
C-N	2-4	(1.329)	0.0467	0.0470	0.0020	0.0021
C-C	4-5	(1.413)	0.0512	0.0518	0.0017	0.0018
S···C	1-4	(2.381)	0.0475	0.0488	0.0005	0.0005
N···N	2-3	(2.486)	0.0521	0.0530	0.0005	0.0006
C···N	2-5	(2.297)	0.0527	0.0535	0.0008	0.0009
C···H	4-7	(2.186)	0.1004	0.1009	0.0086	0.0092
N ₂ ···H ₃	2-6	(2.132)	0.0992	0.0997	0.0092	0.0099
N ₂ ···H ₄	2-7	(3.302)	0.0935	0.0941	0.0055	0.0059
S···H	1-6	(3.436)	0.0884	0.0893	0.0049	0.0052
H···H	6-7	(2.558)	0.1542	0.1549	0.0129	0.0139

Table 2. Mean amplitudes of vibration (l) and perpendicular amplitude correction coefficients (K) for 1,2,5-oxadiazole; Å units.

ON ₂ (CH) ₂	$i-j$	(Equil. dist.)	l		K	
			0°K	298°K	0°K	298°K
C-H	4-6	(1.076)	0.0762	0.0762	0.0172	0.0177
O-N	1-2	(1.380)	0.0453	0.0456	0.0015	0.0016
C-N	2-4	(1.300)	0.0457	0.0459	0.0019	0.0020
C-C	4-5	(1.421)	0.0506	0.0510	0.0017	0.0017
O···C	1-4	(2.138)	0.0480	0.0484	0.0007	0.0007
N···N	2-3	(2.267)	0.0503	0.0509	0.0006	0.0006
C···N	2-5	(2.216)	0.0512	0.0517	0.0007	0.0007
C···H	4-7	(2.270)	0.0973	0.0977	0.0079	0.0083
N ₂ ···H ₃	2-6	(2.069)	0.1000	0.1005	0.0085	0.0089
N ₂ ···H ₄	2-7	(3.264)	0.0893	0.0896	0.0050	0.0052
O···H	1-6	(3.167)	0.0898	0.0902	0.0051	0.0053
H···H	6-7	(2.810)	0.1477	0.1484	0.0112	0.0118

Table 3. Mean amplitudes of vibration (l) and perpendicular amplitude correction coefficients (K) for 1,2,5-selenadiazole; Å units.

SeN ₂ (CH) ₂	$i-j$	(Equil. dist.)	l		K	
			0°K	298°K	0°K	298°K
C-H	4-6	(1.079)	0.0773	0.0773	0.0178	0.0188
Se-N	1-2	(1.830)	0.0439	0.0459	0.0008	0.0010
C-N	2-4	(1.300)	0.0469	0.0472	0.0023	0.0025
C-C	4-5	(1.456)	0.0509	0.0516	0.0017	0.0018
Se···C	1-4	(2.489)	0.0465	0.0495	0.0004	0.0004
N···N	2-3	(2.697)	0.0552	0.0568	0.0005	0.0006
C···N	2-5	(2.370)	0.0552	0.0565	0.0010	0.0011
C···H	4-7	(2.267)	0.0986	0.0991	0.0083	0.0088
N ₂ ···H ₃	2-6	(2.013)	0.0995	0.0999	0.0099	0.0108
N ₂ ···H ₄	2-7	(3.379)	0.0944	0.0952	0.0058	0.0063
Se···H	1-6	(3.526)	0.0891	0.0909	0.0048	0.0052
H···H	6-7	(2.731)	0.1478	0.1484	0.0118	0.0125

Table 4. Mean amplitudes of vibration (l) and perpendicular amplitude correction coefficients (K) for 1,3,4-thiadiazole; Å units.

SN ₂ (CH) ₂	$i-j$	(Equil. dist.)	l		K	
			0°K	298°K	0°K	298°K
C-H	2-6	(1.077)	0.0772	0.0772	0.0182	0.0194
S-C	1-2	(1.721)	0.0430	0.0435	0.0010	0.0011
C-N	2-4	(1.302)	0.0460	0.0462	0.0021	0.0022
N-N	4-5	(1.371)	0.0459	0.0462	0.0017	0.0018
S...N	1-4	(2.554)	0.0436	0.0442	0.0003	0.0003
C...C	2-3	(2.355)	0.0501	0.0505	0.0007	0.0007
C...N	2-5	(2.219)	0.0515	0.0522	0.0010	0.0011
N ₃ ...H ₅	4-7	(3.242)	0.0928	0.0933	0.0057	0.0062
N ₃ ...H ₂	4-6	(2.092)	0.0995	0.1000	0.0095	0.0105
C ₂ ...H ₅	2-7	(3.419)	0.0884	0.0886	0.0052	0.0056
S...H	1-6	(2.473)	0.0966	0.0969	0.0074	0.0082
H...H	6-7	(4.472)	0.1159	0.1161	0.0074	0.0079

Table 5. Mean amplitudes of vibration (l) and perpendicular amplitude correction coefficients (K) for 1,3,4-oxadiazole; Å units.

ON ₂ (CH) ₂	$i-j$	(Equil. dist.)	l		K	
			0°K	298°K	0°K	298°K
C-H	2-6	(1.077)	0.0758	0.0758	0.0167	0.0173
O-C	1-2	(1.360)	0.0431	0.0433	0.0016	0.0016
C-N	2-4	(1.300)	0.0445	0.0447	0.0017	0.0017
N-N	4-5	(1.370)	0.0434	0.0435	0.0016	0.0017
O...N	1-4	(2.015)	0.0472	0.0476	0.0006	0.0006
C...C	2-3	(2.344)	0.0475	0.0477	0.0006	0.0006
C...N	2-5	(2.214)	0.0488	0.0491	0.0006	0.0007
N ₃ ...H ₅	4-7	(3.291)	0.0865	0.0867	0.0047	0.0049
N ₃ ...H ₂	4-6	(2.271)	0.0896	0.0897	0.0078	0.0081
C ₂ ...H ₅	2-7	(3.296)	0.0914	0.0916	0.0048	0.0050
O...H	1-6	(2.072)	0.0983	0.0985	0.0082	0.0087
H...H	6-7	(4.140)	0.1276	0.1278	0.0071	0.0074

Results and discussion

The calculated mean amplitudes of vibration at absolute zero and 298 °K are presented in Tables 1-5 for the diazoles, *viz.* 1,2,5-thia-, oxa-, and selenadiazole, and 1,3,4-thia- and oxa-diazole. The results for thiophene and thiophene- d_4 are found in Table 6, and those for furan and furan- d_4 in Table 7. The various bonded and nonbonded distances are identified in three ways in these tables: (i) the different atoms are specified and (if necessary) subscripted with numbers following the conventions in organic chemistry; *cf.* Fig. 1, (ii) atom pair numbers are given in consistence with the numbering of Ref. 3, (iii) parenthesized values of interatomic separations (in Å) as calculated from the bond distances and angles used as equilibrium parameters are given.

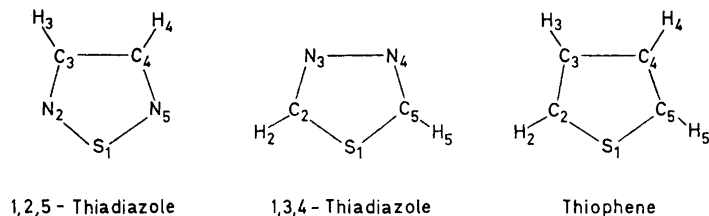


Fig. 1. Identification of atoms in 1,2,5-thiadiazole, 1,3,4-thiadiazole and thiophene.

In the below discussion all quoted values pertain to room temperature. All the l values of bonded CH distances of the present calculations agree well with the characteristic value of about 0.077 Å as found, for instance, in benzene.² All the other bonded distances have values of l between 0.043 and 0.052 Å, which are comparable with the values for other bond distances in planar rings. The value is 0.046 Å in benzene;² in cyclopropene $l(\text{C}=\text{C}) = 0.041$ Å and $l(\text{C}-\text{C}) = 0.050$ Å; and in cyclopropane $l(\text{C}-\text{C}) = 0.051$ Å. For the bonded CC distances in the five-membered heterocyclic rings in particular all l values were found between 0.04₉ and 0.052 Å, which is a trifle more than the benzene value (0.046 Å).

Table 6. Mean amplitudes of vibration (l) and perpendicular amplitude correction coefficients (K) for thiophene and thiophene- d_4 .

Distance ^a	$i-j$	(Equil. dist.)	Thiophene				Thiophene- d_4			
			l	K	l	K	l	K		
			0°K	298°K	0°K	298°K	0°K	298°K	0°K	298°K
C ₃ -H	2-6	(1.078)	0.0765	0.0765	0.0185	0.0194	0.0654	0.0654	0.0132	0.0148
C ₃ -H	4-8	(1.081)	0.0766	0.0766	0.0173	0.0179	0.0655	0.0655	0.0123	0.0134
S-C	1-2	(1.714)	0.0435	0.0442	0.0012	0.0014	0.0434	0.0441	0.0013	0.0016
C ₂ -C ₃	2-4	(1.370)	0.0492	0.0498	0.0024	0.0027	0.0489	0.0496	0.0025	0.0028
C ₃ -C ₄	4-5	(1.423)	0.0505	0.0510	0.0019	0.0021	0.0503	0.0509	0.0020	0.0021
S...C	1-4	(2.555)	0.0489	0.0506	0.0004	0.0005	0.0486	0.0504	0.0005	0.0006
C ₂ ...C ₅	2-3	(2.472)	0.0519	0.0524	0.0008	0.0009	0.0516	0.0522	0.0010	0.0011
C ₂ ...C ₄	2-5	(2.322)	0.0547	0.0556	0.0010	0.0011	0.0543	0.0553	0.0011	0.0013
C ₂ ...H ₃	2-8	(2.161)	0.1019	0.1028	0.0089	0.0095	0.0885	0.0903	0.0063	0.0072
C ₃ ...H ₂	4-6	(2.211)	0.1001	0.1008	0.0087	0.0093	0.0873	0.0887	0.0061	0.0070
C ₃ ...H ₄	4-9	(2.219)	0.1005	0.1010	0.0084	0.0089	0.0873	0.0885	0.0059	0.0067
S...H ₂	1-6	(2.437)	0.1010	0.1015	0.0072	0.0078	0.0866	0.0879	0.0050	0.0058
C ₄ ...H ₅	2-7	(3.519)	0.0894	0.0898	0.0049	0.0051	0.0784	0.0789	0.0033	0.0036
C ₂ ...H ₄	2-9	(3.346)	0.0930	0.0936	0.0054	0.0057	0.0816	0.0826	0.0037	0.0041
C ₄ ...H ₂	4-7	(3.369)	0.0937	0.0944	0.0055	0.0059	0.0827	0.0838	0.0037	0.0042
S...H ₃	1-8	(3.598)	0.0909	0.0921	0.0046	0.0048	0.0793	0.0811	0.0029	0.0033
H ₂ ...H ₃	6-8	(2.638)	0.1594	0.1609	0.0116	0.0122	0.1351	0.1390	0.0079	0.0090
H ₃ ...H ₄	8-9	(2.640)	0.1576	0.1587	0.0113	0.0119	0.1332	0.1364	0.0077	0.0087
H ₂ ...H ₄	6-9	(4.353)	0.1244	0.1252	0.0075	0.0079	0.1062	0.1077	0.0047	0.0053
H ₂ ...H ₅	6-7	(4.541)	0.1187	0.1190	0.0072	0.0076	0.1009	0.1015	0.0044	0.0049

^a H stands for both ¹H and ²H=D.

Table 7. Mean amplitudes of vibration (l) and perpendicular amplitude correction coefficients (K) for furan and furan- d_4 .

Distance ^a	$i-j$	(Equil. dist.)	Furan				Furan- d_4			
			l		K		l		K	
			0°K	298°K	0°K	298°K	0°K	298°K	0°K	298°K
C ₂ -H	2-6	(1.075)	0.0761	0.0761	0.0179	0.0185	0.0650	0.0650	0.0126	0.0139
C ₃ -H	4-8	(1.077)	0.0761	0.0761	0.0175	0.0180	0.0650	0.0651	0.0123	0.0134
O-C	1-2	(1.362)	0.0431	0.0432	0.0017	0.0018	0.0430	0.0432	0.0018	0.0020
C ₂ -C ₃	2-4	(1.361)	0.0485	0.0489	0.0020	0.0021	0.0483	0.0487	0.0020	0.0022
C ₃ -C ₄	4-5	(1.431)	0.0477	0.0479	0.0019	0.0020	0.0476	0.0478	0.0020	0.0021
O...C	1-4	(2.241)	0.0490	0.0495	0.0006	0.0007	0.0488	0.0493	0.0008	0.0008
C ₂ ...C ₅	2-3	(2.181)	0.0472	0.0474	0.0008	0.0009	0.0470	0.0472	0.0010	0.0011
C ₂ ...C ₄	2-5	(2.230)	0.0516	0.0521	0.0008	0.0009	0.0512	0.0518	0.0010	0.0010
C ₂ ...H ₃	2-8	(2.176)	0.1000	0.1005	0.0082	0.0085	0.0868	0.0880	0.0056	0.0062
C ₃ ...H ₂	4-6	(2.239)	0.0968	0.0971	0.0083	0.0087	0.0843	0.0851	0.0058	0.0065
C ₃ ...H ₄	4-9	(2.260)	0.0988	0.0991	0.0079	0.0082	0.0856	0.0867	0.0055	0.0060
O...H ₂	1-6	(2.072)	0.1000	0.1002	0.0086	0.0091	0.0860	0.0869	0.0060	0.0068
C ₂ ...H ₅	2-7	(3.176)	0.0905	0.0906	0.0053	0.0055	0.0787	0.0791	0.0035	0.0039
C ₂ ...H ₄	2-9	(3.279)	0.0897	0.0900	0.0051	0.0052	0.0786	0.0792	0.0033	0.0036
C ₄ ...H ₂	4-7	(3.297)	0.0890	0.0893	0.0052	0.0054	0.0782	0.0787	0.0034	0.0038
O...H ₃	1-8	(3.277)	0.0894	0.0898	0.0050	0.0051	0.0780	0.0787	0.0032	0.0035
H ₂ ...H ₃	6-8	(2.731)	0.1523	0.1531	0.0108	0.0112	0.1287	0.1314	0.0071	0.0079
H ₃ ...H ₄	8-9	(2.757)	0.1564	0.1573	0.0105	0.0109	0.1320	0.1351	0.0070	0.0077
H ₂ ...H ₄	6-9	(4.330)	0.1170	0.1173	0.0072	0.0075	0.0997	0.1003	0.0043	0.0047
H ₂ ...H ₅	6-7	(4.093)	0.1267	0.1270	0.0075	0.0078	0.1072	0.1082	0.0046	0.0051

^a H stands for both ¹H and ²H = D.

It is also interesting to notice the relatively low values of l for the nonbonded ring distances in the molecules of the present investigation. In fact their magnitudes are comparable with those of the bonded ring distances. For comparison we quote here the l values for the *meta* and *para* CC distances in benzene,² *viz.* 0.055 and 0.059 Å, respectively.

It seems not necessary to discuss here the l values of nonbonded distances involving the hydrogen atoms in detail. We only want to mention that they all display reasonable magnitudes when compared with values for similar distances in benzene² and other related molecules.

1,2,5-Thiadiazole and thiophene. Some mean amplitudes of vibration for 1,2,5-thiadiazole and for thiophene have been observed by electron diffraction. They are in satisfactory agreement with the values calculated here when the relatively large experimental error limits are taken into account. The electron diffraction values are (in Å units): 0.078 for C-H in 1,2,5-thiadiazole,⁵ and 0.048 ± 0.008 , 0.040 ± 0.0012 , and 0.045 ± 0.026 for, respectively, S-N, N-C, and C-C in the same molecule.⁶ For thiophene the values of l (in Å) equal to 0.070 and 0.049 have been reported for the C-H and S-C distance, respectively, as observed by electron diffraction in a work⁷ where the C₂-C₃ and C₃-C₄ mean amplitudes were assumed to be 0.044 and 0.046 Å, respectively.

1,3,4-Thiadiazole. From an electron diffraction investigation of 1,3,4-thiadiazole some preliminary results are reported below. The following values (in

Å units with parenthesized standard deviations in 10^{-3} Å) show good agreement with the present calculations.

$$l(\text{C}-\text{H}) = 0.078 \quad (3)$$

$$l(\text{C}-\text{N}) = 0.048 \quad (5)$$

$$l(\text{N}-\text{N}) = 0.049 \quad (8)$$

$$l(\text{C}\cdots\text{N}) = 0.048 \quad (5)$$

The following results from the same investigation show significant discrepancies.

$$l(\text{S}-\text{C}) = 0.065 \quad (3)$$

$$l(\text{S}\cdots\text{N}) = 0.060 \quad (3)$$

$$l(\text{C}\cdots\text{C}) = 0.035 \quad (10)$$

The reason for these discrepancies is not yet explained, but we feel that the spectroscopic values are the more reliable ones since they are based on the elaborate force field studies¹ for a number of related molecules. Furthermore they exhibit reasonable magnitudes according to the above discussion.

PERPENDICULAR AMPLITUDE CORRECTION COEFFICIENTS

The perpendicular amplitude correction coefficients are also referred to as K values;²

$$K = \frac{\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle}{2r} \quad (2)$$

Here $\langle \Delta x^2 \rangle$ and $\langle \Delta y^2 \rangle$ are the mean-square perpendicular amplitudes. The values of K , as well as the mean amplitudes of vibration, are of great interest in molecular structure studies by modern gas electron diffraction methods. As to the K values they may be used to develop the average structure⁸ of molecules. When r_a is the interatomic distance which most directly emerges from the interpretation of electron diffraction data, then the mean distance (r_g) and the distance of the average structure (r_α) are obtainable according to:

$$r_g = r_a + \frac{\langle \Delta z \rangle^2}{r} \quad (3)$$

$$r_\alpha = r_a + \frac{\langle \Delta z \rangle^2}{r} - K \quad (4)$$

The values of K at absolute zero are of special interest. If the distance r_a is extrapolated to $T=0$, eqn. (4) may give the limit of r_α when $T \rightarrow 0$. This limiting value of r_α has great importance⁹ and is referred to as¹⁰ r_z .

The numerical values of K at absolute zero and 298°K are included in Tables 1–7 for the various molecules in question.

ATOMIC VIBRATION MEAN-SQUARE AMPLITUDES

Another type of mean-square quantities have been computed in the present work, namely the atomic vibration amplitudes:

$$\langle x_i^2 \rangle, \langle y_i^2 \rangle, \langle z_i^2 \rangle, \text{ and } \langle y_i z_i \rangle$$

for every type of atoms (i). Here x_i , y_i , and z_i represent the cartesian displacement coordinates. They are oriented in consistence with the cartesian coordinate axes defined elsewhere,³ viz. the X axis perpendicular to the molecule plane, and Z as the two-fold symmetry axis. Hence $\langle x_i y_i \rangle = \langle x_i z_i \rangle = 0$. The atomic vibration mean-square amplitudes are important in modern X-ray structure refinements of molecular crystals,¹¹ where the effect of internal vibrations should be included in order to obtain meaningful results for the rigid-body parameters, as the experimental measurements become more accurate.

Table 8. Atomic vibration mean-square amplitudes (\AA^2 units) for 1,2,5-diazoles.

Atom(i)		$\langle x_i^2 \rangle$	$\langle y_i^2 \rangle$	$\langle z_i^2 \rangle$	$\langle y_i z_i \rangle$
1,2,5-Thiadiazole					
S	0°K	0.00019	0.00023	0.00046	0
	298°K	0.00022	0.00023	0.00049	0
N	0°K	0.00098	0.00107	0.00081	-0.00001
	298°K	0.00113	0.00110	0.00083	-0.00001
C	0°K	0.00094	0.00098	0.00106	0.00015
	298°K	0.00099	0.00101	0.00110	0.00016
H	0°K	0.02160	0.01153	0.00861	-0.00341
	298°K	0.02350	0.01167	0.00872	-0.00350
1,2,5-Oxadiazole					
O	0°K	0.00063	0.00058	0.00075	0
	298°K	0.00070	0.00059	0.00076	0
N	0°K	0.00079	0.00094	0.00066	-0.00006
	298°K	0.00087	0.00096	0.00067	-0.00006
C	0°K	0.00091	0.00095	0.00087	0.00015
	298°K	0.00096	0.00097	0.00088	0.00015
H	0°K	0.01954	0.01027	0.00936	-0.00364
	298°K	0.02071	0.01037	0.00945	-0.00371
1,2,5-Selenadiazole					
Se	0°K	0.00003	0.00006	0.00017	0
	298°K	0.00004	0.00007	0.00021	0
N	0°K	0.00115	0.00132	0.00112	0.00012
	298°K	0.00141	0.00139	0.00122	0.00013
C	0°K	0.00099	0.00104	0.00136	0.00018
	298°K	0.00105	0.00108	0.00150	0.00019
H	0°K	0.02215	0.01057	0.00926	-0.00319
	298°K	0.02437	0.01067	0.00953	-0.00328

Table 9. Atomic vibration mean-square amplitudes (\AA^2 units) for 1,3,4-diazoles.

Atom(<i>i</i>)		$\langle x_i^2 \rangle$	$\langle y_i^2 \rangle$	$\langle z_i^2 \rangle$	$\langle y_i z_i \rangle$
1,3,4-Thiadiazole					
S	0°K	0.00015	0.00021	0.00035	0
	298°K	0.00018	0.00022	0.00036	0
C	0°K	0.00117	0.00111	0.00089	0.00002
	298°K	0.00132	0.00113	0.00090	0.00002
H	0°K	0.02376	0.00650	0.01266	0.00098
	298°K	0.02690	0.00652	0.01278	0.00098
N	0°K	0.00082	0.00079	0.00096	0.00015
	298°K	0.00091	0.00080	0.00098	0.00016
1,3,4-Oxadiazole					
O	0°K	0.00065	0.00055	0.00073	0
	298°K	0.00072	0.00056	0.00074	0
C	0°K	0.00088	0.00091	0.00066	-0.00006
	298°K	0.00093	0.00092	0.00066	-0.00007
H	0°K	0.01965	0.00801	0.01047	0.00303
	298°K	0.02090	0.00804	0.01054	0.00306
N	0°K	0.00069	0.00070	0.00080	0.00013
	298°K	0.00073	0.00071	0.00082	0.00014

Table 10. Atomic vibration mean-square amplitudes (\AA^2 units) for thiophene and thiophene- d_4 .

Atom(<i>i</i>)		$\langle x_i^2 \rangle$	$\langle y_i^2 \rangle$	$\langle z_i^2 \rangle$	$\langle y_i z_i \rangle$
Thiophene					
S	0°K	0.00020	0.00022	0.00046	0
	298°K	0.00025	0.00022	0.00050	0
C ₂	0°K	0.00152	0.00122	0.00087	-0.00003
	298°K	0.00182	0.00126	0.00088	-0.00003
C ₃	0°K	0.00114	0.00098	0.00115	0.00015
	298°K	0.00127	0.00100	0.00120	0.00016
H ₂	0°K	0.02164	0.00691	0.01360	0.00200
	298°K	0.02348	0.00696	0.01378	0.00201
H ₃	0°K	0.01975	0.01164	0.00939	-0.00398
	298°K	0.02104	0.01181	0.00959	-0.00413
Thiophene- d_4					
S	0°K	0.00025	0.00025	0.00049	0
	298°K	0.00033	0.00026	0.00053	0
C ₂	0°K	0.00173	0.00121	0.00089	-0.00003
	298°K	0.00211	0.00125	0.00090	-0.00004
C ₃	0°K	0.00128	0.00104	0.00112	0.00013
	298°K	0.00143	0.00107	0.00118	0.00014
D ₂	0°K	0.01376	0.00491	0.00917	0.00126
	298°K	0.01655	0.00498	0.00963	0.00132
D ₃	0°K	0.01251	0.00785	0.00654	-0.00254
	298°K	0.01451	0.00822	0.00688	-0.00283

We wish to emphasize that there exist other nonvanishing mean-square values of the type $\langle \alpha_i \beta_j \rangle$, where $\alpha, \beta = x, y, \text{ or } z$; and i and j may refer to different atoms. In general these quantities are referred to as mean binary products of cartesian displacements.² All the terms of this kind are easily accessible by our computer programs when the normal-coordinate analysis is done, but those with $i \neq j$ are not supposed to be of prime interest and are therefore not reported here.

Very little has been published of the atomic vibration mean-square amplitudes from rigorous normal-coordinate analyses of molecular vibrations. Besides the direct applicability of calculated atomic vibration amplitudes in studies of crystals it is believed that an accumulation of such data will be useful to provide some general experience as to the orders of magnitude of these quantities.

The numerical results of atomic vibration mean-square amplitudes (at $T=0$ and 298°K) are presented in Tables 8 and 9 for the 1,2,5- and 1,3,4-diazoles, respectively; in Table 10 for thiophene and thiophene- d_4 , and in Table 11 for furan and furan- d_4 .

Table 11. Atomic vibration mean-square amplitudes (\AA^2 units) for furan and furan- d_4 .

Atom(i)		$\langle x_i^2 \rangle$	$\langle y_i^2 \rangle$	$\langle z_i^2 \rangle$	$\langle y_i z_i \rangle$
Furan					
O	0°K	0.00068	0.00051	0.00071	0
	298°K	0.00077	0.00051	0.00072	0
C ₂	0°K	0.00111	0.00089	0.00078	-0.00008
	298°K	0.00121	0.00090	0.00079	-0.00009
C ₃	0°K	0.00102	0.00087	0.00098	0.00013
	298°K	0.00111	0.00088	0.00100	0.00014
H ₂	0°K	0.02058	0.00763	0.01203	0.00301
	298°K	0.02199	0.00766	0.01214	0.00305
H ₃	0°K	0.01883	0.01113	0.00933	-0.00401
	298°K	0.01977	0.01124	0.00942	-0.00409
Furan- d_4					
O	0°K	0.00082	0.00057	0.00074	0
	298°K	0.00095	0.00058	0.00076	0
C ₂	0°K	0.00129	0.00089	0.00083	-0.00007
	298°K	0.00142	0.00090	0.00085	-0.00007
C ₃	0°K	0.00124	0.00093	0.00099	0.00010
	298°K	0.00137	0.00094	0.00101	0.00010
D ₂	0°K	0.01284	0.00528	0.00802	0.00187
	298°K	0.01506	0.00536	0.00831	0.00200
D ₃	0°K	0.01163	0.00747	0.00636	-0.00250
	298°K	0.01320	0.00777	0.00658	-0.00271

REFERENCES

1. Cyvin, B. N. and Cyvin, S. J. *Acta Chem. Scand.* **23** (1969) 3139.
2. Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*, Universitetsforlaget, Oslo, and Elsevier, Amsterdam 1968.
3. Cyvin, B. N., Cyvin, S. J. and Stolevik, R. *Acta Chem. Scand.* **22** (1968) 3034.
4. Cyvin, S. J. and Hagen, G. *To be published*.
5. Momany, F. A. and Bonham, R. A. *J. Am. Chem. Soc.* **86** (1964) 162.
6. Bonham, R. A. and Momany, F. A. *J. Am. Chem. Soc.* **83** (1961) 4475.
7. Bonham, R. A. and Momany, F. A. *J. Phys. Chem.* **67** (1963) 2474.
8. Kuchitsu, K. and Konaka, S. *J. Chem. Phys.* **45** (1966) 4342.
9. Toyama, M., Oka, T. and Morino, Y. *J. Mol. Spectry.* **13** (1964) 193.
10. Morino, Y., Kuchitsu, K. and Oka, T. *J. Chem. Phys.* **36** (1962) 1108.
11. Cruickshank, D. W. J. *Acta Cryst.* **9** (1956) 754, 757; Pawley, G. S. *Acta Cryst.* **17** (1964) 457; **20** (1966) 631; **B 24** (1968) 485.

Received April 24, 1969.