

Vibrational Mean-Square Amplitude Matrices

XVI. In-plane Normal Coordinates and Mean Amplitudes of Vibration in Benzene Molecules

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The theory of mean-square amplitude matrices (Σ) is applied to the in-plane vibrations of benzene and benzene- d_6 . Numerical values at the absolute zero and 298 °K temperatures are given for (i) the symmetrized Σ -matrix elements, and (ii) the ten mean amplitudes of vibration for the various bonded and non-bonded atom pairs. The calculations are based on L -matrices from Albrecht. The L -matrix elements are given and compared with previously unpublished L -matrix elements of Cyvin.

Calculated in-plane force constants for benzene molecules have been reported by several authors¹⁻¹¹. Recently Albrecht¹² has calculated the normal coordinate transformation coefficients for benzenes, using force constants from Whiffen⁸. Mean amplitudes of vibration for benzene¹⁰ and benzene- d_6 ¹³ have been calculated by Cyvin, and those of benzene compared with values from electron-diffraction data¹⁴⁻¹⁶. Quite recently calculated mean amplitudes of vibration for benzene have also been reported by Kimura and Kubo¹⁷ in connection with an electron-diffraction reinvestigation of benzene^{17,18}.

In view of the existing electron-diffraction data of high accuracy for benzene, it was decided to undertake further spectroscopic studies of the mean-square amplitudes of this molecule. In particular it has been planned to perform a calculation of the Bastiansen-Morino shrinkage effects^{19,20} for the linearly situated atoms in benzene. These quantities may be calculated by means of the presently given Σ -matrix elements plus the corresponding quantities for the out-of-plane vibrations. Calculations of the latter mean-square amplitude quantities are in progress. In the present work, the in-plane Σ -matrix elements are used to recalculate the mean amplitudes of vibration (which are square roots of the mean-square parallel amplitudes²¹) for the ten interatomic distances in benzene and benzene- d_6 . The theoretical foundation of these calculations has been outlined in the previous article of this series²².

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Table 1. In-plane symmetry coordinates of benzene.

A_{1g}	S_1	$= 6^{-1/2} (d_1 + d_2 + d_3 + d_4 + d_5 + d_6)$
	S_2	$= 6^{-1/2} (r_1 + r_2 + r_3 + r_4 + r_5 + r_6)$
A_{2g}	S_3	$= 6^{-1/2} R (\beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6)$
B_{1u}	S_{12}	$= 6^{-1/2} D (\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4 + \alpha_5 - \alpha_6)$
	S_{13}	$= 6^{-1/2} (r_1 - r_2 + r_3 - r_4 + r_5 - r_6)$
B_{2u}	S_{14}	$= 6^{-1/2} (d_1 - d_2 + d_3 - d_4 + d_5 - d_6)$
	S_{15}	$= 6^{-1/2} R (\beta_1 - \beta_2 + \beta_3 - \beta_4 + \beta_5 - \beta_6)$
$E_{2g}(a)$	S_{6a}	$= 12^{-1/2} D (2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6)$
	S_{7a}	$= 12^{-1/2} (2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6)$
	S_{8a}	$= 12^{-1/2} (d_1 - 2d_2 + d_3 + d_4 - 2d_5 + d_6)$
	S_{9a}	$= (1/2) R (\beta_2 - \beta_3 + \beta_5 - \beta_6)$
$E_{2g}(b)$	S_{6b}	$= (1/2) D (-\alpha_2 + \alpha_3 - \alpha_5 + \alpha_6)$
	S_{7b}	$= (1/2) (-r_2 + r_3 - r_5 + r_6)$
	S_{8b}	$= (1/2) (-d_1 + d_3 - d_4 + d_6)$
	S_{9b}	$= 12^{-1/2} R (2\beta_1 - \beta_2 - \beta_3 + 2\beta_4 - \beta_5 - \beta_6)$
$E_{1u}(a)$	S_{18a}	$= (1/2) R (\beta_2 + \beta_3 - \beta_5 - \beta_6)$
	S_{19a}	$= 8^{-1/2} (d_1 - d_3 - d_4 + d_6)$ $- 24^{-1/2} D (2\alpha_1 + \alpha_2 - \alpha_3 - 2\alpha_4 - \alpha_5 + \alpha_6)$
	S_{20a}	$= 12^{-1/2} (2r_1 + r_2 - r_3 - 2r_4 - r_5 + r_6)$
$E_{1u}(b)$	S_{18b}	$= 12^{-1/2} R (2\beta_1 + \beta_2 - \beta_3 - 2\beta_4 - \beta_5 + \beta_6)$
	S_{19b}	$= 24^{-1/2} (-d_1 - 2d_2 - d_3 + d_4 + 2d_5 + d_6)$ $- 8^{-1/2} D (-\alpha_2 - \alpha_3 + \alpha_5 + \alpha_6)$
	S_{20b}	$= (1/2) (-r_2 - r_3 + r_5 + r_6)$

Another reason for undertaking the present computations is that the results from benzene may be used as a guide for further calculations on condensed aromatics. Work on naphthalene has been started²³, actuated by the recently published²⁴ results of an electron-diffraction investigation of condensed aromatics.

SYMMETRY COORDINATES

The in-plane symmetry coordinates are specified in Table 1. The valence force coordinates from which the symmetry coordinates are formed are: r -stretching of a C-H bond, d -stretching of a C-C bond, α -bending of a C-C angle, β -bending of a C-H bond. A diagram and more precise definition of coordinates are given in Ref.²²

L-MATRICES

Albrecht¹² gives numerical values for the coefficients L_{ij} of the transformation

$$S_i = \sum_j L_{ij} Q_j$$

Table 2. Mean amplitudes of vibration in benzene (Å units).

Distance	Symbol	Calculated values				Experimental values			
		present		Cyvin ¹⁰ 298°K	Kimura and Kubo ¹⁷ 298°K	Kimura and Kubo ¹⁷ 291°K	Bastiansen and Cyvin ¹⁶		Karle ¹⁴
		$T = 0^\circ\text{K}$	298°K						
C ₁ -C ₂	$\langle d^2 \rangle^{1/2}$	0.0461	0.0464	0.0459	0.0452	0.0456	0.0455	0.0453	0.055
C ₁ -C ₃	$\langle (d^*)^2 \rangle^{1/2}$	0.0539	0.0552	0.0547	0.0548	0.0556	0.054	0.054	0.067
C ₁ -C ₄	$\langle (d^{**})^2 \rangle^{1/2}$	0.0570	0.0590	0.0597	0.0592	0.0614	0.062	0.059	0.075
C ₁ -H ₁	$\langle r^2 \rangle^{1/2}$	0.0771	0.0771	0.0771	0.0771	0.0748	0.073	0.073	0.072
C ₂ -H ₁	$\langle (r^*)^2 \rangle^{1/2}$	0.0994	0.0998	0.1004	0.1000	0.0975	0.094	0.092	0.092
C ₃ -H ₁	$\langle (r^{**})^2 \rangle^{1/2}$	0.0960	0.0969	0.0960	0.0916	0.0925	0.094	0.087	
C ₄ -H ₁	$\langle (r^{***})^2 \rangle^{1/2}$	0.0920	0.0934	0.0942	0.0938	0.0960	0.097	0.099	
H ₁ -H ₂	$\langle t^2 \rangle^{1/2}$	0.1573	0.1580	0.1561	0.1597				
H ₁ -H ₃	$\langle (t^*)^2 \rangle^{1/2}$	0.1322	0.1332	0.1321	0.1388				
H ₁ -H ₄	$\langle (t^{**})^2 \rangle^{1/2}$	0.1171	0.1182	0.1191	0.0966				

relating the symmetry coordinates (S) to the normal coordinates (Q) for both C₆H₆ and C₆D₆. For the calculation of mean-square amplitudes, each of Albrecht's coefficients L_{ij} was multiplied by

$$2\pi 10^{-8} (c\omega_j / hN_o)^{1/2}$$

to give L -matrix elements in $(\text{atomic mass units})^{1/2} \text{ cm } \text{Å}^{-1}$. N_o is Avogadro's number, h is Planck's constant, c is the velocity of light, and ω_j is the vibrational frequency in cm^{-1} as calculated by Albrecht. Further, the coefficients relating S_{19} to the normal coordinates must be multiplied by $2^{1/2}$ because we have followed Crawford and Califano¹¹ in dealing with the redundant coordinates of the E_{1u} symmetry type. There are also some changes of sign where our symmetry coordinates have the opposite sense from Albrecht's. The L_{ij} which we have used as well as those which Cyvin used in his earlier calculations, are given in the Appendix.

Table 3. Mean amplitudes of vibration in benzene-d₆ (Å units).

Distance	Symbol	Calculated values		
		Present		Cyvin ¹³ 298°K
		$T = 0^\circ\text{K}$	298°K	
C ₁ -C ₂	$\langle d^2 \rangle^{1/2}$	0.0459	0.0462	0.0457
C ₁ -C ₃	$\langle (d^*)^2 \rangle^{1/2}$	0.0533	0.0547	0.0543
C ₁ -C ₄	$\langle (d^{**})^2 \rangle^{1/2}$	0.0563	0.0584	0.0593
C ₁ -D ₁	$\langle r^2 \rangle^{1/2}$	0.0658	0.0658	0.0660
C ₂ -D ₁	$\langle (r^*)^2 \rangle^{1/2}$	0.0858	0.0868	0.0898
C ₃ -D ₁	$\langle (r^{**})^2 \rangle^{1/2}$	0.0839	0.0853	0.0848
C ₄ -D ₁	$\langle (r^{***})^2 \rangle^{1/2}$	0.0812	0.0828	0.0839
D ₁ -D ₂	$\langle t^2 \rangle^{1/2}$	0.1324	0.1349	0.1296
D ₁ -D ₃	$\langle (t^*)^2 \rangle^{1/2}$	0.1122	0.1141	0.1112
D ₁ -D ₄	$\langle (t^{**})^2 \rangle^{1/2}$	0.1002	0.1016	0.1028

APPENDIX

A. *L*-matrix elements for the in-plane vibrations of benzene. ($S = LQ$)
Calculated from Albrecht¹²

Symmetry species	Symmetry coordinate	1	2	3	4	5	6	7	8	9
A _{1g}	S ₁	0.274256	-0.0897227							
	S ₂	0.0353057	1.036393							
A _{2g}	S ₃	1.120128								
	S ₁₂	0.949512	0.312328							
B _{1u}	S ₁₃	-0.0370822	1.036262							
	S ₁₄	0.454584	-0.207611							
B _{2u}	S ₁₅	0.676180	0.786109							
	S ₆	0.466921	0.244526	-0.522210	-0.271889					
E _{2g}	S ₇	-0.0105538	1.035481	0.0520144	0.0178191					
	S ₈	0.107411	-0.0623189	0.426104	0.105617					
	S ₉	0.177330	0.0668788	-0.646907	0.827350					
E _{1u}	S ₁₈	0.442477	-1.013556	0.0737579						
	S ₁₉	0.332233	0.354106	-0.118362						
	S ₂₀	0.0222735	0.0373035	1.036050						

B. *L*-matrix for benzene-*d*₆. Calculated from Albrecht.

Symmetry species	Symmetry coordinate	1	2	3	4	5	6	7	8	9
A _{1g}	S ₁	0.256399	-0.132374							
	S ₂	0.0666245	0.758188							
A _{2g}	S ₃	0.871462								
	S ₁₂	0.886128	0.462511							
B _{1u}	S ₁₃	-0.0700937	0.757906							
	S ₁₄	0.496862	-0.0540145							
B _{2u}	S ₁₅	0.362970	0.668948							
	S ₆	0.420911	0.389290	-0.476671	-0.261884					
E _{2g}	S ₇	-0.0176430	0.749349	0.129915	0.0230211					
	S ₈	0.100693	-0.127683	0.425626	0.0234259					
	S ₉	0.237911	0.131132	-0.457242	0.600016					
E _{1u}	S ₁₈	0.501042	-0.681429	0.131097						
	S ₁₉	0.185197	0.423451	-0.190174						
	S ₂₀	0.0206666	0.0894705	0.755538						

C. L -matrix for benzene. Calculated by Cyvin.

		1	2		
A_{1g}	S_1	0.271603	-0.097447		
	S_2	0.064788	1.035015		
		3			
A_{2g}	S_3	1.120176			
		12	13		
B_{1u}	S_{12}	0.942793	0.332066		
	S_{13}	-0.058745	1.035377		
		14	15		
B_{2u}	S_{14}	0.427441	-0.258992		
	S_{15}	0.269399	1.001440		
		6	7	8	9
E_{2g}	S_6	0.492716	0.240582	-0.496631	-0.277777
	S_7	-0.011707	1.035830	0.046600	0.014296
	S_8	-0.094577	-0.059923	0.415108	0.152643
	S_9	0.141868	0.089537	-0.926658	1.002517
		18	19	20	
E_{1u}	S_{18}	1.099641	0.130145	0.051146	
	S_{19}	-0.244451	0.418206	-0.123003	
	S_{20}	-0.010568	0.054548	1.035553	

D. L -matrix for benzene- d_6 . Calculated by Cyvin.

		1	2		
A_{1g}	S_1	0.251153	-0.142055		
	S_3	0.095727	0.755373		
		3			
A_{2g}	S_3	0.871262			
		12	13		
B_{1u}	S_{12}	0.872375	0.487942		
	S_{13}	-0.092132	0.755819		
		14	15		
B_{2u}	S_{14}	0.494209	-0.074402		
	S_{15}	-0.180426	0.739730		
		6	7	8	9
E_{2g}	S_6	0.455988	0.376265	-0.468570	-0.235440
	S_7	-0.020647	0.752364	0.114000	0.016726
	S_8	0.092078	-0.118783	0.426885	0.057728
	S_9	0.215819	0.166889	-0.628119	0.774347
		18	19	20	
E_{1u}	S_{18}	0.805535	-0.271485	0.102316	
	S_{19}	-0.097789	0.446346	-0.202469	
	S_{20}	0.0028194	0.113662	0.752878	

E. Σ -matrix elements for benzene and benzene- d_6

	C_6H_6		C_6D_6	
	$T = 0^\circ K$	$298^\circ K$	$0^\circ K$	$298^\circ K$
$\Sigma_{11}(A_{1g})$	0.00132171	0.00134311	0.00130074	0.00132523
$\Sigma_{22}(A_{1g})$	0.00591422	0.00591458	0.00428785	0.00428963
$\Sigma_{12}(A_{1g})$	-0.00034571	-0.00034296	-0.00043014	-0.00042381
$\Sigma(A_{2g})$	0.01568109	0.01571857	0.01209276	0.01223957
$\Sigma_{11}(B_{1u})$	0.01559043	0.01583273	0.01522904	0.01548456
$\Sigma_{22}(B_{1u})$	0.00594632	0.00594667	0.00432447	0.00432620
$\Sigma_{12}(B_{1u})$	0.00119744	0.00118836	0.00150711	0.00148699

$\Sigma_{11}(B_{2u})$	0.00329626	0.00331094	0.00330690	0.00332257
$\Sigma_{22}(B_{2u})$	0.01498288	0.01507659	0.01089051	0.01124770
$\Sigma_{12}(B_{2u})$	0.00155825	0.00155345	0.00163272	0.00161423
$\Sigma_{11}(E_{2g})$	0.01031969	0.01101335	0.01007457	0.01079070
$\Sigma_{22}(E_{2g})$	0.00595446	0.00595487	0.00436412	0.00436596
$\Sigma_{33}(E_{2g})$	0.00241529	0.00245427	0.00238749	0.00242843
$\Sigma_{44}(E_{2g})$	0.01511555	0.01528531	0.01103279	0.01146547
$\Sigma_{12}(E_{2g})$	0.00090501	0.00088883	0.00115857	0.00112613
$\Sigma_{73}(E_{2g})$	-0.00012713	-0.00013029	-0.00015198	-0.00015777
$\Sigma_{34}(E_{2g})$	-0.00114707	-0.00108133	-0.00125970	-0.00116268
$\Sigma_{13}(E_{2g})$	-0.00144739	-0.00129497	-0.00144913	-0.00129435
$\Sigma_{24}(E_{2g})$	0.00018684	0.00018211	0.00023150	0.00022317
$\Sigma_{14}(E_{2g})$	0.00272803	0.00296881	0.00260111	0.00288971
$\Sigma_{11}(E_{1u})$	0.01490241	0.01496376	0.01120122	0.01142895
$\Sigma_{22}(E_{1u})$	0.00329860	0.00332509	0.00324536	0.00328119
$\Sigma_{33}(E_{1u})$	0.00592361	0.00592375	0.00431720	0.00431801
$\Sigma_{12}(E_{1u})$	-0.00174127	-0.00171537	-0.00191171	-0.00184631
$\Sigma_{23}(E_{1u})$	-0.00040337	-0.00040150	-0.00050039	-0.00049571
$\Sigma_{13}(E_{1u})$	0.00015007	0.00015156	0.00017325	0.00017941

F. Numerical values used in the calculations.

R	= 1.084 Å (equilibrium C-H distance)
D	= 1.397 Å (equilibrium C-C distance)
h	= 6.6252×10^{-27} erg sec
N_0	= 6.02472×10^{23} atomic mass units gm^{-1}
c	= 2.997929×10^{10} cm sec^{-1}
k	= 1.38042×10^{-16} erg deg^{-1}

 Σ -MATRIX

The L -matrix elements quoted above were used to calculate the Σ -matrices ($\Sigma = L\tilde{A}\tilde{L}$) for benzene and benzene- d_6 . A is a diagonal matrix whose elements are

$$(h/8\pi^2c\omega_i) \coth(hc\omega_i/2kT)$$

where k is the Boltzmann factor and T is the temperature in degrees Kelvin. We used the observed frequencies of gaseous benzene (Brodersen and Langseth²⁵) here; thus there is a small inconsistency between the Σ -matrix and the set of force constants from which Albrecht calculated the L -matrix elements. An F -matrix calculated from

$$F = \tilde{L}^{-1} A L^{-1}$$

would be exactly consistent with our Σ -matrix. The observed and calculated frequencies are sufficiently close that the effect of the inconsistency should be negligible. The Σ -matrix elements are given in the appendix.

MEAN AMPLITUDES OF VIBRATION

The mean-square amplitudes of vibration were calculated from the Σ -matrix using the expressions given in Ref.²² and the square roots of these are the mean amplitudes of vibration. The calculated mean amplitudes for benzene and benzene- d_6 are given in Tables 2 and 3 along with calculated and observed mean amplitudes from other work.

Note: The digits as given in these and the other tables are not necessarily all significant.

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