

Mean Amplitudes of Vibration and Shrinkage Effect for Allene and Its Isotopically Substituted Compounds

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Calculated mean amplitudes of vibration and the linear shrinkage effects are presented for allene, allene-d₄, and allene-t₄; and all partially deuterated allenes, *viz.* allene-d, allene-1,1-d₂, allene-1,3-d₂, and allene-d₃. The temperature-dependence of the calculated quantities is shortly discussed. The calculations are based on a harmonic force field, which shows excellent agreement with observed vibration frequencies. For Coriolis constants on the other hand there are some significant discrepancies. One may therefore still await improvements of the force field, but the mean amplitudes and shrinkage effects are not expected to be changed substantially by the future refinements.

Allene and deuterated allenes have been subjected to many spectroscopic investigations. Lord and Venkateswarlu¹ seem to have made the most complete study of the infrared spectrum of both allene and allene-d₄. This last statement is a quotation from the most recent work on allenes due to Maki and Toth,² which may be consulted for a summary of the earlier work. Here we only wish to add some comments. Mills and Duncan³ were the first ones to point out an error in the current tables of ζ -sum rules, which gave a wrong result when applied to allene. Simultaneously they reinterpreted the measurements on perpendicular bands of the *E* species in allene and allene-d₄, using the correct ζ -sum rule. In a subsequent publication Mills, Smith and Duncan⁴ have reported a reinvestigation of two perpendicular bands in allene. By their new analysis of the measurements quite drastic changes of some of the *E* × *E* (*z*) type ζ constants were introduced, when compared to those of the previous work.³ Maki and Toth² also estimated one second-order

ζ value of the $A \times E(x,y)$ type in allene. Here we finally want to mention an infrared work on allene-1,1-d₂ by Shuler and Fletcher.⁵

Mean amplitudes of vibration (u) for allene and allene-d₄ have been calculated by Cyvin,⁶ using vibrational frequencies from Lord and Venkateswarlu.¹ Some values of u from gaseous electron diffraction are now available,⁷ and a linear shrinkage effect for the CCC chain has been reported in the same work. The shrinkage in allene has been studied in some details by Morino *et al.*⁸

The purpose of the present work was to recalculate the mean amplitudes and shrinkage effects in allene (and allene-d)₄ by means of an improved force field. At the same time one wanted to explore the temperature-dependence of the same quantities. One also wished to study the effect of isotopic substitutions; we therefore extended the computations of mean amplitudes and shrinkage effect to include the molecules of allene-t₄, and all partilly deuterated allenes, *viz.* allene-d, allene-1,1-d₂, allene-1,3-d₂, and allene-d₃.

MOLECULAR STRUCTURE AND SYMMETRY

The equilibrium structure of allene is known to belong to a twisted model of symmetry D_{2d} . As structural parameters we have adopted ^{3,7,9}

$$\text{CH} = 1.083 \text{ \AA}, \text{CC} = 1.309 \text{ \AA}, \text{HCH} = 117.9^\circ$$

They are in good correspondence with some quite recent estimates.² The equilibrium structure is assumed to be unaffected by the isotopic substitutions.

Presently it is not intended to specify fully the applied symmetry coordinates of molecular vibrations. One only wishes to make some comments in

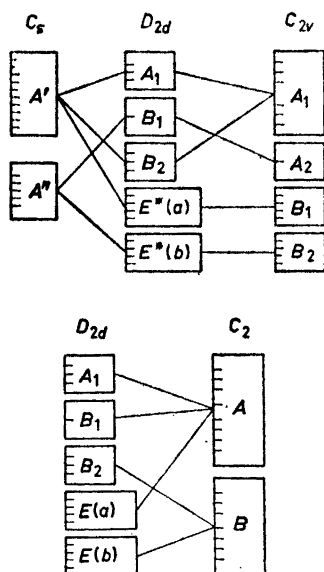


Fig. 1. Correlation diagrams for some symmetry groups pertaining to vibrations of substituted allenes.

connection with the correlations of symmetry species for the various symmetry groups, to which the considered molecules belong. It was found necessary to employ two versions of symmetry coordinates for the most symmetrical compound (say allene itself), in order to achieve the maximal separation into symmetry species for all the compounds of lower symmetries. Take the cartesian principal axes as z along the CCC chain, and x, y along the two other two-fold symmetry axes. Hence x and y intersect the right angles between the two CH_2 planes. The degenerate coordinates belonging to $E(a)$ and $E(b)$ have been constructed as to transform as the rigid translations of T_x and T_y , respectively. In the alternative set of symmetry coordinates the degenerate species are presently denoted by $E^*(a)$ and $E^*(b)$, and the corresponding coordinates transform like $(T_x + T_y)$ and $(T_x - T_y)$, respectively. In this latter case they are oriented as parallel and perpendicular to the CH_2 planes. A complete account on the correlations of the various symmetry species pertaining to the vibrations of the here considered molecules is given in Fig. 1.

Fig. 2 shows the presently adopted numbering of atoms in allene and deuterated allenes.

FORCE FIELD

The same harmonic force field was applied for the whole series of isotopic allene molecules. It is not the intention to specify the complete set of our force constants on this place, but in Table 1 we give the calculated frequencies, along with the available observed frequencies for three of the compounds. The correspondence between observed and calculated frequencies is very good, the deviations being mostly within 1 %.

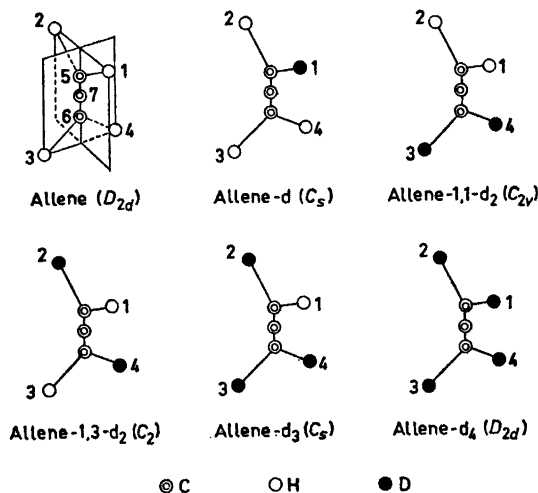


Fig. 2. Adopted numbering of atoms in allene and deuterated allenes.

Table 1. Calculated and observed vibrational frequencies (in cm^{-1}) for isotopic allene molecules.

D_{2d}		Allene		D_{2d}		Allene-d ₄		D_{2d}		Allene-t ₄	
		Calc.	Obs.			Calc.	Obs.			Calc.	
A_1	{	3024.43	2996 ^a	A_1	{	2174.73	2195 ^a	A_1	{	1820.44	
		1457.36	1440 ^a			1274.96	1288 ^a			1220.45	
		1088.10	1076 ^a			865.52	874 ^a			721.32	
		867.21	865 ^a			613.44	615 ^a			501.30	
		3022.34	3006.7 ^b			2217.36	2228.92 ^b			2021.39	
B_1	{	1968.00	1957 ^a	B_1	{	1910.38	1920.27 ^b	B_1	{	1736.37	
		1402.34	1398 ^a			1033.66	1034 ^a			870.14	
B_2	{	3105.10	3085.5 ^c	B_2	{	2315.48	2330 ^c	B_2	{	1987.36	
		1001.14	999.1 ^c			822.54	824.5 ^c			754.01	
E	{	839.32	840.8 ^c	E	{	667.87	666.4 ^c	E	{	595.95	
		355.68	355.3 ^c			306.15	306.5 ^c			274.10	

C_s		Allene-d	C_{2v}		Allene-1,1-d ₂	C_2		Allene-1,3-d ₂	C_s		Allene-d ₂	
		Calc.	Calc.	Obs.	Calc.	Obs.	Calc.	Calc.	Calc.			
A'	{	3067.22	A_1	{	3022.89	3011 ^d	A	{	3067.51	A'	{	3066.99
		3023.12			2197.60	2226 ^d			2242.13			2254.97
		2252.10			1939.25	1942 ^d			1364.49			2193.34
		1954.77			1436.47	1418 ^d			1060.27			1925.67
		1439.43			1199.14	1176 ^d			870.92			1340.95
A''	{	1309.07	A_2	{	924.45	—	B	{	812.60	A''	{	1168.13
		1071.82			751.12	—			649.46			933.92
A'	{	879.75	B_1	{	3105.10	3100 ^d	B	{	326.66	A''	{	840.71
		804.32			998.23	1022 ^d			3066.68			676.16
		338.45			686.18	670 ^d			2261.43			318.67
		3105.10			334.36	336 ^d			1941.25			2315.48
		999.66			2315.48	2334 ^d			1268.85			846.84
A''	{	856.40	B_2	{	872.61	858 ^d	B	{	870.15	A''	{	770.36
		715.40			776.87	825 ^d			752.79			635.18
		346.06			324.82	327 ^d		331.49			315.60	

^a Lord and Venkateswarlu.¹^c Mills, Smith and Duncan.⁴^b Maki and Toth.²^d Shuler and Fletcher.⁵

Unfortunately the Coriolis coupling constants (ζ) calculated with our force field show partially poor agreement with observed values, as is seen in Table 2. One observes, however, also great diversities among the various experimental values. This applies also to the two sets from Mills *et al.*,^{3,4} published with the interval of three years. In general the Coriolis constants are known to be rather sensitive properties in all respects (*e.g.* force-constant dependence, isotopic shift, experimental determination), and one has therefore not hesitated to apply the derived force field in further computations. This seems particularly justified for calculations of mean amplitudes of vibration, since these quantities are much less sensitive than the Coriolis constants with respect to the force-constant dependence.

Table 2. Calculated and observed Coriolis constants for allene and allene-d₄.

Allene	Calc. Present	<i>a</i>	<i>b</i>	Observed <i>c</i>	<i>d</i>
$ \zeta_{1,8}^x $	0.001				0.05
ζ_8	0.001	(0.09)	0.05 ₂	0.00 ₂	-0.0067
ζ_9	0.336	(0.16)	0.02 ₂	0.13 ₇	
ζ_{10}	-0.236	(0.12)	0.07 ₀	0.01 ₇	
ζ_{11}	0.868	(0.66)	0.82 ₄	0.81 ₄	
$ \zeta_{9,10} $	0.461	0.55	0.57 ₂	0.56 ₃	
Allene-d ₄	Calc. Present	<i>a</i>	<i>b</i>	Observed <i>c</i>	
$ \zeta_{1,8}^x $	0.071				
ζ_8	0.004	(0.09)	0.04 ₂	0.01 ₃	
ζ_9	0.528	(0.07)	0.27 ₃	0.35 ₄	
ζ_{10}	-0.355	(0.03)	-0.08 ₃	-0.12 ₂	
ζ_{11}	0.776	(0.86)	0.72 ₀	0.70 ₇	
$ \zeta_{9,10} $	0.320	0.42	0.52 ₀	0.53 ₄	

^a Lord and Venkateswarlu.¹ Values in parantheses are based on a wrong ζ -sum rule.

^b Mills and Duncan.³

^c Mills, Smith and Duncan.⁴

^d Maki and Toth.²

MEAN AMPLITUDES OF VIBRATION AND SHRINKAGE EFFECT

Table 3 shows the mean amplitudes of vibration and shrinkage effects for allene, allene-d₄, and allene-t₄ from the present calculations. The results are in good correspondence with the earlier computations of mean amplitudes by Cyvin.⁶ Also the agreement with electron-diffraction values from Almenningen *et al.*⁷ is satisfactory. As to the (linear C...C) shrinkage effect Morino *et al.*⁸ have found 0.0107–0.0079 Å from an interpretation of electron-diffraction data of Almenningen *et al.*⁷ They have reported the upper limit (0.0107 Å)

Table 3. Mean amplitudes of vibration and shrinkage effect for light and heavy allenes; Å units.

Distance	Allene-d ₀		Allene-d ₄	Allene-t ₄
	<i>T</i> = 0°K	<i>T</i> = 298.16°K	<i>T</i> = 298.16°K	<i>T</i> = 298.16°K
C–H (1.083 Å)	0.07696	0.07696	0.06593	0.06060
C–C (1.309 Å)	0.04077	0.04083	0.04077	0.04074
C ₇ ...H ₁ (2.085 Å)	0.09776	0.09822	0.08538	0.07940
C ₉ ...H ₁ (3.309 Å)	0.11331	0.11735	0.10443	0.09865
C...C (2.618 Å)	0.04792	0.04810	0.04800	0.04793
H ₁ ...H ₂ (1.856 Å)	0.12073	0.12080	0.10207	0.09283
H ₇ ...H ₃ (3.959 Å)	0.16162	0.16979	0.15032	0.14168
Shrinkage C...C	0.00686	0.00935	0.00933	0.00931

to be the most probable one. These results are seen to be in excellent agreement with the spectroscopic computations. The calculated and observed quantities in question are shown in Table 4.

Table 4. Calculated and observed mean amplitudes of vibration (u) and shrinkage effect for allene; Å units.

Quantity	Calculated	(298.16°K)	Obs.
$u(\text{C}-\text{H})$	0.0772 ^a	0.0770	0.0795 ^c
$u(\text{C}-\text{C})$	0.0401 ^a	0.0408	0.0390 ^c
$u(\text{C}_7\cdots\text{H}_1)$	0.1015 ^a	0.0982	0.1046 ^c
$u(\text{C}_8\cdots\text{H}_1)$	0.1144 ^a	0.1174	0.1272 ^c
$u(\text{C}\cdots\text{C})$	0.0451 ^a	0.0481	0.0519 ^c
$u(\text{H}_1\cdots\text{H}_4)$	0.1273 ^a	0.1208	—
$u(\text{H}_1\cdots\text{H}_3)$	0.1716 ^a	0.1698	—
Shrinkage	0.0100 ^b	0.0094	0.0107 — 0.0079 ^{b,c}

^a Cyvin.⁶

^b Morino *et al.*⁸ Referred to at 300°K.

^c Almenningen *et al.*⁷

In Fig. 3 one has drawn the curves of temperature-dependence for the mean amplitudes and shrinkage effect in allene and allene-d₄. One finds a very small variation with temperature for the mean amplitudes of the bonded O—H and C=C distances, but quite drastic variations for the longest C⋯H and H⋯H distances, with the mean amplitudes for the other distances in between.

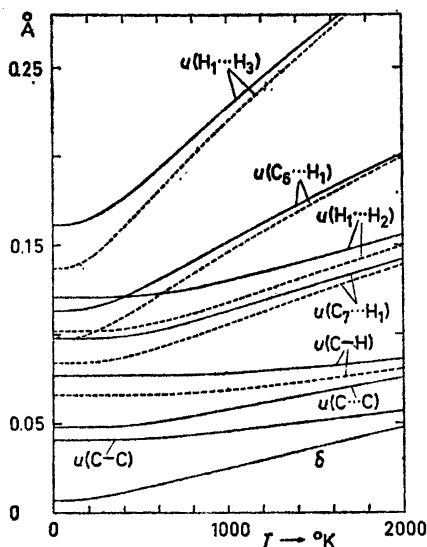


Fig. 3. Mean amplitudes of vibration and shrinkage effect for allene (fully drawn curves) and allene-d₄ (stippled curves) as functions of temperature. For the quantities pertaining to bonded or non-bonded CC atom pairs the curves of the two isotopic molecules are practically coincident.

One has also computed the mean amplitudes of vibration and shrinkage effect for all deuterated allenes. The results at 298.16°K for the partially deuterated compounds are given in Table 5. One finds all the quantities to have characteristic magnitudes for the various types of atom pairs, quite independent of the isotopic substitutions elsewhere in the molecules.

Table 5. Mean amplitudes of vibration and shrinkage effect for partially deuterated allenes at 298.16°K; Å units.

Distance	allene-d	allene-1,1-d ₂	allene-1,3-d ₂	allene-d ₃
C—H ₁ (1.083 Å)		0.07696	0.07696	0.07696
C—H ₂	0.07696	0.07696		
C—H ₃	0.07696		0.07696	
C—D ₁	0.06594			
C—D ₂			0.06594	0.06594
C—D ₃		0.06594		0.06593
C ₅ —C ₇ (1.309 Å)	0.04081	0.04080	0.04080	0.04079
C ₆ —C ₇	0.04081	0.04080	0.04080	0.04079
C ₇ ...H ₁ (2.085 Å)		0.09820	0.09815	0.09814
C ₇ ...H ₂	0.09816	0.09820		
C ₇ ...H ₃	0.09821		0.09815	
C ₇ ...D ₁	0.08544			
C ₇ ...D ₂			0.08543	0.08541
C ₇ ...D ₃		0.08541		0.08540
C ₅ ...H ₁ (3.309 Å)		0.11731	0.11725	0.11723
C ₆ ...H ₂	0.11727	0.11731		
C ₆ ...H ₃	0.11733		0.11725	
C ₆ ...D ₁	0.10451			
C ₆ ...D ₂			0.10448	0.10446
C ₆ ...D ₃		0.10448		0.10445
C...C (2.618 Å)	.04808	0.04805	0.04805	0.04802
H ₁ ...H ₂ (1.856 Å)		0.12080		
H ₃ ...H ₄	0.12080			
H ₁ ...D ₂			0.11207	0.11207
D ₁ ...H ₂	0.11208			
D ₃ ...D ₄		0.10207		0.10207
H ₁ ...H ₃ (3.959 Å)			0.16968	
H ₂ ...H ₄	0.16973			
H ₁ ...D ₄		0.16035	0.16031	0.16029
D ₁ ...H ₄	0.16037			
D ₂ ...D ₄			0.15035	0.15033
Shrinkage C...C	0.00935	0.00934	0.00934	0.00933

Note added in proof. Since this work was completed the results from a continuation of the work of Mills *et al.* have appeared; Nemes, L., Duncan, J. L. and Mills, I. M. *Spectrochim. Acta* 23 A (1967) 1803.

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