

Mean Amplitudes of Vibration and Related Quantities in Isotopic Butatrienes

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Mean amplitudes of vibration were calculated for butatriene, and in the same connection recalculated for ethylene and allene. The results of these calculations show altogether satisfactory agreement with electron-diffraction data. The force field for butatriene was established with the aid of initial force constants transferred from ethylene and allene. In addition to the mentioned quantities the following ones are reported as results of the calculations for butatriene and a number of its isotopic compounds: vibrational frequencies, shrinkage effects, and mean-square perpendicular amplitudes. Substantial secondary isotope effects on the mean-square perpendicular amplitudes are found, while they are negligible for the mean amplitudes of vibration and shrinkage effects.

The main purpose of this work is to report the spectroscopic calculations of the mean amplitudes¹ and related quantities in butatriene and its isotopic compounds. In the same connection we have included some recalculations of the same quantities for ethylene and allene. The force fields derived for these simpler molecules were used as a starting point in the studies of butatriene.

The computations of the present work were completed before the appearance of two recent and independent works^{2,3} reporting spectroscopic mean amplitudes for butatriene. We feel that the publication of these works have not made ours superfluous. On the contrary it has prompted us to write the present paper. A short discussion of its justification seems relevant here.

Significant differences between mean amplitude values for most of the atom pairs from the two works^{2,3} might be enough reason to perform a recalculation. Nagarajan *et al.*² in their calculations of mean amplitudes have assumed that the effect of the off-diagonal elements of the Σ matrix^{1,4} is negligible. This approximation, however, is usually not a very good one, and gives in general only rough estimates of the mean amplitudes. The calculated results by Nagarajan *et al.*² therefore cannot be accepted without great precaution. It is possible that Venkateswarlu *et al.*³ have used the same approximation of neglecting off-diagonal Σ -matrix elements, although it is

not explicitly stated in their paper. But in common with Nagarajan *et al.*,² they do refer to solving of the secular equation

$$|\Sigma G^{-1} - \Delta E| = 0$$

as a part of their method of calculations. Furtheron, Venkateswarlu *et al.*³ have reported mean-square perpendicular amplitudes¹ for butatriene largely different from ours. The same is the case for the shrinkage effects¹ reported by the same workers.³

Mean amplitudes of vibration and related quantities for isotopically substituted butatriene have not been published previously. In the present work we have included the mean amplitudes and shrinkage effects for butatriene- d_0 , butatriene- d_4 , butatriene- t_4 , and all partially deuterated butatrienes. The study of mean-square perpendicular amplitudes for isotopic butatrienes with hydrogen and deuterium also showed to be interesting; the results of calculations of these quantities are included here.

The three molecules in question have all been subjected to modern gas electron-diffraction investigations. The observed mean amplitudes for ethylene,^{5,6} allene,⁷ and butatriene⁸ are given in Table 1, along with calculated results from the present work (see below). The agreement between observed and calculated values is altogether very satisfactory.

ETHYLENE

The force field for ethylene was recalculated using a least-squares adjustment of the force constants to observed frequencies for all the seven isotopic ethylenes containing hydrogen and deuterium. The applied frequencies were taken from the quotations of Cyvin and Cyvin.⁹ An experimental Coriolis constant from Smith and Mills¹⁰ was used as additional constraint. The derived force field was not substantially different from that of the mentioned work by Cyvin and Cyvin,⁹ which also contains a detailed account of calculated mean amplitudes of vibration and generalized mean-square amplitudes of vibration for all the mentioned isotopic compounds. It seems therefore not necessary to give a detailed report on the recalculated results here. We only wish to give the mean amplitudes of vibration for light ethylene at 298°K. They are found in Table 1 along with the corresponding quantities in allene and butatriene from the present calculations (see below). The calculated mean amplitudes for ethylene shown in Table 1 are in excellent agreement not only with the previous calculations by Cyvin and Cyvin^{1,9} but also with independently calculated data by Kuchitsu.^{11,17}

ALLENE

In the present reinvestigation of allene two initial force fields were produced by tentative transferring of force constants and compliants, respectively, from ethylene. The agreement between calculated and observed frequencies were very promising in both cases. A final force field was produced by adjusting the force constants to observed frequencies^{12,13} for allene and allene- d_4 . The

Table 1. Calculated (Spectr.) and observed (E.D.) mean amplitudes of vibration (\AA units) for ethylene, allene and butatriene. Calculated results taken at 298°K.

Distance	Ethylene		Allene		Butatriene	
	Spectr.	E.D.	Spectr.	E.D. ^c	Spectr.	E.D. ^d
C—H	0.077	{0.076 ₃ ± 0.003 ^a 0.0798 ± 0.002 ^b }	0.078	0.0795	0.078	0.080 ± 0.005
C ₁ =C ₂	0.042	{0.043 ₉ ± 0.002 ^a 0.0443 ± 0.002 ^b }	0.040	0.0390	0.041	0.040 ± 0.005
C ₂ =C ₃ (middle)					0.040	0.039 ± 0.005
C ₁ ···C ₃			0.047	0.0519	0.048	0.051
C ₁ ···C ₄					0.053	0.055
C ₂ ···H ₁	0.097	{0.102 ± 0.006 ^a 0.0993 ± 0.004 ^b }	0.100	0.1046	0.096	0.061
C ₃ ···H ₁			0.119	0.1272	0.115	0.102
H ₁ ···H ₁ '(com)	0.125		0.132		0.126	
H ₁ ···H ₄ '(trans)	0.117		} 0.174		0.145	
H ₁ ···H ₄ '(cis)	0.169				0.216	

^a Ref. 5. ^b Ref. 6. ^c Ref. 7. ^d Ref. 8.

effect on calculated mean amplitudes from this last refinement was quite small. In Table 1 the results for allene- d_0 at 298°K are included, as calculated from the final force field. These results are practically the same as those of previous calculations, and especially the recent work of Andersen *et al.*,¹⁴ which also contains the calculated mean amplitudes for all isotopic allenes with hydrogen and deuterium. The only difference of some significance occurs for the H₁···H₁'(com) distance, where the value from Andersen *et al.*¹⁴ is 0.12080 \AA for allene- d_0 at 298.16°K. As a matter of fact this value would fit better the values for the other members of the series ethylene-allene-butatriene as far as the characteristic values for similar distances are concerned. But the anomaly of the present value (in Table 1) is not so great that a closer inspection and further refinement of the force field seems worth while performing.

BUTATRIENE

Vibrational assignment

Two initial sets of frequencies for butatriene were calculated by transferring (a) force constants and (b) compliants from ethylene and allene. The results were quite similar (see Table 2) and served as the basis for our final assignment of frequencies. The experimental frequencies were taken from Miller *et al.*,¹⁵ who have furnished a more complete assignment than Cyvin *et al.*¹⁶ in a simultaneous work; *cf.* Table 2. The assignment of Miller *et al.*¹⁵ for species a_g , b_{1u} , b_{2u} , and the highest frequencies in b_{3g} and b_{3u} were adopted at once because of their nice agreement with our calculated frequencies. In species b_{2g} and for the lower frequencies in b_{3g} the previous assignments^{15,16} seem to be doubtful. Firstly, $\nu_8(b_{3g})=663 \text{ cm}^{-1}$ seems much too low, and we have

Table 2. Assignments of vibrational frequencies for butatriene.

Species and	No.	Present work		Assigned	Observed	
		Calculated ^a	(b)		Cyvin <i>et al.</i> ¹⁶	Miller <i>et al.</i> ¹⁵
a_g	1	3010	3013	2995		2995
	2	1978	1983	2079		2079
	3	1424	1447	1430		1430
	4	881	897	878		878
b_{2g}	5	945	951	878	859	544
	6	526	524	544	323	234
b_{3g}	7	3125	3125	3059		3059
	8	1147	1156	1090		663
	9	505	501	458	372	330
a_u	10	1019	1019	736		736
b_{1u}	11	2988	2994	2994	3001	2994
	12	1579	1614	1608	1607	1608
	13	1411	1449	1370	1364	1370
b_{2u}	14	3124	3125	3080	3059	3080
	15	953	955	1060	1070	1060
	16	210	209	215	<300	215
b_{3u}	17	1061	1072	854	852	854
	18	224	222	215	<300	

^a Transferred (a) force constants and (b) compliants from ethylene and allene.

replaced it by 1090 cm^{-1} , which Miller *et al.*¹⁵ have assigned to $2\nu_5(b_{2g})$. Next we have replaced $\nu_9(b_{3g})=330\text{ cm}^{-1}$ by 458 cm^{-1} , another frequency observed in Raman by Miller *et al.*¹⁵ In species b_{2g} the calculated frequencies favour the assignment of Cyvin *et al.*¹⁶ rather than that of Miller *et al.*¹⁵ Venkateswarlu *et al.*,³ who also noticed the difficulties of assignments of b_{2g} and b_{3g} frequencies solved the problem by adopting (in the notation of Table 2) $\nu_5(b_{2g})=859\text{ cm}^{-1}$ from Cyvin *et al.*¹⁶ and interchanging $\nu_6(b_{2g})$ with $\nu_9(b_{3g})$ in the assignment of Miller *et al.*¹⁵ Their solution may be as good as ours; we have maintained 544 cm^{-1} from Miller *et al.*¹⁵ as one of the frequencies in b_{2g} , and taken $\nu_5(b_{2g})=878\text{ cm}^{-1}$ equal to $\nu_4(a_g)$. Another frequency value which we have used twice is 215 cm^{-1} for $\nu_{16}(b_{2u})$ and $\nu_{18}(b_{3u})$. The latter frequency is left open in the Miller *et al.*¹⁵ assignment. Finally, we have adopted $\nu_{10}(a_u)=736\text{ cm}^{-1}$ for the torsional frequency, which is inactive in both infrared and Raman. The value is significantly smaller than our calculated values, but it fits the trend of decrease in the torsional frequency through the series ethylene-allene-butatriene.

Force field

A final force field was produced by adjusting the force constants to fit exactly the frequencies according to the present assignment (see Table 2 and the above text). It is clear that several details of the assignment are still questionable, but the force field seems good enough to give meaningful mean amplitudes of vibration.

In the present calculations we have used the following data as equilibrium parameters:^{8,15}

$$R(C-H) = 1.083 \text{ \AA}, D(C_1 = C_2) = 1.318 \text{ \AA},$$

$$T(C_2 = C_3; \text{ middle bond}) = 1.283 \text{ \AA}, 2A(\angle HCH) = 119.0^\circ$$

Table 3. Calculated frequencies (cm^{-1}) for isotopic butatrienes. The species notation applies only to the compounds with D_{2h} symmetry: (i) C_4H_4 , (vii) C_4D_4 , and (viii) C_4T_4 .

Species and No.	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)	(viii)	
a_g	1	2995	2250	2211	2253	2229	2206	2200	2091
	2	2079	2071	2059	2065	2061	2051	2041	1800
	3	1430	1406	1399	1300	1307	1276	1093	985
	4	878	843	833	812	829	808	797	705
b_{2g}	5	878	869	868	842	813	814	751	716
	6	544	530	516	499	526	498	492	456
b_{3g}	7	3059	3032	2995	3027	3028	3031	2265	1933
	8	1090	1076	1076	936	970	936	908	838
	9	458	444	435	431	430	421	410	378
a_u	10	736	663	637	621	585	569	521	425
b_{1u}	11	2994	2993	2992	2238	2271	2239	2209	1924
	12	1608	1598	1587	1586	1588	1574	1560	1486
	13	1370	1266	1045	1248	1236	1046	994	828
b_{2u}	14	3080	3070	3068	3041	3034	2300	2318	2005
	15	1060	939	872	941	891	866	840	744
	16	215	207	200	199	200	193	187	169
b_{3u}	17	854	816	722	776	817	719	691	629
	18	215	210	205	208	204	200	195	181

Table 3 shows the calculated frequencies for a number of isotopic butatrienes, as calculated with our final force field. For the sake of brevity we are using the designations:

- (i) butatriene,
- (ii) butatriene- d ,
- (iii) *asym*-butatriene-1,1'- d_2 ,
- (iv) *cis*-butatriene-1,4'- d_2 ,

- (v) *trans*-butatriene-1,4- d_2 ,
- (vi) butatriene- d_3 ,
- (vii) butatriene- d_4 ,
- (viii) butatriene- t_4 .

These designations are used in Table 3 and some of the subsequent tables.

Mean amplitudes of vibration and shrinkage effects

Mean amplitudes of vibration for butatriene- d_0 were calculated with the both initial force fields, which correspond to the frequencies (a) and (b) in Table 2, and with the final force field. The results of all three calculations were very similar. Hence we reproduce here only the final set; *cf.* Tables 1 and 4. In Table 4 also the calculated mean amplitudes from our final force field applied to butatriene- d_4 and butatriene- t_4 are included.

Table 4. Mean amplitudes of vibration (u) and shrinkage effects (δ) in Å units for isotopic butatrienes with D_{2h} symmetry.

Molecule	C_4H_4		C_4D_4		C_4T_4	
	$u(0^\circ K)$	$u(298^\circ K)$	$u(0^\circ K)$	$u(298^\circ K)$	$u(0^\circ K)$	$u(298^\circ K)$
Distance						
C—H	0.0777	0.0777	0.0665	0.0666	0.0611	0.0612
$C_1=C_2$	0.0410	0.0410	0.0409	0.0410	0.0409	0.0410
$C_2=C_3$ (middle)	0.0397	0.0398	0.0396	0.0398	0.0395	0.0397
$C_1 \cdots C_3$	0.0471	0.0475	0.0470	0.0474	0.0469	0.0473
$C_1 \cdots C_4$	0.0526	0.0533	0.0524	0.0531	0.0522	0.0530
$C_2 \cdots H_1$	0.0958	0.0963	0.0825	0.0836	0.0759	0.0776
$C_3 \cdots H_1$	0.1105	0.1153	0.0956	0.1027	0.0881	0.0970
$C_4 \cdots H_1$	0.1191	0.1299	0.1035	0.1180	0.0956	0.1127
$H_1 \cdots H_4'$ (<i>com</i>)	0.1259	0.1260	0.1061	0.1065	0.0960	0.0970
$H_1 \cdots H_4'$ (<i>trans</i>)	0.1423	0.1454	0.1210	0.1264	0.1102	0.1176
$H_1 \cdots H_4'$ (<i>cis</i>)	0.1845	0.2161	0.1583	0.1991	0.1446	0.1919
Distance						
$C_1 \cdots C_3$	0.0066	0.0093	0.0064	0.0093	0.0063	0.0093
$C_1 \cdots C_4$	0.0139	0.0227	0.0134	0.0227	0.0131	0.0226
Distance						
$\delta(0^\circ K)$						
$\delta(298^\circ K)$						

Table 4 also shows the calculated linear shrinkage effects¹ from our final force field.

The quantities in question were also calculated for all partially deuterated butatrienes. All secondary isotope effects on both mean amplitudes and shrinkage effects were found to be negligible for all practical purposes. For most of the quantities we obtained completely the same figures for the partially deuterated compounds as those for C_4H_4 and C_4D_4 in Table 4 within the reported decimals in that table. To give an idea of this correspondence we

may for instance take the $C_2 \cdots H_1$ type distance, for which the mean amplitude at 298°K for all isotopic molecules came out with magnitudes between 0.0961₅ and 0.0962₆ Å. Such differences are quite negligible, since even the last ones of the decimals reported in Table 4 are hardly significant. In consequence of these considerations it is sufficient to give the values of mean amplitudes for the different $H \cdots D$ distances in the partially deuterated molecules to give full account of the data. These supplementary mean amplitudes at 298°K are given in Table 5.

Table 5. Mean amplitudes of vibration (Å units) for the $H \cdots D$ distances in partially deuterated butatrienes at 298°K.

Distance	
$H_1 \cdots D_1'$ (<i>com</i>)	{ 0.1168 (in C_4HD_3) 0.1169
$H_1 \cdots D_4$ (<i>trans</i>)	0.1362
$H_1 \cdots D_4'$ (<i>cis</i>)	{ 0.2076 (in C_4HD_3) 0.2077 (in <i>tr</i> - $C_4H_2D_2$) 0.2078

Mean-square perpendicular amplitudes

The mean-square perpendicular amplitudes¹ are interesting for several reasons. They enter into the values of K according to

$$K = (\langle \Delta x^2 \rangle + \langle \Delta y^2 \rangle) / 2R$$

These quantities are used to calculate the linear shrinkage effects,¹ as it was done for butatriene (*cf.* Table 4). Nonlinear shrinkage effects² cannot be calculated in general without taking into account the anharmonic contribu-

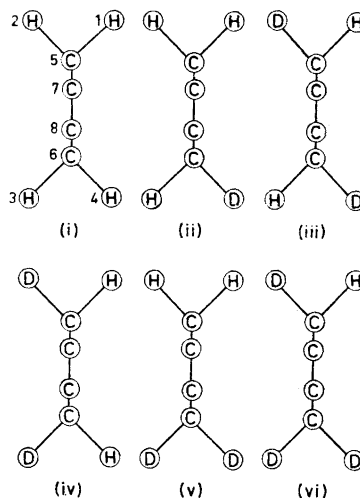


Fig. 1. Numbering of atoms in isotopic butatrienes, as used in Tables 6 and 7.

Table 6. In-plane mean-square perpendicular amplitudes in \AA^2 for isotopic butatriene at 298°K.

Distance	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)
C(5)H(1)	0.0237	0.0240	0.0235	0.0235	0.0243	0.0238	
C(5)H(2)	0.0237	0.0240			0.0243		
C(6)H(3)	0.0237	0.0232	0.0235				
C(6)H(4)	0.0237			0.0235			
C(5)D(2)			0.0195	0.0195		0.0198	0.0194
C(6)D(3)				0.0195	0.0188	0.0191	0.0194
C(6)D(4)		0.0192	0.0195		0.0188	0.0191	0.0194
C(5)C(7)	0.0116	0.0120	0.0115	0.0115	0.0124	0.0118	0.0114
C(6)C(8)	0.0116	0.0110	0.0115	0.0115	0.0106	0.0110	0.0114
C(7)C(8)	0.0062	0.0063	0.0064	0.0064	0.0064	0.0065	0.0066
C(5)C(8)	0.0107	0.0118	0.0110	0.0110	0.0128	0.0120	0.0113
C(6)C(7)	0.0107	0.0100	0.0110	0.0110	0.0094	0.0103	0.0113
C(5)C(6)	0.0006	0.0008	0.0009	0.0009	0.0011	0.0010	0.0011
C(7)H(1)	0.0398	0.0409	0.0394	0.0395	0.0419	0.0404	
C(7)H(2)	0.0398	0.0410			0.0419		
C(8)H(3)	0.0398	0.0384	0.0394				
C(8)H(4)	0.0398			0.0395			
C(7)D(2)			0.0357	0.0357		0.0367	0.0354
C(8)D(3)				0.0357	0.0334	0.0344	0.0354
C(8)D(4)		0.0346	0.0357		0.0334	0.0344	0.0354
C(8)H(1)	0.0327	0.0347	0.0328	0.0328	0.0366	0.0346	
C(8)H(2)	0.0327	0.0327			0.0366		
C(7)H(3)	0.0327	0.0309	0.0328				
C(7)H(4)	0.0327			0.0328			
C(8)D(2)			0.0293	0.0293		0.0311	0.0294
C(7)D(3)				0.0293	0.0258	0.0277	0.0294
C(7)D(4)		0.0273	0.0293		0.0258	0.0277	0.0294
C(6)H(1)	0.0129	0.0139	0.0128	0.0129	0.0150	0.0138	
C(6)H(2)	0.0129	0.0140			0.0150		
C(5)H(3)	0.0129	0.0119	0.0128				
C(5)H(4)	0.0129			0.0129			
C(6)D(2)			0.0095	0.0094		0.0104	0.0094
C(5)D(3)				0.0094	0.0078	0.0086	0.0094
C(5)D(4)		0.0085	0.0095		0.0078	0.0086	0.0094
H(1)H(2)	0.0529	0.0539			0.0547		
H(1)D(2)			0.0484	0.0484		0.0492	
H(3)D(4)		0.0475	0.0484				
D(3)D(4)					0.0425	0.0434	0.0442
H(1)H(3)	0.0236	0.0233	0.0228				
H(1)D(3)				0.0200	0.0195	0.0189	
H(2)D(4)		0.0195			0.0195		
D(2)D(4)			0.0153			0.0152	0.0149
H(1)H(4)	0.0171			0.0169			
H(2)H(3)		0.0171					
H(1)D(4)		0.0139	0.0137		0.0141	0.0138	
D(2)D(3)				0.0107		0.0107	0.0106

Table 7. Out-of-plane mean-square perpendicular amplitudes in Å² for isotopic butatrienes at 298°K.

Distance	(i)	(ii)	(iii)	(iv)	(v)	(vi)	(vii)
C(5)H(1)	0.0207	0.0216	0.0236	0.0272	0.0245	0.0261	
C(5)H(2)	0.0207	0.0248			0.0245		
C(6)H(3)	0.0207	0.0241	0.0236				
C(6)H(4)	0.0207			0.0272			
C(5)D(2)			0.0149	0.0129		0.0154	0.0168
C(6)D(3)				0.0129	0.0143	0.0145	0.0168
C(6)D(4)		0.0116	0.0149		0.0143	0.0170	0.0168
C(5)C(7)	0.0128	0.0131	0.0128	0.0128	0.0136	0.0132	0.0128
C(6)C(8)	0.0128	0.0125	0.0128	0.0128	0.0120	0.0124	0.0128
C(7)C(8)	0.0052	0.0052	0.0053	0.0053	0.0053	0.0054	0.0055
C(5)C(8)	0.0119	0.0127	0.0121	0.0122	0.0137	0.0131	0.0124
C(6)C(7)	0.0119	0.0114	0.0121	0.0122	0.0107	0.0115	0.0124
C(5)C(6)	0.0009	0.0011	0.0012	0.0014	0.0015	0.0015	0.0017
C(7)H(1)	0.0406	0.0387	0.0432	0.0525	0.0458	0.0491	
C(7)H(2)	0.0406	0.0487			0.0458		
C(8)H(3)	0.0406	0.0463	0.0432				
C(8)H(4)	0.0406			0.0525			
C(7)D(2)			0.0343	0.0265		0.0329	0.0359
C(8)D(3)				0.0265	0.0320	0.0304	0.0359
C(8)D(4)		0.0272	0.0343		0.0320	0.0379	0.0359
C(8)H(1)	0.0370	0.0348	0.0385	0.0493	0.0437	0.0462	
C(8)H(2)	0.0370	0.0466			0.0437		
C(7)H(3)	0.0370	0.0415	0.0385				
C(7)H(4)	0.0370			0.0493			
C(8)D(2)			0.0320	0.0228		0.0305	0.0326
C(7)D(3)				0.0228	0.0272	0.0257	0.0326
C(7)D(4)		0.0238	0.0320		0.0272	0.0343	0.0326
C(6)H(1)	0.0178	0.0180	0.0193	0.0249	0.0233	0.0241	
C(6)H(2)	0.0178	0.0239			0.0233		
C(5)H(3)	0.0178	0.0197	0.0193				
C(5)H(4)	0.0178			0.0249			
C(6)D(2)			0.0127	0.0087		0.0126	0.0132
C(5)D(3)				0.0087	0.0093	0.0094	0.0132
C(5)D(4)		0.0082	0.0127		0.0093	0.0134	0.0132
H(1)H(2)	0.0241	0.0337			0.0384		
H(1)D(2)			0.0232	0.0266		0.0289	
H(3)D(4)		0.0180	0.0232				
D(3)D(4)					0.0096	0.0153	0.0189
H(1)H(3)	0.0190	0.0251	0.0273				
H(1)D(3)				0.0200	0.0176	0.0202	
H(2)D(4)		0.0151			0.0176		
D(2)D(4)			0.0068			0.0097	0.0110
H(1)H(4)	0.0430			0.0439			
H(2)H(3)		0.0434					
H(1)D(4)		0.0364	0.0368		0.0367	0.0373	
D(2)D(3)				0.0289		0.0294	0.0299

tion. This difficulty arises for instance for all distances outside the linear chain in butatriene. Nevertheless the values of K are useful for all distance types when interpreting electron-diffraction data, since they to the first approximation connect the mean distances (R_g) and the distances of the average structure¹⁷ (R_α) according to

$$R_\alpha = R_g - K$$

The in-plane ($\langle \Delta x^2 \rangle$) and out-of-plane ($\langle \Delta y^2 \rangle$) mean-square perpendicular amplitudes from the present calculations for all isotopic butatrienes containing hydrogen and deuterium are given in Tables 6 and 7, respectively. The numbering of atoms used in these tables is explained on Fig. 1.

It is interesting to notice the drastic secondary isotope effect on the mean-square perpendicular amplitudes. The same effect is previously found for isotopic ethylenes.⁹ For the $C_1 \cdots C_4$ (longest) distance taken as example the in-plane mean-square perpendicular amplitude at 298°K varies from 0.00063 Å² in C_4H_4 to 0.001064 Å² in C_4D_4 . The corresponding figures for the out-of-plane quantities are 0.00092 and 0.001674 Å². For the shorter CC distances the variations are not so drastic, but still much greater than the case is for the mean-square amplitudes of vibration (or mean-square parallel amplitudes¹). These features may be explained by the fact that the normal vibrations of CCH or CCD type in-plane bendings contribute significantly to $\langle \Delta x^2 \rangle$, especially for the longest CC distance, and the CH_2 or CD_2 type out-of-plane bendings contribute to $\langle \Delta y^2 \rangle$. But all details of the secondary isotope effects on mean-square perpendicular amplitudes, as they are seen in Tables 5 and 6, could hardly be predicted.

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