

## Calculation of Fundamental Frequencies of 2,5-Dimethyl-2,3,4-hexatriene

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Tetramethylbutatriene has been analyzed using force constant calculations, which demonstrated that force constants may be transferred from structurally related compounds such as butatriene and tetramethylethylene.

Recently, the vibrational spectra of tetramethylbutatriene were analyzed by one of us.<sup>1</sup> The ambiguities in the assignments due to incomplete vibrational spectral data suggested to us that we use force constant calculations as a tool for obtaining more reliable assignments. Further, tetramethylbutatriene has recently been subjected to a gas electron-diffraction investigation by the Oslo group<sup>2</sup> and mean amplitudes of vibration are needed in the analysis. The scope of this paper is to demonstrate that the approximate, transferred force constants may be applied in studying fundamental modes of vibration for tetramethylbutatriene.

Some of the constants of an approximate internal valence force field for tetramethylbutatriene can be

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transferred from butatriene and tetramethylethylene. Previously, Cyvin and Hagen<sup>3</sup> established a force field for butatriene by transferring initial force constants from ethylene and allene and producing a final force field by adjusting the force constants to fit exactly the observed frequencies of butatriene. Different types of force fields have been reported for propene,<sup>4</sup> *cis*-2-butene<sup>5</sup> and *trans*-2-butene,<sup>6</sup> but no force field has been published for tetramethylethylene.

### VIBRATIONAL ASSIGNMENTS

*Butatriene.* The vibrational spectra of butatriene have been published by Miller *et al.*<sup>7</sup> and by Cyvin *et al.*<sup>8</sup> The assignment of the fundamental modes of vibration given by the former, was later modified by Cyvin and Hagen.<sup>3</sup> The reassignment was in part confirmed by our calculations. However, there are no experimental criteria to distinguish between the  $\nu_7(b_{2g})$  mode at  $544\text{ cm}^{-1}$  and the  $\nu_{10}(b_{3g})$  mode at  $459\text{ cm}^{-1}$ , as was stated by Cyvin and Hagen.<sup>3</sup> For tetramethylbutatriene the normal coordinate calculations give better results if the values of  $\nu_7$  and

Table 1. Structural parameters used in normal coordinate calculations.

	Ethylene	Tetramethyl-ethylene	Butatriene	Tetramethylbutatriene
C=C (Å)	1.34	1.34	{ 1.33 1.27	{ 1.33 1.27
C-C (Å)		1.51		1.51
C-H (Å)	1.085	1.09	1.085	1.09
C=C-H <sub>1</sub> (°)		122	121	122
C=C-C <sub>1</sub> (°)	121			
C-C-H (°)		109.47		109.47

$\nu_{10}$  are interchanged. It also seems reasonable to assume that the out-of-plane mode will appear at a lower frequency than the corresponding in-plane mode.

**2,3-Dimethyl-2-butene.** Several research groups have analyzed the vibrational spectra of tetramethylethylene.<sup>9-12</sup> Apart from the uncertainty in the assignment of the methyl torsional modes  $\nu_{17}(b_{1g})$ ,  $\nu_{22}(b_{2g})$  and  $\nu_{49}(b_{3u})$  some inconsistencies appear in the assignments of  $\nu_6(a_g)$ ,  $\nu_{12}(b_{2g})$ ,  $\nu_{43}(b_{2u})$  and  $\nu_{47}(b_{3u})$ . We have assigned the latter modes to bands at 947, 505, 272 and 308  $\text{cm}^{-1}$ , respectively, as first suggested by Scott *et. al.*<sup>9</sup> The alternative assignments<sup>12</sup> of these modes do not agree with our calculations.

### FORCE CONSTANT CALCULATIONS

In the present work, the force field for tetramethylbutatriene was constructed by transferring a common force field for ethylene, butatriene and tetramethylethylene, derived by the overlay technique. The structural parameters used in the normal coordinate analyses, are given in Table 1. Definitions of the internal valence coordinates are shown in Fig. 1. The methyl torsions have been defined as the normalized sum of the three  $\text{C}=\text{C}-\text{C}-\text{H}$  torsions, while the  $\text{C}=\text{C}$  torsions were defined as the normalized sum of the two *trans*  $\text{X}-\text{C}=\text{C}-\text{X}$  torsions.

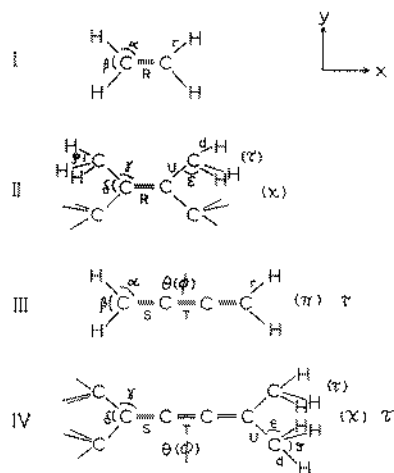


Fig. 1. Definition of the internal coordinates in ethylene (I), tetramethylethylene (II), butatriene (III) and tetramethylbutatriene (IV). The out-of-plane deformations are in the direction of the z-axis.

Table 2. Suggested valence force constants, with reference to Fig. 1, for ethylene (I), tetramethylethylene (II), butatriene (III) and tetramethylbutatriene (IV).

Constant	Value <sup>a</sup>	Used in molecule
$K_R$	9.63	I, II
$K_S$	9.25	III, IV
$K_T$	10.83	III, IV
$K_U$	4.40	II, IV
$K_V$	5.06	I, III
$K_d$	4.62	II, IV
$H_z$	0.551	I, III
$H_\beta$	0.383	I, III
$H_\theta$	0.437	III, IV
$H_\phi$	0.328	III, IV
$H_\gamma$	1.09	II, IV
$H_\delta$	1.24	II, IV
$H_\epsilon$	0.614	II, IV
$H_\zeta$	0.530	II, IV
$H_\pi$	0.198	III
$H_\nu$	0.267	II, IV
$H_\tau$	0.139	III, IV
$F_{ST}$	0.68	III, IV
$F_{RU}$	0.96	II, IV
$F_{SU}$		
$F_{dd}$	0.05	II, IV
$F_{Rz}$	0.30	I, III
$F_{Sz}$		
$F_{Ry}$	0.53	II, IV
$F_{Sy}$		
$F_{Uy}$	0.48	II, IV
$F_{Uz}$	0.33	II, IV
$F_{dc}$	0.10	II, IV
$f_{zz}^1$	0.06	I
$f_c^1$	-0.04	I
$f_{zz}^2$	-0.04	III, IV
$f_{\theta\theta}$	0.02	III, IV
$f_{\phi\phi}$	0.33	II
$f_{\gamma\gamma}^1$	0.60	II
$f_{\gamma\gamma}^2$	-0.02	II, IV
$f_{\delta\delta}$	-0.01	II, IV
$f_{\phi\gamma}^1$	-0.05	IV
$f_{\phi\gamma}^2$	-0.05	IV
$f_{\phi\kappa}$	-0.045	IV
$f_{\kappa\kappa}$	-0.045	II
$H_{\tau-\text{Me}}$	0.018	II, IV

<sup>a</sup>Stretching force constants in  $\text{mdyn}/\text{\AA}$ , bending force constants in  $\text{mdyn}/\text{\AA}$  and stretch-bend interactions in  $\text{mdyn}$ .

Table 3. Observed and calculated frequencies ( $\text{cm}^{-1}$ ) for tetramethylethylene.<sup>a</sup>

Species	Obs.	Calc.	Species	Obs.	Calc.	
$a_g$	$v_1$	2930	$b_{1u}$	$v_{30}$	2930	
	$v_2$	2860		$v_{31}$	2879	
	$v_3$	1683		$v_{32}$	1460	
	$v_4$	1456		$v_{33}$	1382	
	$v_5$	1397		$v_{34}$	1172	
	$v_6$	947		$v_{35}$	902	
	$v_7$	690		$v_{36}$	417	
	$v_8$	411				
$b_{1g}$	$v_{14}$	2930	$b_{2u}$	$v_{37}$	2930	
	$v_{15}$	1456		$v_{38}$	2879	
	$v_{16}$	947		$v_{39}$	1453	
	$v_{17}$	—		$v_{40}$	1382	
$b_{2g}$	$v_{18}$	2930		$v_{41}$	1165	
	$v_{19}$	1456		$v_{42}$	972	
	$v_{20}$	1071		$v_{43}$	272	
	$v_{21}$	505		$b_{3u}$	$v_{44}$	2930
	$v_{22}$	—			$v_{45}$	1460
$b_{3g}$	$v_{23}$	2930		$v_{46}$	1028	
	$v_{24}$	2862			$v_{47}$	308
	$v_{25}$	1456			$v_{48}$	—
	$v_{26}$	1374				164
	$v_{27}$	1269				
	$v_{28}$	947				
	$v_{29}$	505				

<sup>a</sup>Experimental data from Refs. 9–12.Table 4. Observed and calculated frequencies ( $\text{cm}^{-1}$ ) for butatriene<sup>a</sup> and tetramethylbutatriene.<sup>b</sup>

Species	Butatriene		Tetramethylbutatriene			
	No.	Obs.	Calc.	No.	Obs.	Calc.
$a_g$	$v_1$	2995	2995	$v_1$	2904	2932
	$v_2$	2079	2079	$v_2$	2850	2870
	$v_3$	1430	1450	$v_3$	2064	2073
	$v_4$	878	877	$v_4$	1459	1459
				$v_5$	1377	1383
				$v_6$	1280	1296
				$v_7$	966	902
				$v_8$	595	606
				$v_9$	291	344
$b_{1g}$	$v_5$	736	736	$v_{15}$	2924	2928
				$v_{16}$	1436	1454
				$v_{17}$	948	965
				$v_{18}$	177	172
$b_{2g}$	$v_6$	878	871	$v_{19}$	2924	2929
	$v_7$	459	459	$v_{20}$	1459	1457
				$v_{21}$	1059	1044

Table 4. Continued.

				$\nu_{22}$	528	541
				$\nu_{23}$	329	303
				$\nu_{24}$	130	157
$b_{3g}$	$\nu_8$	3059	3097	$\nu_{25}$	2924	2929
	$\nu_9$	1090	1081	$\nu_{26}$	2860	2870
	$\nu_{10}$	546	544	$\nu_{27}$	1436	1456
				$\nu_{28}$	1364	1384
				$\nu_{29}$	1280	1224
				$\nu_{30}$	948	952
				$\nu_{31}$	748	728
				$\nu_{32}$	275	269
$b_{1u}$	$\nu_{11}$	2994	2994	$\nu_{33}$	2934	2931
	$\nu_{12}$	1608	1605	$\nu_{34}$	2863	2870
	$\nu_{13}$	1370	1393	$\nu_{35}$	1661	1629
				$\nu_{36}$	1447	1455
				$\nu_{37}$	1374	1383
				$\nu_{38}$	1010	1037
				$\nu_{39}$	808	826
				$\nu_{40}$	401	442
$b_{2u}$	$\nu_{14}$	3080	3097	$\nu_{41}$	2918	2932
	$\nu_{15}$	1060	1049	$\nu_{42}$	2863	2870
	$\nu_{16}$	215	215	$\nu_{43}$	1447	1456
				$\nu_{44}$	1374	1384
				$\nu_{45}$	1211	1216
				$\nu_{46}$	956	952
				$\nu_{47}$	533	576
				$\nu_{48}$	85	83
$b_{3u}$	$\nu_{17}$	854	861	$\nu_{49}$	2918	2929
	$\nu_{18}$	215	215	$\nu_{50}$	1459	1458
				$\nu_{51}$	1063	1045
				$\nu_{52}$	433	456
				$\nu_{53}$	—	161
				$\nu_{54}$	100	110

<sup>a</sup>Experimental data from Refs. 7 and 8. <sup>b</sup>Experimental data from Ref. 1.

A total of 35 force constants was fitted to reproduce the vibrational fundamental modes of the three molecules: ethylene, butatriene and tetramethylethylene (Table 2). All interaction constants between valence coordinates not involving common atoms were assumed vanishingly small. Two additional interaction constants,  $f_{\theta\gamma}$  and  $f_{\theta\gamma'}$ , were introduced for tetramethylbutatriene in order to reproduce the lowest bending modes.

The observed and calculated vibrational frequencies for tetramethylethylene are given in Table 3, while the corresponding results for butatriene and tetramethylbutatriene are given in Table 4. In general the agreement is within 1%. The

magnitudes of the force constants of Table 2 seem to be physically reasonable. The fact that the interaction constants are refined to fit several molecules increases our confidence in the force constants.

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