

## Approximate Valence Force Fields for Isobutene, *trans*-2-Butene, *cis*-2-Butene and 1-Butene

S. H. SCHEI

Department of Chemistry, University of Trondheim, NLHT Rosenborg, N-7000 Trondheim, Norway

For the butenes, valence force fields containing relatively few force constants have been developed for the purpose of serving as a basis for the composition of approximate valence force fields for substituted butenes. One distinct set of force constants was developed for each butene. However, the consistency between the various force fields was good. The vibrational frequencies of the butenes were calculated to an average deviation of 11–17  $\text{cm}^{-1}$  from observations. Particular features in the force fields indicate that three sequential carbon-carbon bonds in a planar *cis*-like position should be associated with angle bend force constants of increased magnitude relatively to staggered position. The force fields have shown suitable transferability.

The vibrational spectra of the butenes have been extensively studied and the interpretation of the vibrational frequencies should be quite well established.<sup>1-13</sup> Several normal coordinate calculations have been carried out.<sup>3,6,10,11,14-16</sup> However, most of these calculations have applied different types of force fields for the various butenes. The fundamental frequencies of isobutene and *cis*- and *trans*-2-butene have been calculated from a consistent force field as part of a molecular mechanics (MM) calculation.<sup>16</sup> There is no doubt that this combined use of a valence force field (VFF) and nonbonded interactions was a good approach; however, "pure" VFF are still widely used as a tool in the calculation of vibrational quantities, like vibrational amplitudes for use in electron diffraction studies.<sup>17</sup> For such purpose the mentioned consistent force field is not always immediately accessible for combination and transference to other

molecules. Further, it is convenient having comparable force fields for all butenes.

During the development of a new VFF one should bear in mind the answers to the following questions:

1. What purpose should the force field serve?
2. What is the needed accuracy for the quantities to be calculated from the force field?

For the present calculation, the answers were:

1. Primarily, it was desirable to have access to relative simple VFF for the parent molecules during the work with several halo-substituted butenes, both for the calculation of quantities like vibrational amplitudes and for the calculation of vibrational frequencies. Thus, the force fields were not primarily developed for the sake of the butenes themselves.

2. The force fields should reproduce all main features of the vibrational spectra quite accurately.

It was obviously no straightforward matter to meet the mentioned criteria, simplicity and accuracy, simultaneously, so some personal judgement was inevitable.

### CALCULATIONS

Generally, the following limitations were imposed on the calculations:

1. To meet the simplicity requirement:
  - a. As few non-diagonal force constants as possible should be introduced. A thorough study of

several possible interactions was carried out.

b. The interactions should preferably be of equal type for all the butenes. Exceptions were made only when obviously linked to structural differences.

c. The interactions were chosen to be very local. This was assumed to enhance the chances of carrying out reliable calculations for the halo-substituted butenes and other related molecules, because it would avoid unwanted ambiguity in the process of transferring the force fields.

d. No attempt was made to discern force constants associated with in-plane and out-of-plane positioned H-atoms.

2. In order to maintain consistency within the butene series, a particular type of force constant, diagonal or non-diagonal, should be of comparable magnitude.

3. When the requirements of simplicity and consistency had to be balanced against accuracy of the calculated frequencies:

a. It was considered most important to fit skeletal frequencies well.

b. Among the many frequencies mainly due to various types of CCH bends, it was occasionally necessary to accept less accurate values for some of these. Because there have been most ambiguity as to the interpretation among the rock frequencies, less emphasis was put on the calculation of CCH bends between 900 and 1200  $\text{cm}^{-1}$  when a few larger deviations had to be tolerated.

The calculations were carried out with a least squares program.<sup>18</sup>

*Isobutene.* Several studies of isobutene have included assignment of the fundamental frequencies,<sup>5-7,9,14</sup> and a few dissimilarities have occurred. For the present calculation the interpretation of Ref. 7 has been used, except for the torsional frequencies for which gas phase values of Ref. 8 were preferred. The geometrical parameters were taken from Ref. 19. The calculation was initiated with a VFF similar to the one obtained for 3-butenenitrile.<sup>20</sup> The final force field is listed in Table 1. Calculated frequencies are compared with the observed ones in Table 2.

Most frequencies mainly associated with the  $\text{CH}_3$  groups were well calculated. However, the frequency approximately described as  $=\text{CH}_2$  rock,  $\nu_{23}$ , was poorly fitted, calculated 79  $\text{cm}^{-1}$  too low. Efforts to make a better agreement with observation failed within the preset limitations. Improvement was only possible by allowing

$f(\text{C}=\text{C}-\text{H})$ , the  $\text{C}=\text{C}-\text{H}$  force constant, to take an unreasonable value as compared with related molecules<sup>20-23</sup> or by introducing more interactions or less local interactions. The corresponding frequencies were also calculated too low when the isobutene force field was combined with those of 3-halo-1-propenes in a normal coordinate analysis of 3-halo-2-methyl-1-propene,<sup>24</sup> while other frequencies seemed to be well reproduced.

For the calculation of vibrational quantities the value of the torsional force constant,  $f_\tau$ , is often a problem. For some halogenated propenes and butenes it has been found useful to estimate  $f_\tau$  from MM calculations.<sup>24,25</sup> Therefore, it was interesting to know how well corresponding MM calculations<sup>26</sup> on the butenes could estimate the  $f_\tau$  values. For isobutene a value of  $f_\tau=0.07$   $\text{mdyn} \cdot \text{\AA} \cdot \text{rad}^{-2}$  was obtained, yielding torsional frequencies of 193( $A_2$ ) and 201  $\text{cm}^{-1}$ ( $B_2$ ). The  $B_2$  torsional frequency was observed to 197  $\text{cm}^{-1}$  in the gaseous phase,<sup>8</sup> while the  $A_2$  torsional frequency was estimated to 167  $\text{cm}^{-1}$ .<sup>8</sup> Thus, the MM obtained  $f_\tau$  had a satisfactory value.

*trans-2-Butene.* A normal coordinate calculation based on a VFF has earlier been made for *trans-2-butene*.<sup>10</sup> Also that force field had relatively few terms, 21 force constants, but the type of interactions are quite different from the VFF presented here.

The *trans-2-butene* geometry from Ref. 27 was used. The initial calculation used force constants from isobutene and 3-butene-nitrile.<sup>20</sup> The final force constants are given in Table 1.

The  $=\text{C}-\text{H}$  out-of-plane and  $\text{C}=\text{C}$  torsion frequencies could be fairly well calculated by a much simpler approach than that used in Ref. 10. The acceptance of the calculated values (Table 3) was based on the assumption that the 260  $\text{cm}^{-1}$  frequency belongs to  $A_u$  and 294  $\text{cm}^{-1}$  to  $B_u$ , contrary to the conclusion from the earlier calculation<sup>10</sup> but in agreement with Ref. 14. Whether the lowest  $B_u$  fundamental actually is 260 or 294  $\text{cm}^{-1}$  is not possible to judge from a normal coordinate analysis. By varying  $f(\text{C}=\text{C}-\text{C})$  and an interaction  $f(\text{C}=\text{C}-\text{C}/\text{C}=\text{C}-\text{C})$  both alternatives could easily be fitted, and at the same time obtaining *ca.* 500  $\text{cm}^{-1}$  for the  $A_g$   $\text{C}=\text{C}-\text{C}$  frequency. As for isobutene the  $\text{CH}_3$  rock frequencies were reasonably well reproduced. The largest deviation appeared for  $\text{C}=\text{C}-\text{H}$  bend, and this discrepancy could not be

Table 1. Approximate valence force fields for isobutene, *trans*-2-butene, *cis*-2-butene and 1-butene *gauche/syn*. Force constants in  $\text{mdyn} \cdot \text{\AA}^{-1}$  and  $\text{mdyn} \cdot \text{\AA} \cdot \text{rad}^{-2}$  <sup>a</sup> and corresponding units for the interaction force constants.

Type	Coordinate	Iso-butene	<i>trans</i> -2-Butene	<i>cis</i> -2-Butene	1-Butene
str.	C=C	9.14	9.21	9.05	9.34/9.27
	=C-C	4.24	5.07	5.07	4.72
	-C-C				4.29
	=C-H(=CH <sub>2</sub> )	5.00			5.06
	=C-H(=CH)		4.91	4.87	4.94
	-C-H(CH <sub>3</sub> )	4.71	4.66	4.64	4.81
bend	-C-H(CH <sub>2</sub> )				4.62
	C=C-C	0.98	0.95	1.21	0.97/1.39
	C-C-C(=CC <sub>2</sub> )	0.73			
	C-C-C				0.61/1.25
	C=C-H(=CH <sub>2</sub> )	0.52			0.53
	C=C-H(=CH)		0.50	0.52	0.55
	C-C-H(=CH)		0.49	0.48	0.52
	H-C-H(=CH <sub>2</sub> )	0.42			0.39
	C-C-H(CH <sub>3</sub> )	0.63	0.64	0.64	0.64
	C-C-H(CH <sub>2</sub> )				0.69
	H-C-H(CH <sub>3</sub> )	0.57	0.53	0.54	0.57
	H-C-H(CH <sub>2</sub> )				0.56
tors.	C=C	0.49	0.59	0.58	0.55
	=C-C	0.07	0.06	0.02	0.06/0.11
	-C-C				0.10/0.15
o.o.p.	=CH <sub>2</sub>	0.21			0.23
	=CH		0.23	0.26	0.28
	=CC <sub>2</sub>	0.35			
str./str.	=C-C/C=C-C	0.78			
	-C-H/-C-H(CH <sub>3</sub> )	0.05	0.05	0.04	0.07
	-C-H/-C-H(CH <sub>2</sub> )				0.06
str./bend	C=C/C=C-H	0.39	0.41	0.38	0.44
	C=C/C-C-C(=CC <sub>2</sub> )	-0.43			
	C=C/C-C-H(=CH)		-0.21	-0.36	
	C-C/C-C-C	0.32			0.22
	C-C/C-C-H(CH <sub>3</sub> )	0.33	0.25	0.24	0.36
	C-C/C-C-H(CH <sub>2</sub> )				0.27
bend/bend	C-C-H/C-C-H(CH <sub>3</sub> ) (C-C common)	-0.04	-0.02	-0.02	-0.01
	C-C-H/C-C-H(CH <sub>2</sub> ) (C-C common)				-0.03/-0.22
	C-C-H/C-C-H( <i>anti</i> )				0.11
	C=C-H/C=C-H( <i>cis</i> )			0.10	
	C=C-C/C=C-C		0.18	0.43	
	C=C-C/C-C-C( <i>syn</i> )				-/0.52
tors./o.o.p.	C=C/CH				-0.06/-0.02
o.o.p./o.o.p.	=CH/CH			-0.03	

<sup>a</sup> Conversion to SI units:  $1 \text{ mdyn} \text{\AA}^{-1} = 10^2 \text{ Nm}^{-1}$  and  $1 \text{ mdyn} \text{\AA} \text{ rad}^{-2} = 10^{-18} \text{ Nm rad}^{-2}$ .

Table 2. Vibrational frequencies of isobutene as calculated from the valence force field in Table 1. Potential energy distribution (P.E.D) includes contributions larger than 20 %.

		Frequencies (cm <sup>-1</sup> )		P.E.D. <sup>b</sup>
		Obs. <sup>a</sup>	Calc.	
A <sub>1</sub>	v <sub>1</sub>	2988	2981	=C-H(99)
	v <sub>2</sub>	2942	2956	-C-H(100)
	v <sub>3</sub>	2916	2904	-C-H(97)
	v <sub>4</sub>	1653	1653	C=C(84)
	v <sub>5</sub>	1438	1437	H-C-H(72)
	v <sub>6</sub>	1421	1417	H-C-H(=CH <sub>2</sub> ) (47)C=C-H(29)
	v <sub>7</sub>	1376	1382	C-C-H(53)H-C-H(50)
	v <sub>8</sub>	1058	990	C-C-H(75)
	v <sub>9</sub>	809	807	C-C(74)
	v <sub>10</sub>	389	390	C-C-C(56)C=C-C(38)
A <sub>2</sub>	v <sub>11</sub>	2956	2954	-C-H(100)
	v <sub>12</sub>	1438	1436	H-C-H(91)
	v <sub>13</sub>	969	965	C-C-H(84)
	v <sub>14</sub>	685	689	tC=C(98)
	v <sub>15</sub>		193	tC-C(100)
B <sub>1</sub>	v <sub>16</sub>	3077	3082	=C-H(99)
	v <sub>17</sub>	2968	2955	-C-H(100)
	v <sub>18</sub>	2898	2903	-C-H(98)
	v <sub>19</sub>	1430	1439	H-C-H(88)
	v <sub>20</sub>	1386	1383	H-C-H(52)C-C-H(46)
	v <sub>21</sub>	1271	1278	C-C(59)C=C-H(22)C-C-C(20)
	v <sub>22</sub>	996	959	C-C-H(63)C=C-H(26)
	v <sub>23</sub>	958	879	C-C(53)C=C-H(44)
	v <sub>24</sub>	438	435	C=C-C(77)C-C(20)
B <sub>2</sub>	v <sub>25</sub>	2956	2954	H-C-H(100)
	v <sub>26</sub>	1458	1441	H-C-H(88)
	v <sub>27</sub>	1085	1061	C-C-H(90)
	v <sub>28</sub>	889	892	w=CH <sub>2</sub> (91)
	v <sub>29</sub>	438	430	w=CC <sub>2</sub> (90)
	v <sub>30</sub>	197 <sup>c</sup>	201	tC-C(100)

<sup>a</sup> Observed frequencies from Ref. 7 when otherwise not indicated. <sup>b</sup> w and t denote out-of-plane and torsion, <sup>c</sup> Ref. 8.

removed without introducing further complexity in the force field. Both torsional frequencies, gas phase values from Ref. 12, were well reproduced by  $f_{\tau}=0.06 \text{ mdyn} \cdot \text{\AA} \cdot \text{rad}^{-2}$ , equal to the  $f_{\tau}$  value obtained from a MM calculation.

The most noticeable difference between the present VFF and the one presented in Ref. 10 is, besides the simpler calculation of the =C-H out-of-plane wag frequencies, the value of the C=C-H force constant. The value obtained in the present work is similar to values used for other alkenes<sup>21-23</sup> and the value used in another in-plane normal coordinate analysis of the 2-butenes.<sup>27</sup>

*cis*-2-Butene. As for *trans*-2-butene, there has been developed a VFF for *cis*-2-butene.<sup>11</sup> That calculation<sup>11</sup> was based upon Raman observed frequencies. By taking into consideration infrared observations as well, it appears that one band of strong intensity in the IR spectrum was not included there. This is an obvious fundamental, at  $566 \text{ cm}^{-1}$ ,<sup>9</sup> which actually was used in an early calculation.<sup>14</sup>

The *cis*-2-butene geometry was found in Ref. 28. When the force field of the *trans*-2-butene was directly transferred to *cis*-2-butene, the B<sub>2</sub> frequency associated with C=C-C bend was calculated noticeably below  $566 \text{ cm}^{-1}$ . It was

Table 3. Vibrational frequencies of *trans*-2-butene as calculated from the valence force field in Table 1. Potential energy distribution (P.E.D), includes contributions larger than 20 %.

	Frequencies (cm <sup>-1</sup> )		P.E.D. <sup>b</sup>
	Obs. <sup>a</sup>	Calc.	
A <sub>g</sub> v <sub>1</sub>	2998	3022	=C-H(97)
v <sub>2</sub>	2936	2947	-C-H(100)
v <sub>3</sub>	2854	2874	-C-H(97)
v <sub>4</sub>	1668	1667	C=C(84)
v <sub>5</sub>	1441	1443	H-C-H(90)
v <sub>6</sub>	1386	1379	C-C-H(24)C-C(24)H-C-H(22)
v <sub>7</sub>	1304	1334	C-C-H(36)H-C-H(28)C=C-H(20)
v <sub>8</sub>	1138	1094	C-C-H(30)C-C-H(=C-H) (30)
v <sub>9</sub>	861	906	C-C-H(55)C-C(20)
v <sub>10</sub>	501	500	C=C-C(42)C-C(27)
B <sub>g</sub> v <sub>11</sub>	2970	2945	-C-H(100)
v <sub>12</sub>	1452	1442	H-C-H(93)
v <sub>13</sub>	1041	1044	C-C-H(77)
v <sub>14</sub>	755	758	w=CH(84)
v <sub>15</sub>	216 <sup>c</sup>	217	tC-C(98)
A <sub>u</sub> v <sub>16</sub>	2969	2946	-C-H(100)
v <sub>17</sub>	1444	1443	H-C-H(93)
v <sub>18</sub>	1042	1024	C-C-H(76)
v <sub>19</sub>	973	974	tC=C(55)w=CH(28)
v <sub>20</sub>	260	232	w=CH(55)tC=C(41)
v <sub>21</sub>	164 <sup>c</sup>	173	tC=C(94)
B <sub>u</sub> v <sub>22</sub>	3016	2997	=C-H(100)
v <sub>23</sub>	2937	2946	-C-H(100)
v <sub>24</sub>	2961	2874	-C-H(97)
v <sub>25</sub>	1451	1493	H-C-H(93)
v <sub>26</sub>	1373	1369	C-C-H(47)H-C-H(37)C-C(26)
v <sub>27</sub>	1364	1305	C-C-H(=CH) (35)C=C-H(30)
v <sub>28</sub>	1062	1064	C-C(60)
v <sub>29</sub>	983	998	C-C-H(63)
v <sub>30</sub>	294	289	C=C-C(91)

<sup>a</sup> Observed frequencies from Ref. 10 when otherwise not indicated. <sup>b</sup> w and t denote out-of-plane and torsion, respectively. <sup>c</sup> Ref. 12.

necessary to increase  $f(\text{C}=\text{C}-\text{C}/\text{C}=\text{C}-\text{C})$  as compared to the *trans* case and at the same time also increase  $f(\text{C}=\text{C}-\text{C})$ .

It is not surprising that there should be a more pronounced  $\text{C}=\text{C}-\text{C}/\text{C}=\text{C}-\text{C}$  interaction in *cis*-2-butene than in *trans*-2-butene. However, the calculations in Refs. 10 and 11 showed a larger negative value for  $f(\text{C}=\text{C}-\text{C}/\text{C}=\text{C}-\text{C})$  when passing from *trans* to *cis*. As a qualitative aid, the valence force constant matrices obtained from the MM calculations were investigated. Of course, comparative conclusions from such a calculation must be made carefully, since the interactions in the actual VFF have been chosen

from criteria which make it less general than the one obtained from the MM calculations. However, it should be reasonable to make a search for outstanding large values among the non-diagonal terms, as well as indications of relative magnitude. In fact, comparison between MM obtained force constant matrices of *trans*- and *cis*-2-butene showed the *cis*  $\text{C}=\text{C}-\text{C}/\text{C}=\text{C}-\text{C}$  interaction to be definitely larger than the corresponding *trans* interaction,  $0.50 \text{ m dyn} \cdot \text{\AA} \cdot \text{rad}^{-2}$ . It was also noted that  $f(\text{C}=\text{C}-\text{C})$  increased by ca. 25 % from *trans* to *cis*-2-butene, again in agreement with what had already been obtained (Table 1). In Ref. 11 the  $\text{C}=\text{C}-\text{C}$  bend frequency was

taken as  $687\text{ cm}^{-1}$ , which has been assigned to  $=\text{C}-\text{H}$  out-of-plane in another work.<sup>9</sup> The latter interpretation goes along well with the initial calculation,  $642\text{ cm}^{-1}$ . The  $B_1$  ( $687\text{ cm}^{-1}$ ) and the lowest  $A_2$  ( $394\text{ cm}^{-1}$ ) frequencies associated with  $=\text{C}-\text{H}$  out-of-plane and  $\text{C}=\text{C}$  torsion were well reproduced without introducing much complementary in the force field. However, it was not possible, in a simple way, to bring the third of these frequencies down to  $852\text{ cm}^{-1}$ , the observation used in Ref. 11. There might well be pronounced interactions between the out-of-plane modes in *cis*-2-butene. The actual force constants were adjusted to fit the 394 and  $687\text{ cm}^{-1}$  observations. Then the third frequency was

calculated to  $962\text{ cm}^{-1}$ , which at least is not an unreasonable value. The final force field is given in Table 1, and frequency data in Table 4. Only one gas phase  $\text{C}-\text{C}$  torsional frequency has been observed.<sup>12</sup> This frequency was well fitted (see Table 4) by  $f_\tau = 0.02\text{ mdyn} \cdot \text{\AA} \cdot \text{rad}^{-2}$ , only  $0.01\text{ mdyn} \cdot \text{\AA} \cdot \text{rad}^{-2}$  lower than the MM calculated value.

1. *Butene*. 1-Butene is different from the other butenes in that there is one ethyl group instead of two methyl groups. This may cause more difficulties in the calculation of the frequencies associated with the various CCH bends. Several investigations have established the frequency assignments.<sup>1,4,9,13</sup> The interpretation given in Ref. 13

Table 4. Vibrational frequencies of *cis*-2-butene as calculated from the valence force field in Table 1. Potential energy distribution (P.E.D) includes contributions larger than 20 %.

	Frequencies ( $\text{cm}^{-1}$ )		P.E.D. <sup>b</sup>	
	Obs. <sup>a</sup>	Calc.		
$A_1$	$v_1$	3011	2996	$=\text{C}-\text{H}(98)$
	$v_2$	2932	2941	$-\text{C}-\text{H}(100)$
	$v_3$	2862	2869	$-\text{C}-\text{H}(98)$
	$v_4$	1662	1661	$\text{C}=\text{C}(81)\text{C}-\text{C}(21)$
	$v_5$	1462	1443	$\text{H}-\text{C}-\text{H}(91)$
	$v_6$	1384	1395	$\text{C}-\text{C}-\text{H}(54)\text{H}-\text{C}-\text{H}(50)$
	$v_7$	1257	1260	$\text{C}=\text{C}-\text{H}(47)\text{C}-\text{C}-\text{H}(=\text{CH})$ (44)
	$v_8$	1010	1049	$\text{C}-\text{C}-\text{H}(56)\text{C}-\text{C}(28)$
	$v_9$	874	872	$\text{C}-\text{C}(43)\text{C}-\text{C}-\text{H}(30)$
	$v_{10}$	302	302	$\text{C}=\text{C}-\text{C}(58)$
$A_2$	$v_{11}$	2958	2940	$-\text{C}-\text{H}(100)$
	$v_{12}$	1438	1444	$\text{H}-\text{C}-\text{H}(91)$
	$v_{13}$	1038	1069	$\text{C}-\text{C}-\text{H}(45)\text{w}=\text{CH}(39)$
	$v_{14}$	852	962	$\text{C}-\text{C}-\text{H}(40)\text{tC}=\text{C}(38)\text{w}=\text{CH}(24)$
	$v_{15}$	394	392	$\text{tC}=\text{C}(47)\text{w}=\text{CH}(38)$
	$v_{16}$		106	$\text{tC}-\text{C}(98)$
$B_1$	$v_{17}$	2958	2939	$-\text{C}-\text{H}(100)$
	$v_{18}$	1438	1443	$\text{H}-\text{C}-\text{H}(91)$
	$v_{19}$	974	1018	$\text{C}-\text{C}-\text{H}(84)$
	$v_{20}$	$685^c$	675	$\text{w}=\text{CH}(93)$
	$v_{21}$	$101^d$	103	$\text{tC}-\text{C}(98)$
$B_2$	$v_{22}$	2980	2992	$=\text{C}-\text{H}(99)$
	$v_{23}$	2929	2940	$-\text{C}-\text{H}(100)$
	$v_{24}$	2862	2869	$-\text{C}-\text{H}(98)$
	$v_{25}$	1445	1443	$\text{H}-\text{C}-\text{H}(91)$
	$v_{26}$	1427	1425	$\text{C}-\text{C}(36)\text{C}-\text{C}-\text{H}(30)\text{H}-\text{C}-\text{H}(28)$
	$v_{27}$	1357	1360	$\text{C}=\text{C}-\text{H}(28)\text{C}-\text{C}-\text{H}(25)\text{H}-\text{C}-\text{H}(23)$
	$v_{28}$	$1134^c$	1083	$\text{C}-\text{C}-\text{H}(46)$
	$v_{29}$	974	968	$\text{C}-\text{C}-\text{H}(35)\text{C}-\text{C}(33)$
	$v_{30}$	$566^c$	576	$\text{C}=\text{C}-\text{C}(94)$

<sup>a</sup> Observed frequencies from Ref. 11 when otherwise not indicated. <sup>b</sup> w and t denote out-of-plane and torsion, respectively. <sup>c</sup> Ref. 9. <sup>d</sup> Ref. 12.

was used, and the geometry was that of Ref. 28. Initial force constants were taken from 3-butenenitrile<sup>20</sup> and isobutene.

In the region 900–1200 cm<sup>-1</sup> it was not possible to simultaneously calculate all frequencies well. Those frequencies attributed to C–C stretch were considered most important, although such a preference must be somewhat arbitrary since the potential energy distribution description (Table 5) showed highly mixed contributions in this region.

By introducing one additional interaction within the ethyl group (C–C–H/C–C–H<sub>anti</sub>) the CCH bends outside 900–1200 cm<sup>-1</sup> were repro-

duced well. Some of the CCH rock frequencies were not well fitted. To correct this required alterations which made the force field extend beyond the scope of this work. The frequencies of the *syn* conformer was not successfully calculated by use of the *gauche* VFF. The necessary changes in the force field were mainly made among the interactions. The positioning of the CH<sub>3</sub> group relative to the =CH<sub>2</sub> group in the *syn* form is similar to the mutual position of the two CH<sub>3</sub> groups in *cis*-2-butene. In fact, the alterations in force constants found to work best for *syn* 1-butene was an increase of the values of  $f(C=C-C)$  and  $f(C-C-C)$  along with the intro-

Table 5. Vibrational frequencies of 1-butene as calculated from the valence force field in Table 1. Potential energy distribution (P.E.D.) includes contributions larger than 15 %.

		Frequencies (cm <sup>-1</sup> )				P.E.D. <sup>b</sup>
		<i>syn</i>		<i>gauche</i>		
		Obs. <sup>a</sup>	Calc.	Obs. <sup>a</sup>	Calc.	
A'	v <sub>1</sub>	3090	3098	3090	3098	=C <sub>1</sub> -H(99)
	v <sub>2</sub>	3019	3021	3019	3021	=C <sub>2</sub> -H(81)
	v <sub>3</sub>	3008	2997	3008	2997	=C <sub>1</sub> -H(82)
	v <sub>4</sub>	2982	2985	2982	2984	-C <sub>4</sub> -H(100)
	v <sub>5</sub>	2952	2936	2948	2936	-C <sub>4</sub> -H(97)
	v <sub>6</sub>	2888	2895	2888	2894	-C <sub>3</sub> -H(98)
	v <sub>7</sub>	1643	1646	1647	1648	C=C(81)
	v <sub>8</sub>	1460	1466	1463	1465	H-C <sub>4</sub> -H(82)
	v <sub>9</sub>	1450	1442	1444	1442	H-C <sub>3</sub> -H(72)
	v <sub>10</sub>	1426	1410	1421	1412	H-C <sub>1</sub> -H(46)C=C <sub>1</sub> -H(32)
	v <sub>11</sub>	1380	1379	1380	1377	C-C <sub>4</sub> -H(53)H-C <sub>4</sub> -H(50)
	v <sub>12</sub>	1342	1345	1296	1285	C-C <sub>3</sub> -H(76)
	v <sub>13</sub>	1306	1300	1318	1329	C-C <sub>3</sub> -H(20)C=C <sub>2</sub> -H(19)C=C <sub>1</sub> -H(15)
	v <sub>14</sub>	1128	1007	1128	977	C-C <sub>4</sub> -H(28)C=C <sub>1</sub> -H(18)
	v <sub>15</sub>	1071	1109	1079	1133	C-C <sub>3</sub> -H(22)C=C <sub>1</sub> -H(17)C=C <sub>2</sub> -H(15)
	v <sub>16</sub>	988	987	1020	1020	C-C-H <sub>3</sub> (76)
	v <sub>17</sub>	836	818	854	851	=C-C(34)C-C <sub>4</sub> -H(25)C=C <sub>1</sub> -H(22)
	v <sub>18</sub>	540	540	439	440	C=C-C(60)
	v <sub>19</sub>	311	311	301	302	C-C-C(69)
A''	v <sub>20</sub>	2978	2985	2987	2985	-C <sub>4</sub> -H(100)
	v <sub>21</sub>	2936	2927	2936	2929	-C <sub>3</sub> -H(100)
	v <sub>22</sub>	1469	1459	1469	1461	H-C <sub>4</sub> -H(91)
	v <sub>23</sub>	1264	1268	1264	1253	C-C <sub>3</sub> -H(73)
	v <sub>24</sub>	1177	1076	1177	1047	C-C <sub>4</sub> -H(36)C-C <sub>3</sub> -H(25)
	v <sub>25</sub>	999	1002	993	988	C=C <sub>1</sub> -H(23)tC=C(20)w=CH <sub>2</sub> (19)w=CH(16)
	v <sub>26</sub>	915	922	912	912	w=CH <sub>2</sub> (56)tC=C(39)
	v <sub>27</sub>	784	782	784	784	C-C <sub>3</sub> -H(53)C-C <sub>4</sub> -H(41)
	v <sub>28</sub>	551	551	634	632	w=CH(48)tC=C(22)
	v <sub>29</sub>	285 <sup>c</sup>	294	230 <sup>c</sup>	228	tC-CH <sub>3</sub> (93)
	v <sub>30</sub>	154	153	103	105	t=C-C(93)

<sup>a</sup> Observed frequencies from Ref. 13 when otherwise not stated. <sup>b</sup> The carbon skeleton is numbered as C<sub>1</sub>=C<sub>2</sub>-C<sub>3</sub>-C<sub>4</sub>; w and t denote out-of-plane and torsion, respectively, <sup>c</sup> Ref. 4.

duction of an interaction between them. This parallels the increase in  $f(\text{C}=\text{C}-\text{C})$  and  $f(\text{C}=\text{C}-\text{C}/\text{C}=\text{C}-\text{C})$  when passing from *trans*- to *cis*-2-butene. Again, an MM calculation of the general VFF for 1-butene showed exactly the same trend. Final force constants and the corresponding calculated frequencies are listed in Tables 1 and 5, respectively.

The torsional frequencies were initially calculated from the MM obtained  $f_t$ 's, 0.06/0.07 and 0.10/0.15  $\text{mdyn} \cdot \text{\AA} \cdot \text{rad}^{-2}$  for  $=\text{C}-\text{C}$  and  $\text{C}-\text{CH}_3$  torsion, respectively, of *gauche/syn* conformer. Only the  $=\text{C}-\text{C}$  torsional frequencies were assigned in Ref. 13, and by increasing the *syn*  $f_t$  ( $=\text{C}-\text{C}$ ) to 0.11  $\text{mdyn} \cdot \text{\AA} \cdot \text{rad}^{-2}$  the observations were practically reproduced. The calculated *gauche*  $\text{C}-\text{CH}_3$  torsional frequency of  $228 \text{ cm}^{-1}$  and the *syn* value of  $294 \text{ cm}^{-1}$  are in good agreement with an assignment proposed earlier.<sup>4</sup>

The present VFF has been combined with a 3-chloro-1-propene VFF to serve a normal coordinate analysis of 3-chloro-1-butene.<sup>29</sup> That calculation seemed to give reliable frequencies, just as was the case when a combination was made with an acetylchloride VFF in a normal coordinate analysis of propionylchloride.<sup>30</sup>

**Comparison.** Taking into consideration the low number of force constants relative to the number of frequencies, it is almost surprising that the value of each type of force constant shows only small variation from molecule to molecule. There are only a couple of exceptions. The first has already been discussed, namely the increase of certain force constants when two CCC angles are in an eclipsed position. This may be accounted for as due to increased strain when such a positioning occurs.

The  $=\text{C}-\text{C}$  stretch force constant of isobutene, being  $4.24 \text{ mdyn} \cdot \text{\AA}^{-1}$  is distinctly lower than the other  $f(\text{C}=\text{C})$  in Table 1. However, the corresponding value obtained for 3-butenitrile<sup>20</sup> was  $4.17 \text{ mdyn} \cdot \text{\AA}^{-1}$  and  $4.24 \text{ mdyn} \cdot \text{\AA}^{-1}$  for  $f(\text{C}=\text{C})$ . One similarity between isobutene and 3-butenitrile may in this connection be that both molecules have two sequential  $\text{C}-\text{C}$  bonds, both of which are connected to an unsaturated bond; although it is not obvious how this should be linked to the low  $f(\text{C}=\text{C})$  value, which may merely be accidental because of the particular construction of the force field.

Both for the 2-butenes and the 1-butene the  $f(\text{C}=\text{C})$  values are close to what was expected from similar molecules,<sup>21-23</sup> while  $f(\text{C}-\text{CH}_3)$  is more like the alkane VFF value.<sup>31</sup> Regarding the  $\text{C}-\text{C}$  stretch force constants in 1-butene, their values were of course dependent upon the interpretation of the frequencies between  $900$  and  $1200 \text{ cm}^{-1}$ .

## CONCLUSION

The present work was undertaken because of the need for consistent, simple VFF for the various butenes. Since the force fields were intended to be used for separate related molecules, no effort was made to calculate an overlay force field, although such a calculation could most likely be well performed on the basis of the present results.

To some extent the transferability of the force fields presented here have been tested, and with promising results.<sup>24,29,30</sup> All essential features of the observed spectra were reproduced by the calculations, and good agreements were obtained for the skeleton frequencies. Even a more accurate force field for the butene would hardly give a better combined force field for the substituted molecule.

The force fields were not aimed at doing a complete job in calculating the butene frequencies. And, as anticipated it was not possible to obtain good calculated values for all CCH bend frequencies. Associated with two  $\text{CH}_3$  groups there are 10 such frequencies, which should be reproduced by the 4 distinct force constants  $f(\text{C}-\text{C}-\text{H})$ ,  $f(\text{H}-\text{C}-\text{H})$ ,  $f(\text{C}-\text{C}/\text{C}-\text{C}-\text{H})$  and  $f(\text{C}-\text{C}-\text{H}/\text{C}-\text{C}-\text{H})$ . Despite the choice to keep the number of CCH related force constants low and rather accept a few larger deviations among the CCH rock frequencies, the average deviations from experimental frequencies were satisfactory. The 30 fundamental frequencies of isobutene, *trans*-2-butene, *cis*-2-butene and 1-butene were calculated to an average deviation of 12, 17, 11 and  $15 \text{ cm}^{-1}$  totally and 6, 14, 6 and  $5 \text{ cm}^{-1}$  when disregarding frequencies described as CCH rock.

Altogether, the intended level of accuracy, the wanted simplicity and consistency, as well as satisfactory transferability was obtained, all with force constants of reasonable magnitude and interactions of reasonable types. Even the choice



of the less obvious CCC/CCC interaction and increase of  $f(\text{CCC})$  when eclipsing arrangement of two bonds occurs, has been justified *a posteriori* by the MM calculations.

## REFERENCES

1. Sheppard, N. J. *Chem. Phys.* 17 (1949) 74.
2. Richards, C. M. and Nielsen, J. R. *J. Opt. Soc. Am.* 40 (1950) 442.
3. Sverdlov, L. M. *Opt. Spectrosk.* 1 (1956) 752.
4. Harrah, L. A. *Wright Air Development Division (U.S.A.F.) TR-61-82* (1961).
5. Lüttke, W. and Braun, S. *Ber. Bunsenges. Phys. Chem.* 71 (1967) 34.
6. Pathak, C. M. and Fletscher, W. H. *J. Mol. Spectrosc.* 31 (1969) 32.
7. Harris, W. C. and Levin, I. W. *J. Mol. Spectrosc.* 39 (1971) 441.
8. Dwig, J. R., Hawley, W. C. and Bragin, J. J. *Chem. Phys.* 57 (1972) 1426.
9. Barnes, A. J. and Howells, J. D. R. *J. Chem. Soc. Faraday Trans 2*, 69 (1973) 532.
10. Levin, I. W., Pearce, R. A. R. and Harris, W. C. *J. Chem. Phys.* 59 (1973) 3048.
11. Levin, I. W. and Pearce, R. A. R. *J. Mol. Spectrosc.* 49 (1974) 91.
12. Durig, J. R., Hudson, S. D. and Natters, W. J. *J. Chem. Phys.* 70 (1979) 5747.
13. Durig, J. R. and Compton, D. A. C. *J. Phys. Chem.* 84 (1980) 773.
14. Kilpatrick, J. E. and Pitzer, K. S. *J. Res. Natl. Bur. Stand.* 38 (1947) 191.
15. Shimanouchi, T., Yasuaki, A. and Alaki, Y. *Polym. J.* 2 (1971) 199.
16. Ermer, O. and Lifson, S. *J. Am. Chem. Soc.* 95 (1973) 4121.
17. Cyvin, S. J. *Molecular Vibrations and Mean Square Amplitudes*, Universitetsforlaget, Oslo 1968.
18. Hilderbrandt, R. L. and Wieser, J. D. *J. Chem. Phys.* 55 (1971) 4648.
19. Tokue, I., Fukuyama, T. and Kuchitsu, K. *J. Mol. Struct.* 23 (1974) 33.
20. Schei, S. H. *J. Mol. Struct.* 98 (1983) 141.
21. Zerbi, G. and Gusoni, M. *Spectrochim. Acta* 22 (1966) 2111.
22. Califano, S. *Pure Appl. Chem.* 18 (1969) 353.
23. Mannik, L. and Phibbs, M. K. *Report RR. 75.2A*, Research Centre, Kingston, Ontario 1975.
24. Schei, S. H. *Spectrochim. Acta Part A* 39 (1983) 327.
25. Schei, S. H. *Spectrochim. Acta Part A* 39 (1983) 1043.
26. Abraham, R. J. and Stølevik, R. *Chem. Phys. Lett.* 58 (1978) 622.
27. Almenningsen, A., Anfinson, I. M. and Haaland, A. *Acta Chem. Scand.* 24 (1970) 43.
28. Van Hemelrijk, D., Van den Enden, L., Geise, H. J., Sellers, H. L. and Schäfer, L. *J. Am. Chem. Soc.* 102 (1980) 2189.
29. Schei, S. H. and Klæboe, P. *Acta Chem. Scand. A* 37 (1983) 315.
30. Dyngeseth, S., Schei, S. H. and Hagen, K. *J. Mol. Struct.* 116 (1984) 257.
31. Snyder, R. G. and Schachtschneider, J. H. *Spectrochim. Acta* 21 (1965) 169.

Received December 14, 1983.