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Conclusions

Energy levels in a phen chromophore are particularly sensitive to electron-donating substituents in the 4,7 positions. Other substituent groups in these positions should lead to a series of singlet manifold. This theory is currently being tested and will be the subject of a future report.

Improved Force Field of (E)-1,3,5-Hexatriene Based on Deuterated Derivatives

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Raman and infrared spectra of ground-state (E)-1,3,5-hexatriene-3,4-d2 (d34EHT), (E)-1,3,5-hexatriene-3-d (d3EHT), (E)-1,3,5-hexatriene-1,2-d2 (d11EHT), and (E)-1,3,5-hexatriene-2,5-d2 (d25EHT) are reported. Together with previously published spectra of (E)-1,3,5-hexatriene (EHT), these spectra are used to refine a scaled ab initio force field from the literature, calculated at the HF/6-31G level, and the spectra of EHT, d34EHT, d3EHT, d11EHT, and d25EHT are interpreted by use of the resulting refined force field. The changes in the force field are discussed, as are the changes in normal modes upon deuteration.

Introduction

Vibrational analysis of 1,3,5-hexatriene has been a matter of interest since Lippincott's early reports.12 We have studied the vibrations of 1,3,5-hexatriene and methylated derivatives both in the ground state23 and in the lowest excited triplet state.5-9 The analysis of excited-state vibrational spectra is difficult, since the knowledge of geometry and bond properties in excited states is limited. One effort to understand the excited-state vibrations is the investigation of excited states of isotopically substituted compounds, and we have started work in this direction.9 Another effort is the correlation between excited-state and ground-state vibrations, although it should be applied with caution due to the rotation of normal modes (Duschinsky effect). Here, it is important that the vibrational analysis of the ground state is complete and correct. Consequently, isotopically substituted compounds should be investigated in the ground state as well.

Recently, four groups have published calculations on the vibrations of (E)-1,3,5-hexatriene: Hemley et al. (HBK),10 Bock et al. (BPKP),11 Fogarasi et al. (FSLBP),12 and Yoshida et al. (YFT).13 Furthermore, a detailed study of the influence of electron correlation on the force field of the in-plane vibrations has appeared (SKL).14 The calculations by HBK are semiempirical, whereas the latter four are ab initio. The results of

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Capillaries were cooled briefly, sealed, and kept in a freezer. Small samples were isolated by use of preparative gas chromatography. Earlier,9 From the mixture of triene and toluene thus obtained in toluene. Is This method is far superior to the pyrolysis we used for the above reasons, we found it important to investigate additional deuterated analogues of (E)-1,3,5-hexatriene (EHT). We have recently published the ground-state Raman and resonances. Raman spectra of (E)-1,3,5-hexatriene-3,4-d4 (d34EHT) and the resonances Raman spectrum of (E)-1,3,5-hexatriene-2,5-d2 (d25EHT).9 In the present paper we report the ground-state Raman and Fourier transform (FT) infrared spectra of d34EHT, (E)-1,3,5-hexatriene-3-d (d3EHT), and (E)-1,3,5-hexatriene-1,1-d2 (d11EHT). These spectra are used together with the previously published spectra of EHT1,5 to establish a force field.

Among these, EHT, d34EHT, d25EHT, and d2345EHT transform according to C2v symmetry and so obey the exclusion principle between Raman and infrared-active vibrational transitions; d3EHT and d11EHT transform according to C1 symmetry.

Materials

The synthesis of (E)-1,3,5-hexatriene-3,4-d4 and (E)-1,3,5-hexatriene-2,5-d2 has been described previously.9 (E)-1,3,5-Hexatriene-3,4-d4 was prepared by reduction of 3-hexyne-2,5-diol with lithium aluminum hydride/D2O2 acetylation, and elimination of acetic acid using palladium(II) acetate and triphenylphosphine in toluene. 18 This method is far superior to the pyrolysis we used earlier.9 From the mixture of triene and toluene thus obtained small samples were isolated by use of preparative gas chromatography (Varian 2700, Ucon column, He carrier gas, 60 °C). (E)-1,3,5-Hexatriene-1,1-d2 was synthesized starting from (E): (E)-2,4-hexadienoic acid. Reduction with LiAlD4 in ether/THF afforded hexa-2,4-dien-1-ol-1,1-d2, which was acetylated and converted to the triene as described above. The purified samples were distilled into glass capillaries under reduced pressure. The capillaries were cooled briefly, sealed, and kept in a freezer.

Capillary gas chromatography (DB225 column, 30-55 °C, carrier gas He) showed the sample of d34EHT to contain 98% of the E isomer and 2% of the Z isomer and the sample of d11EHT to contain 96% of the E isomer and 4% of the Z isomer, whereas for d34EHT and d25EHT no isomeric or other impurities were found. A high deuterium content (>95%) of the deuteriated products was indicated by 1H NMR spectrometry (Bruker WM300, 300 MHz).

Experimental Methods

The Raman spectra were obtained of the samples in the capillary glass tubes, with outer diameter 3 (d34EHT and d11EHT) or 4 mm (d3EHT), thermostated at 10 °C. Afterward, the samples were transferred under argon to a vacuum line and from this to spectroscopic cells for gas-phase FT-infrared spectra at room temperature.

The Raman and FT-infrared spectrometers have been described in detail previously.14 Raman spectra were recorded in the region 3400-10 cm-1 with 514.5-nm excitation. Perpendicular illumination with vertically polarized light was used in a horizontal scattering plane; spectra were obtained in I(IV) and I(VI) configurations. The spectral slit width was 2.9 cm-1 or less.

Mid infrared spectra were obtained in the region 4000-500 cm-1 with a resolution of 0.5 cm-1. A Ge/KBr beam splitter and a liquid nitrogen cooled MCT detector with KBr windows were used. The spectroscopic cell was a 10-cm gas cell with KBr windows. For d34EHT and d3EHT, infrared spectra were obtained in the region 700-50 cm-1, with 1-cm-1 resolution, a 3.5-μm Myler beam splitter, a room temperature DTGS detector with polyethylene (PE) windows, and a 20-cm cell with PE windows. For d11EHT, an infrared spectrum was obtained in the region 700-300 cm-1, with 1-cm-1 resolution, a Ge/KBr beam splitter, the DTGS detector, and a 10-cm cell with KBr windows.

Experimental Results

The Raman spectra of neat d34EHT and d11EHT are shown in Figures 1 and 2, respectively. For d34EHT and d25EHT, the Raman spectra and their experimental conditions are found in ref 9. For d25EHT, the Raman spectrum was only obtained in connection with time-resolved resonance Raman studies of the lowest excited triplet state,9 from acetonitrile solution with 317.5-nm excitation, and only the strongest Raman bands were observed. Due to a very limited amount of sample of d25EHT, we could not obtain in full Raman and infrared spectra of this compound. The infrared and Raman spectra of EHT, and their experimental conditions, are found in ref 3. The Raman spectra in the R(0) representation6,9 of the region below 400 cm-1 are shown in parts A, B, and C of Figure 3 for d34EHT, d3EHT, and d11EHT, respectively. The infrared spectra of d34EHT, d3EHT, and d11EHT are only listed in the tables (see below); however, they are available on request.

The wavenumbers, intensities, and depolarization ratios of Raman bands, and wavenumbers, intensities, and band contours of infrared bands, are listed in Tables I, II, and III for d34EHT, d3EHT, and d11EHT, respectively, together with calculated frequencies and potential energy distributions (PED) of the normal modes (see below). The Raman wavenumbers, intensities, and depolarization ratios listed in Tables I-III for bands below 400 cm-1 were obtained from the R(0) spectra. For d25EHT, the wavenumbers and intensities of Raman bands are listed in Table IV, together with calculated frequencies and PED of the normal modes. The experimentally observed wavenumbers of fundamentals of EHT from ref 3 are listed in Table V, together with calculated frequencies and PED of the normal modes from the present study.

If one accepts the view proposed previously9 that the observed EHT Raman bands at 1637 and 1623 cm-1 are due to a Fermi resonance between an 1188 + 444 cm-1 combination and the + + + C=C stretching mode, the unperturbed + + + mode is predicted at 1628 cm-1. This value is entered in Table V. The value observed previously by us for the highest wavenumber C=C torsion of b2 symmetry (428 cm-1) is too far from the calculated value (612 cm-1) and has been replaced in Table V by the frequency observed in the crystalline phase in a later study (615 cm-1).13

For the region 3400–2000 cm⁻¹, only those Raman and infrared bands are reported that may possibly be attributed to CH or CD stretch fundamentals. This is done in Table VI for the four compounds EHT, d34EHT, d3EHT, and d11EHT. In Table VII, these CH and CD stretches are assigned to the calculated frequencies and the PED of the normal modes are listed.

Theoretical Methods
In the analysis of the observed vibrational spectra we used two computer programs, VIBROT and FLINDA, both based on a valence force field. FLINDA is used to refine a valence force field from starting values of the force constants. The input consists of the molecular geometry, the internal coordinates, the nuclear masses, the experimentally observed frequencies, and starting values for the valence force field. For each force constant, it is specified whether it should be kept fixed or varied in the refinement. By least-squares analysis, FLINDA iterates a new force field.

VIBROT subsequently calculates the wavenumbers and internal-coordinate compositions of the normal modes from the molecular geometry, the internal coordinates, the nuclear masses, and the refined valence force field. The VIBROT and FLINDA calculations were carried out on an RC 8000 computer.

With respect to the equilibrium molecular structure of (E)-1,3,5-hexatriene a choice has to be made: On the one hand, the only experimental study of the geometry of EHT (gas-phase electron diffraction) is more than 20 years old; on the other hand, the geometry has been calculated theoretically in several recent studies, using mainly ab initio methods. Theoretical geometries agree well with each other, but the agreement between the theoretical geometries on one side and the experimental one


important geometrical parameters, especially the length of the central C=C bond. The internal coordinates used in the present study are defined in Figure 4 and Table IX. They are identical with those of BPKP, although our numbering is different. (Although we use the term internal coordinates, the coordinates in Table IX are strictly speaking group coordinates.)

As mentioned above, d3EHT and d11EHT transform according to D3h symmetry. For this reason, we performed the calculations for all molecules investigated under the assumption of C3v symmetry, i.e., with the in-plane vibrations of a′ symmetry and the out-of-plane vibrations of a″ symmetry. The experimental frequencies used for d3EHT and d11EHT, where vibrations may be both Raman and infrared active, were mostly Raman values.

The starting values in the iteration of the refined valence force field were taken from BPKP. The iteration was carried out using the experimentally observed frequencies for EHT, d3EHT, d34EHT, and d11EHT.

Theoretical Results

The calculated wavenumbers and potential energy distributions of the normal modes are listed in Tables I, II, III, and V for d34EHT, d3EHT, d11EHT, and EHT, respectively. The same is done in part for d25EHT in Table IV. The PED are calculated as the square of the coefficient of an internal coordinate in a normal mode, multiplied by the pertinent diagonal force constant. However, the sign of the coefficients is retained in the PED, as shown in Tables I–V. Only the dominant internal coordinates are shown; they appear in order of the size of their contribution. The calculated wavenumbers and PED of the CH and CD stretches are listed in Table VII for the four compounds EHT, d34EHT, d3EHT, and d11EHT and assigned to the observed bands from Table VI. The calculated wavenumbers and the symmetry of normal modes are summarized in Table X for EHT, d34EHT, d3EHT, d11EHT, and d25EHT, together with the observed values.

For the in-plane vibrations, only 19 force constants were changed in the iteration: The 13 diagonal ones, 1 C–H stretch–stretch coupling constant, and 5 coupling constants for the interaction between CC stretches. Our final refined values are listed in Table XI, together with the starting ones from BPKP, and those of YFT,28 FSLBP, and SKL.

For the out-of-plane vibrations, a large part of the force constants were refined. The refined force field is listed on Table XII, together with those of BPKP, YFT, and FSLBP.

Discussion

Deuterium substitution in (E)-1,3,5-hexatriene has two general effects on the molecular vibrations. First, it shifts downward the frequency of the vibrations where hydrogen is directly involved: CH stretch, CH in-plane rock, CH out-of-plane wag. Second, it decouples the CH vibrations being deuteriated from other vibrations of similar frequencies and induces new couplings with vibrations at lower frequencies, causing the whole vibrational pattern to change.

Most of the fundamentals are assigned unambiguously in the experimental spectra in Tables I–V and VII. All C–C and C–C stretching of the four compounds EHT, d34EHT, d3EHT, and d11EHT are described well by our calculations. This also applies to the CH2 (CD2) scissorings and in-plane rocks and the CCC deformations. The discrepancies between theory and experiment are slightly larger for the CH (CD) in-plane rocks. This may be partly explained by the fact that our calculations do not take anharmonicity into account. The out-of-plane modes are generally described very well. The largest discrepancies are found for d34EHT and d3EHT for out-of-plane CH wags (d34EHT, 999 cm⁻¹; d3EHT, 1002 and 987 cm⁻¹; calculated).

However, in a few cases the assignment is doubtful; these cases shall be mentioned here. In Table I for d34EHT, the observed
TABLE I: Observed Wavenumbers (cm⁻¹) and Depolarization Ratios of Raman Bands and Wavenumbers and Band Contours of Infrared Bands of (E)-1,3,5-Hexatriene-3,4-d₂ in the Region 2000–10 cm⁻¹, Together with Calculated Wavenumbers and Potential Energy Distributions of Normal Modes

<table>
<thead>
<tr>
<th>Raman (liquid)</th>
<th>R</th>
<th>Q</th>
<th>P</th>
<th>contour</th>
<th>calc wavenumber</th>
<th>calc PED$^a$</th>
</tr>
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<tbody>
<tr>
<td>1913 w</td>
<td>1974</td>
<td></td>
<td>1965</td>
<td>w</td>
<td>B</td>
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<tr>
<td>1741 w</td>
<td>0.31</td>
<td>1734</td>
<td>1726</td>
<td>m A/B</td>
<td>1563</td>
<td>7 – 5 – 18 – 8 – 20</td>
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<td>1638 m</td>
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<td>1628</td>
<td>1623</td>
<td>1619</td>
<td>s A</td>
<td>1623 5 – 18</td>
</tr>
<tr>
<td>1461 w</td>
<td>0.49</td>
<td>1458</td>
<td>1448</td>
<td>w A/B</td>
<td>1427 8 – 20</td>
<td></td>
</tr>
<tr>
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<td>1370</td>
<td>w A/B</td>
<td>1394 8 – 20</td>
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<tr>
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<td>1294</td>
<td>1290</td>
<td>m A</td>
<td>1291 11 – 23</td>
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<td></td>
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<td>1189</td>
<td>1177</td>
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<td>1129</td>
<td>m B</td>
<td>1140 6 – 19 – 9 + 21 + 11 – 23</td>
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<td>1131 w</td>
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<td>1084</td>
<td>w B</td>
<td>1033 13 – 25 + 6 – 19</td>
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<tr>
<td>1025 w</td>
<td>0.32</td>
<td>1000</td>
<td></td>
<td></td>
<td>1000 9 + 21 + 13 + 25</td>
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<tr>
<td>1001 s</td>
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<td>984</td>
<td>983</td>
<td>s C</td>
<td>999 30 + 31 + 35 + 36</td>
<td></td>
</tr>
<tr>
<td>925 w</td>
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<td>901</td>
<td>902</td>
<td>894</td>
<td>900 32 + 33</td>
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<tr>
<td>871 s</td>
<td>0.37</td>
<td>851</td>
<td>(846)</td>
<td>841</td>
<td>857 13 – 25 – 9 + 21</td>
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<tr>
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<td>786</td>
<td>w B</td>
<td>875 13 – 25 – 9 – 21 – 6 – 19</td>
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</tr>
<tr>
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<td>736</td>
<td>722</td>
<td>w C</td>
<td>734 28 + 29 + 34</td>
<td></td>
</tr>
<tr>
<td>558 w</td>
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<td>517</td>
<td>(512)</td>
<td>506</td>
<td>513 10 – 22 + 12 – 24</td>
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</tr>
<tr>
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<td>420</td>
<td></td>
<td>w</td>
<td>434 12 + 24 + 6 + 19</td>
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<tr>
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<td>0.49</td>
<td>342</td>
<td>247</td>
<td>w</td>
<td>342 10 + 22</td>
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</tr>
<tr>
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<td>247</td>
<td>w</td>
<td>34 + 26 + 27</td>
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<td>202</td>
<td>26 – 27</td>
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<td></td>
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<tr>
<td>58 m</td>
<td>dp</td>
<td></td>
<td></td>
<td></td>
<td>87 26 – 27 + 34</td>
<td></td>
</tr>
</tbody>
</table>

$s =$ strong, $m =$ medium, $w =$ weak, $sh =$ shoulder; $P =$ polarized, $dp =$ depolarized. Values in parentheses indicate average values referred to in text. $^a$PED = potential energy distributions of normal modes; only the dominant internal-coordinate contributions are shown. For the numbering of internal coordinates, see Table IX and Figure 4.
### TABLE II: Observed Wavenumbers (cm\(^{-1}\)) and Depolarization Ratios of Raman Bands and Wavenumbers and Band Contours of Infrared Bands of (E)-1,3,5-Hexatriene-3-d in the Region 2000–10 cm\(^{-1}\), Together with Calculated Wavenumbers and Potential Energy Distributions of Normal Modes

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<th>(Q)</th>
<th>(P)</th>
<th>contour</th>
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<td>w</td>
<td>B</td>
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<tr>
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<td>P</td>
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<td>1809</td>
<td>1805</td>
<td>m</td>
<td>A</td>
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<td>P</td>
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<td>P</td>
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<td>P</td>
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<td>P</td>
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<td>A</td>
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<td>18 - 5 - 19</td>
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<td>w</td>
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<td>8 - 20</td>
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<td>w</td>
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<td>b</td>
<td>1204</td>
<td>19 - 21 + 6 - 24</td>
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<td>1132 m</td>
<td>0.36</td>
<td>1126</td>
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<td>A/B</td>
<td>1136</td>
<td>6 - 9 + 11 - 19</td>
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<td>1104</td>
<td></td>
<td></td>
<td>w</td>
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</tr>
<tr>
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<td>P</td>
<td></td>
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<td></td>
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</tr>
<tr>
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<td></td>
<td></td>
<td>C</td>
<td>1021</td>
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</tr>
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<td>1001 w</td>
<td>P</td>
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<td>s</td>
<td>C</td>
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<td></td>
<td></td>
<td></td>
<td>s</td>
<td>901</td>
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<tr>
<td>932 w</td>
<td>P</td>
<td>938</td>
<td></td>
<td>Q</td>
<td>895</td>
<td>895</td>
<td>29 - 33</td>
</tr>
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<td>921 sh</td>
<td>dp</td>
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<td>909</td>
<td>s</td>
<td>C</td>
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<td>857</td>
<td>857</td>
<td>w</td>
<td>Q</td>
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<td>808</td>
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<td>C</td>
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<td>780</td>
<td>770</td>
<td>761</td>
<td>w</td>
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<td>596</td>
<td>580</td>
<td>564</td>
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<td>dp</td>
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<td>532</td>
<td>521</td>
<td>m</td>
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<td></td>
<td></td>
<td></td>
<td>A/B</td>
<td>528</td>
<td>22 - 10 - 12</td>
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<tr>
<td>441 w</td>
<td>dp?</td>
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<td></td>
<td></td>
<td>w</td>
<td>251</td>
<td>34 + 26 + 27</td>
</tr>
<tr>
<td>213 w</td>
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<td></td>
<td></td>
<td></td>
<td>w</td>
<td>153</td>
<td>12 - 24 - 10 - 22</td>
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<td></td>
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</tr>
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<td>56 m</td>
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<td></td>
<td></td>
<td></td>
<td>intermolecular</td>
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</tr>
</tbody>
</table>

*Q = Q branch. For further comments, see Table I.*

Infrared band around 846 cm\(^{-1}\) is not likely to represent the calculated 875 cm\(^{-1}\) normal mode, because of the large discrepancy between theory and experiment. The 875 cm\(^{-1}\) (calculated) band is probably not observed but is hidden under the strong 902 cm\(^{-1}\) (observed) band. In Table II for d34EHT, the band calculated at 575 cm\(^{-1}\) may be assigned to any of the observed infrared bands at 596, 580, 564, and 545 cm\(^{-1}\), so for this band the agreement between theory and experiment cannot be determined.

For the CH and CD stretches in Table VII, we find some modes where the difference between theory and experiment is rather large: For EHT at 3037 and 3019 cm\(^{-1}\) and for d34EHT at 3037 cm\(^{-1}\) (a\(_\Sigma\) symmetry, calculated values). The discrepancy may be partly explained by the fact that the Raman spectra were obtained from the liquid phase, whereas the infrared spectra were obtained...
TABLE III: Observed Wavenumbers (cm⁻¹) and Depolarization Ratios of Raman Bands and Wavenumbers and Band Contours of Infrared Bands of (E)-1,3,5-Hexatriene-1,1-d₂ in the Region 2000–10 cm⁻¹, Together with Calculated Wavenumbers and Potential Energy Distributions of Normal Modes

<table>
<thead>
<tr>
<th>Raman (liquid)</th>
<th>$I_{VV}/I_{VY}$</th>
<th>infrared (gas)</th>
<th>calc wavenumber</th>
<th>calc PED</th>
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</thead>
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<tr>
<td>1976 w</td>
<td>P</td>
<td>1962</td>
<td>1953</td>
<td>w B</td>
</tr>
<tr>
<td>1923 w</td>
<td>P</td>
<td>1884</td>
<td>1875</td>
<td>w B</td>
</tr>
<tr>
<td>1893 w</td>
<td>P</td>
<td>1864</td>
<td>1856</td>
<td>m B</td>
</tr>
<tr>
<td>1738 w</td>
<td>P</td>
<td>1830</td>
<td>1825</td>
<td>w</td>
</tr>
<tr>
<td>1633 s</td>
<td>0.21</td>
<td>1811</td>
<td>1803</td>
<td>m B</td>
</tr>
<tr>
<td>1617 sh</td>
<td>P</td>
<td>1770</td>
<td>1760</td>
<td>w A/B</td>
</tr>
<tr>
<td>1600 sh</td>
<td>P</td>
<td>1612</td>
<td>1600</td>
<td>s</td>
</tr>
<tr>
<td>1589 sh</td>
<td>P</td>
<td>16411</td>
<td>1637</td>
<td>m A</td>
</tr>
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<td>P</td>
<td>1611</td>
<td>1613</td>
<td>s A</td>
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<td>1545 s</td>
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<td>1551</td>
<td>m A/B</td>
</tr>
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<td>1524 w</td>
<td>P</td>
<td>1519</td>
<td>1519</td>
<td>w</td>
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<td>P</td>
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<td>1438</td>
<td>m B</td>
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<td>1416</td>
<td>m A</td>
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<td>1372</td>
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<tr>
<td>1311 w</td>
<td>P</td>
<td>1304</td>
<td>(1298)</td>
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</tr>
<tr>
<td>1284 s</td>
<td>0.17</td>
<td>1292</td>
<td>1283</td>
<td>m B</td>
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<td>1266 sh</td>
<td>P</td>
<td>1243</td>
<td>1249</td>
<td>1245</td>
</tr>
<tr>
<td>1210 m</td>
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<td>1006</td>
<td>1002</td>
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<td>1184 s</td>
<td>0.32</td>
<td>1034</td>
<td>1025</td>
<td>w B</td>
</tr>
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<td>1002</td>
<td>993</td>
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<td>959</td>
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<td>947</td>
<td>937</td>
<td>C</td>
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<td>932</td>
<td>928</td>
<td>C</td>
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<td>894</td>
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<td>908</td>
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</tr>
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<td>dp</td>
<td>896</td>
<td>959</td>
<td>m C</td>
</tr>
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<td>945</td>
<td>937</td>
<td>m C</td>
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<td>914</td>
<td>902</td>
<td>s C</td>
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<td>902 m</td>
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<td>908</td>
<td>901</td>
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<td>874 w</td>
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<td>802</td>
<td>796</td>
<td>m C</td>
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<td>800</td>
<td>792</td>
<td>m A</td>
</tr>
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<td>794 w</td>
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<td>730</td>
<td>722</td>
<td>s C</td>
</tr>
<tr>
<td>759 w</td>
<td>P</td>
<td>664</td>
<td>654</td>
<td>m C</td>
</tr>
<tr>
<td>722 m</td>
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<td>609</td>
<td>586</td>
<td>w</td>
</tr>
<tr>
<td>659 w</td>
<td>0.70</td>
<td>548</td>
<td>540</td>
<td>m B</td>
</tr>
<tr>
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<td>0.43</td>
<td>522</td>
<td>514</td>
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</tr>
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<td>508 sh</td>
<td>dp</td>
<td>511</td>
<td>511</td>
<td>34 - 26</td>
</tr>
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<td>466 w</td>
<td>P</td>
<td>437</td>
<td>466</td>
<td>w</td>
</tr>
<tr>
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<td>435</td>
<td>435</td>
<td>24 + 12 + 6 + 19</td>
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<td>P</td>
<td>422</td>
<td>422</td>
<td>32</td>
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<td>332 m</td>
<td>0.35</td>
<td>327</td>
<td>10 + 22</td>
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<td>242 w</td>
<td>0.21</td>
<td>238</td>
<td>34 + 26 + 27</td>
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</tr>
<tr>
<td>210 w</td>
<td>0.21</td>
<td>213</td>
<td>27 + 26</td>
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<td>147</td>
<td>12 + 24 - 10 + 22</td>
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</tr>
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<td>82 sh</td>
<td>0.21</td>
<td>84</td>
<td>26 + 27 + 34</td>
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</tr>
<tr>
<td>48 m</td>
<td></td>
<td>48</td>
<td>48</td>
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</tr>
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</table>

from the gas phase. For molecules of $C₄$ symmetry where vibrations may be both Raman and infrared active, gas-phase infrared bands are often observed at 5–10-cm⁻¹ higher frequencies than corresponding liquid phase Raman bands (see Tables II, III,
TABLE IV: Observed Wavenumbers (cm⁻¹) of Raman Bands of ca. 5 mM (E)-1,3,5-Hexatriene-2,5-d₂ in Ar-Saturated CH₂CN Solution, Excited at 317.5 nm, in the Region 1800-200 cm⁻¹, Together with Calculated Wavenumbers and Potential Energy Distributions of Normal Modes

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<thead>
<tr>
<th>Raman (solution) wavenumber</th>
<th>calc PED</th>
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<tr>
<td>1618 s</td>
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<tr>
<td>1571 m</td>
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</tr>
<tr>
<td>1381 m</td>
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<td>1296 m</td>
<td>1293</td>
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<tr>
<td>1215 m</td>
<td>1211</td>
</tr>
<tr>
<td>1023 m</td>
<td>1024</td>
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TABLE V: Observed Wavenumbers (cm⁻¹) and Symmetries of Fundamentals of (E)-1,3,5-Hexatriene in the Region 3000-10 cm⁻¹, Together with Calculated Wavenumbers and Potential Energy Distributions of Normal Modes

| obs calc calc PED |
|--------------------|---------|
| 1628 1621          | 4       |
| 1574 1576          | 5 + 18  |
| 1397 1395          | 8 + 20  |
| 1288 1300          | 13 + 25 |
| 1283 1288          | 11 + 15 |
| 1188 1191          | 6 + 19  |
| 930 931            | 9 + 21  |
| 444 441            | 12 + 24 |
| 353 349            | 10 + 22 |

<table>
<thead>
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<th>b_k</th>
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<tbody>
<tr>
<td>985 987</td>
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</tr>
<tr>
<td>868 866</td>
</tr>
<tr>
<td>615 612</td>
</tr>
<tr>
<td>215 217</td>
</tr>
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</table>

<table>
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</tr>
<tr>
<td>1433 1432</td>
</tr>
<tr>
<td>1296 1292</td>
</tr>
<tr>
<td>1255 1257</td>
</tr>
<tr>
<td>1132 1133</td>
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<td>966 959</td>
</tr>
<tr>
<td>541 544</td>
</tr>
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<td>152 154</td>
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<table>
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<td>938 941</td>
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<td>900 899</td>
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<tr>
<td>683 684</td>
</tr>
<tr>
<td>248 252</td>
</tr>
<tr>
<td>94 87</td>
</tr>
</tbody>
</table>

*From ref 13, crystalline phase.

and VI). These differences shall be discussed further below. Only in the case of undeuterated (E)-1,3,5-hexatriene can we compare our theoretical results with those of previous calculations. For practically all vibrations, the fit with experiment is improved in our calculation compared to the previous ones. Only for the CH stretches, the improvement is limited. Here, however, the assignment of experimentally observed bands is difficult. The assignment was made by introducing large discrepancies between theory and experiment; the calculated EHT modes at 3096 (a, and 3037 cm⁻¹ (b, are found nearly unchanged for d₃EHT, d₄EHT, and d₁₁EHT, in both theory and experiment; the calculated EHT modes at 3096 (a, and 3037 cm⁻¹ (b, are found nearly unchanged for d₃EHT and d₄EHT, and the calculated EHT mode at 3025 cm⁻¹ (b, is found nearly unchanged for d₄EHT and d₁₁EHT.

In contrast, CH stretch normal modes involving the same internal coordinates but differing in symmetry (a, or b, show a strong splitting between observed Raman and infrared frequencies, a splitting that is not reproduced in the calculated frequencies. The EHT modes observed at 3017 (a, and 3046 cm⁻¹ (b,), the d₃EHT modes at 3015 (a, and 3051 cm⁻¹ (b,), and even the d₁₁EHT modes at 3022 (a, and 3049 cm⁻¹ (b, are all calculated at 3037 cm⁻¹. The only way we could lift this discrepancy between theory and experiment was by introducing large coupling constants between CH stretches located at opposite ends of the molecule, which is an unacceptable solution.

CC Stretches. It is seen from Table X that central deuteration (d₃EHT, d₄EHT) barely affects the b, (or b, like) C-C (EHT, 1629; d₃EHT, 1623; d₄EHT, 1628 cm⁻¹; observed) and C-C (EHT, 1132; d₃EHT, 1133; d₄EHT, 1132 cm⁻¹; observed) stretches. This agrees with expectation, since the central C-C stretch does not contribute to b, normal modes. For the a, (or

TABLE VI: Observed Wavenumbers (cm⁻¹) and Depolarization Ratios of Raman Bands and Wavenumbers and Band Contours of Infrared Bands in the Region 3400-2000 cm⁻¹ for (E)-1,3,5-Hexatriene (EHT), (E)-1,3,5-Hexatriene-3,4-d₂ (d₃EHT), (E)-1,3,5-Hexatriene-3,4,5-d₃ (d₃₄EHT), and (E)-1,3,5-Hexatriene-1,1,2-d₃ (d₁₁EHT)*

<table>
<thead>
<tr>
<th>Raman (Liquid)</th>
<th>EHT</th>
<th>d₃EHT</th>
<th>d₄EHT</th>
<th>d₁₁EHT</th>
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<tbody>
<tr>
<td></td>
<td>Iᵥ₁/</td>
<td>Iᵥ₂/</td>
<td>Iᵥ₃/</td>
<td>Iᵥ₄/</td>
</tr>
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<td>3089</td>
<td>0.46</td>
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<td>d₃EHT contour</td>
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<td>0.09</td>
<td>2999</td>
<td>0.04</td>
</tr>
<tr>
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<td>0.10</td>
<td>2997</td>
<td>0.41</td>
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<tr>
<td>d₁₁EHT contour</td>
<td>2241</td>
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<td>2238</td>
<td>0.27</td>
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</table>

*Only those bands are listed that may be assigned as CH or CD stretches. From ref 13, liquid phase.
TABLE VII: Observed Wavenumbers (cm\(^{-1}\)) and Symmetries of Fundamentals in the Region 3400-2000 cm\(^{-1}\) of (E)-1,3,5-Hexatriene (EHT), (E)-1,3,5-Hexatriene-3-d (d3EHT), (E)-1,3,5-Hexatriene-4-d (d4EHT), and (E)-1,3,5-Hexatriene-1,4-d (d11EHT). Together with Calculated Wavenumbers and Potential Energy Distributions of Normal Modes

<table>
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<th>d3EHT</th>
<th>d11EHT</th>
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</tr>
<tr>
<td>calc</td>
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<tr>
<td>PED</td>
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</tr>
</tbody>
</table>

*Experimental values\(^2\) in parentheses.

**TABLE VIII:** Equilibrium Molecular Structure of (E)-1,3,5-Hexatriene Used in the Present Study

<table>
<thead>
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<th></th>
<th>C(<em>{6})H(</em>{8})</th>
<th>H(<em>{2})C(</em>{2})C(_{2})</th>
<th>deg</th>
<th>121.8</th>
<th>(120.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(<em>{5})H(</em>{5})</td>
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<td>(1.104)</td>
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<td>(121.7)</td>
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<td>(115.0)</td>
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**TABLE IX:** Definition of Internal Coordinates; for Atom and Angle Numbering, See Figure 4

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**CH\(_{2}\), CH, CCC In-Plane Deformations.** For d11EHT we find the CH\(_{2}\) scissoring at 1412 cm\(^{-1}\). This is close to the average of the \(a_g\) and \(b_1\) CH\(_{2}\) scissorings found in EHT, d3EHT, and d3EHT. The CH\(_{2}\) scissorings in d25EHT are lowered compared to EHT, d34EHT, and d3EHT, a sign that the CH rock at C\(_3\) couples with the neighboring CH\(_{2}\) scissoring and pushes it upward.

The 1296-cm\(^{-1}\) (EHT; observed) \(b_1\) normal mode is quite unaffected in d34EHT, d3EHT, and d11EHT and must thus belong to the CH rock at C\(_4\), whereas the 1255-cm\(^{-1}\) \(b_1\) mode must belong to the CH rock at C\(_4\). The 1283-cm\(^{-1}\) (EHT; observed) \(a_g\) normal mode is nearly unchanged in d34EHT, d3EHT, and d11EHT and must belong to the CH rock at C\(_2\). Generally, there is a strong coupling between CD rock and CH2 rock. For d11EHT, the CH\(_{2}\) rock is found at 947 cm\(^{-1}\), close to the average of 966 and 930 cm\(^{-1}\) from EHT. Among the CCC deformations, only the \(b_1\) central deformation (EHT, 152 cm\(^{-1}\), observed) is unaffected by deuteration.

**Out-of-Plane Vibrations.** For the out-of-plane vibrations, the terminal CH\(_{2}\) wags are influenced by deuteration in d11EHT and d25EHT, but not in d34EHT and d3EHT, whereas the CH wags are changed little by the terminal deuteration in d11EHT compared to EHT. Generally, only those CH wags being directly deuterated are shifted substantially. These observations can be interpreted by assuming that the range of coupling between the CH/CH\(_{2}\) out-of-plane wags is quite short, being efficient only for wags situated on neighboring carbon atoms. This empirical observation is supported by remarks below about the out-of-plane force field.

The vibrations that are dominated by terminal C=C torsion are influenced strongly by central (d34EHT) and, especially terminal (d11EHT) deuteration, whereas the C=C torsions generally are influenced little by deuteration.

**In-Plane Force Field.** The ab initio force field of BPKP was calculated at the HF/6-31G level. Subsequently, the diagonal force constants were scaled to improve the fit with the experimentally observed frequencies. The same force field was also the basis of YFT, but here the scaling factors were different. The ab initio force field of BPKP was calculated at the HF/4-21G level and subsequently scaled. The ab initio force field of SKL was calculated at the SCF level with DZ+P and TZ+P basis sets and subsequently scaled. In the present study, we used the scaled force field of BPKP as the starting point in our force field refinement. We shall now look closer at the modifications resulting from our refinement, as listed in Table XI for the in-plane force field.

Among the diagonal force constants connected with the CH (CD) stretches, only one is changed appreciably in the present study; for the CH\(_{2}\) stretch the force constant is lowered by about 2%. This lowering seems reasonable, since our calculated normal modes dominated by CH\(_{2}\) stretch generally agree quite well with experiment. Moreover, the coupling between the CH\(_{2}\) and CH\(_{3}\) stretches is increased in our final force field. The scaling factors for the CH stretch diagonal force constants were not changed between BPKP and YFT but were increased in FSLBP.

The diagonal force constants for the CH\(_{2}\) stretches are all increased in our refinement, especially the one for the terminal C=C.
TABLE XI: In-Plane Force Constants for (E)-1,3,5-Hexatriene and EHT, EHT-3-d,d (d34EHT), EHT-3-d (d3EHT), EHT-1,1-d (d11EHT), and EHT-2,5-d (d25EHT)

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Out-of-Plane

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Our refined CC stretch diagonal force constants agree well with those of SKL. The scaling factors for the C=C stretch were barely changed between BPKP and YFT, whereas that of C=C stretch was increased by 2%. Our study supports the view that the terminal C=C bonds in (E)-1,3,5-hexatriene are stronger, and consequently shorter, than the central one.

In our refinement, all coupling constants between CC stretches are increased numerically. This is in agreement with the view proposed by YFT that interaction force constants between skeletal stretching coordinates are underestimated in absolute value by the view proposed by SKL that inclusion of electron correlation leads to an increase in absolute value of all CC stretch-stretch coupling constants.

It is interesting to note the agreement between our refined CC stretch coupling constants and those of SKL. However, our value for the coupling constant between the C=C stretches is numerically larger than in any of the previous studies. The correctness of our analysis is supported by the agreement between our calculated and observed frequencies of the C=C stretches.

The diagonal force constants corresponding to internal coordinates 9 (CH_2 rock) and 11 (CH rock) are decreased by about 3% in our refinement; the corresponding to internal coordinate 13 (CH rock) is increased by a similar amount. This has the effect of bringing closer together the force constants connected with CH in-plane rock. It is particularly remarkable that the force constants connected with the CH rocks at C_2 and C_3 are brought much closer to each other. These changes are qualitatively the same as the changes from BPKP to YFT, but the changes in the present study are larger. The three CH rock diagonal force constants of FSLBP are even closer to each other than in our study.
TABLE XII: Out-of-Plane Force Field for (E)-1,3,5-Hexatriene and Deuteriated Derivatives

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</table>


For the diagonal force constants connected with CCC in-plane deformation, the situation is reversed. In the initial force field, internal coordinates 10 and 12 are close together, whereas in our refinement, 10 is left nearly unchanged and 12 is increased by as much as 12%. This change seems to be correct, since the agreement with experiment is improved strongly for the four lowest in-plane modes that are quite pure CCC deformations. The CCC force constants are barely changed among BPKP, YFT, and FSLBP.

**Out-of-Plane Force Field.** Among the diagonal out-of-plane force constants listed in Table XII, those connected with C=C torsion, internal coordinates 26 and 27, are increased in our refinement. The refined value, 0.0366, is close to those obtained by YFT and FSLBP. The force constants connected with C=C torsion, internal coordinates 34, 35, and 36, are decreased. Here, the central C=C torsion force constant (34) is decreased more than the terminal C=C torsion ones (35, 36), again indicating a weakening of the central C=C bond compared to the terminal ones. The force constants for the CH out-of-plane wags, internal coordinates 28-31, are increased. The diagonal force constants connected with C=C torsion and CH wag of YFT and FSLBP are close to those of BPKP. For the CH2 wags, internal coordinates 32 and 33, the diagonal force constants of the present study are close to those of BPKP, YFT, and FSLBP.

For the out-of-plane interaction force constants, the absolute size of the changes resulting from our refinement is small; however, the relative changes are large. However, none of the interaction constants change sign between BPKP and the present calculation. There is a tendency in the changes such that interactions between internal coordinates that are close to each other in the molecule tend to increase, whereas interactions between internal coordinates that are further apart tend to decrease. Thus, our calculation shows larger values and a stronger range for the interaction force constants between out-of-plane vibrations. This was also observed experimentally above. It should be noted that this tendency also holds for torsional interactions. In particular, the long-range interactions between CC torsions do not increase as one might expect from the results for the in-plane force field.

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