

# Radical Cation of 1,3-Butadiene: Resonance Raman Spectrum of Deuterated Derivatives and Improved Force Field

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The resonance Raman spectra of the radical cations of three deuterated derivatives of 1,3-butadiene are reported. Together with the data for the parent compound (cf.: Keszthelyi, T.; Wilbrandt, R.; Bally, T. *J. Phys. Chem.* **1996**, *100*, 16843), 22 frequencies of totally symmetric fundamentals are available to complement 29 previously obtained IR data for the same compounds (Tang, W; Zhang, X.-L., Bally, T. *J. Phys. Chem.* **1993**, *97*, 4373) and to generate a new and improved scaled quantum mechanical force field of butadiene radical cation based on B3LYP/6-31G\* second derivatives. After fitting those with 13 scaling factors, the resulting force field reproduces all 51 observed fundamental vibrations of the four isotopomers with a root-mean-square deviation of 6.03 cm<sup>-1</sup> (10.6 cm<sup>-1</sup> for the 11 strongly anharmonic C–H/C–D stretches, 3.92 cm<sup>-1</sup> for the remaining 40 modes). It allows the first experimentally based prediction of the stretching force constant for the central C–C bond and corrects the previous ones for the terminal C=C stretch. As in the case of the parent compound, evidence is presented for the presence of the *s-cis* rotamer after ionization whose vibrations are predicted very accurately by scaling a B3LYP/6-31G\* force field of *cis*-butadiene<sup>•+</sup> with the optimized scaling factors of the *s-trans* rotamer.

## Introduction

In 1993 a scaled quantum mechanical (SQM) force field was established for the radical cation of 1,3-butadiene (BD<sup>•+</sup>), based on 43 observed IR-active fundamentals of six C<sub>2h</sub> isotopomers and a set of UMP2/6-31G\* Cartesian second derivatives which were fitted according to a model involving 13 independent scaling factors applied to force constants in internal symmetry coordinates.<sup>1</sup> A comparison to the force field of the parent neutral butadiene<sup>2</sup> (BD) revealed changes in valence force constants in agreement with expectations based on qualitative and quantitative MO models. However, it suffered from the flaw that no experimental frequencies of totally symmetric vibrations were available. Therefore, the important stretching force constant for the central C–C bond had to be estimated and that for the terminal C=C stretches was possibly biased because it was based exclusively on data for the antisymmetric vibrations. Also, the force constants for twisting around the central and the terminal C=C bonds of BD<sup>•+</sup> were not very well defined due to the difficulty to observe low-frequency a<sub>u</sub> modes in the IR experiment.

After demonstrating that it was possible to obtain good resonance Raman (RR) spectra of BD<sup>•+</sup>,<sup>3</sup> we decided to extend this study to include some of the deuterated derivatives that had been investigated in the previous IR work.<sup>1</sup> Thus we were hoping to complete and update the force field of BD<sup>•+</sup> such as to produce a reference for future studies of this kind on longer polyene radical cations. After some exploratory SQM force-field calculations based on the previously obtained UMP2/6-31G\* second derivatives which did not yield satisfactory agreement with the new experimental data, we turned to density functional (DF) calculations to serve as a basis for the scaling procedure. These have recently been demonstrated by others<sup>4a–e</sup>

and by us<sup>4f,g</sup> to provide molecular structures and harmonic force fields of substantially higher accuracy than obtained via Hartree–Fock calculations, and it was found that they are often better suited for scaling than even MP2 force fields. Initially we worked with the BLYP procedure used in the initial RR study,<sup>3</sup> but then we found that the more recently introduced B3LYP combination of functionals<sup>5</sup> gives force fields which are better suited for scaling according to the procedure advanced by Pulay et al.<sup>6,7</sup>

This paper presents the results of our study of the radical cations of BD-*d*<sub>6</sub>, BD-*d*<sub>4</sub>, and BD-*d*<sub>2</sub> and integrates these findings with those on BD-*d*<sub>0</sub><sup>3</sup> to obtain an improved force field of BD<sup>•+</sup> based on B3LYP Cartesian second derivatives which were scaled after transformation into symmetrized internal coordinates as described previously.<sup>1,8</sup> In analogy to the preceding paper<sup>3</sup> we identify some peaks which cannot be assigned to fundamentals of *s-trans*-BD<sup>•+</sup> or combinations thereof with those of *s-cis*-BD<sup>•+</sup> which appears to be formed concomitantly during ionization.

## Methods

The experimental methods are identical with those described in some detail in the preceding paper.<sup>3</sup> The RR spectra were obtained from samples of BD-*d*<sub>6</sub>, BD-*d*<sub>4</sub>, and BD-*d*<sub>2</sub> (obtained via the corresponding 3-sulfolenes as described previously<sup>1</sup>) exposed to  $\gamma$ -rays in a 1:1 mixture of CF<sub>2</sub>Br–CF<sub>2</sub>Br and CF<sub>3</sub>Cl at 77 K. The samples were of >99% chemical and >97% isotopic purity as assessed by GC/MS and <sup>1</sup>H NMR. We refrained from returning to the rather difficult synthesis and purification of the terminally dideuterated derivatives of C<sub>2h</sub> symmetry<sup>1</sup> because we did not expect any invaluable additional information on the valence force constants of interest to us from these.

The SQM force field procedure<sup>6,8</sup> was applied as described previously,<sup>1,2</sup> i.e., the Cartesian force constants of a B3LYP/

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, October 1, 1996.

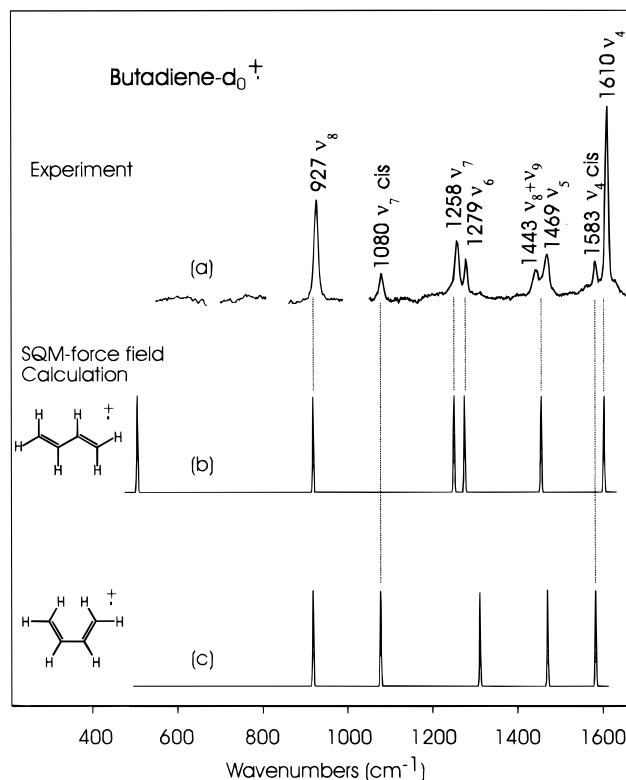
**TABLE 1: Symmetry-Adapted Internal Coordinates of Butadiene (for Definition of Internal Valence Coordinates  $q_1$ – $q_{24}$  See Ref 2)**

| no. | definition | sym   | no. | definition | sym   | scaling factor <sup>a</sup> |
|-----|------------|-------|-----|------------|-------|-----------------------------|
| s1  |            | $a_g$ |     |            |       | 0.965                       |
| s2  |            | $a_g$ | s17 |            | $b_u$ | 0.947                       |
| s3  |            | $a_g$ | s18 |            | $b_u$ | 0.922                       |
| s4  |            | $a_g$ | s19 |            | $b_u$ | 0.904                       |
| s5  |            | $a_g$ | s20 |            | $b_u$ | 0.915                       |
| s6  |            | $a_g$ | s21 |            | $b_u$ | 1.015                       |
| s7  |            | $a_g$ | s22 |            | $b_u$ | 0.935                       |
| s8  |            | $a_g$ | s23 |            | $b_u$ | 0.927                       |
| s9  |            | $a_g$ | s24 |            | $b_u$ | 0.977                       |
| s10 |            | $b_g$ | s13 |            | $a_u$ | 0.950                       |
| s11 |            | $b_g$ | s14 |            | $a_u$ | 1.000                       |
| s12 |            | $b_g$ | s16 |            | $a_u$ | 0.935                       |
|     |            |       | s15 |            | $a_u$ | 0.920                       |

<sup>a</sup> factor used to scale the corresponding B3LYP force constant to achieve optimal agreement with observed vibrational frequencies listed in Table 2.

6-31G\* calculation were transformed into the set of symmetrized internal coordinates shown in Table 1 for the purpose of scaling. Thereby, an independent scaling factor was assigned to every different type of internal coordinate (stretches, bends, torsions, etc.) of which there are 13 in the present case. In the spirit of the Pulay method,<sup>6</sup> off-diagonal elements were scaled by the geometric mean of the scaling constants for the corresponding diagonal elements. The optimization of the scaling constants was first conducted manually such as to ascertain the correct assignment of RR bands to fundamentals. Only after this was unambiguous was the final optimization achieved by a Simplex algorithm. Finally, the set of optimized scaling factors was used to scale a B3LYP/6-31G\* force field of *s-cis*-BD<sup>•+</sup> which provided an immediate assignment of some of those peaks in the RR spectra that could not be explained in terms of the predominant *s-trans* rotamer.

The B3LYP calculations (geometry optimization and second derivatives) were carried out with the Gaussian 94 program<sup>9</sup> on SGI and HP workstations. The B3LYP geometries of *s-trans*- and *s-cis*-BD<sup>•+</sup> are very similar to those obtained with the BLYP procedure,<sup>3</sup> except that the C–C bonds are generally shorter by  $\approx 1$  pm which is due to the fact that the Hartree–Fock density with its incorrect dissociation behavior enters the B3LYP but not the BLYP functional. However, these minor geometry differences are insignificant in the present context.



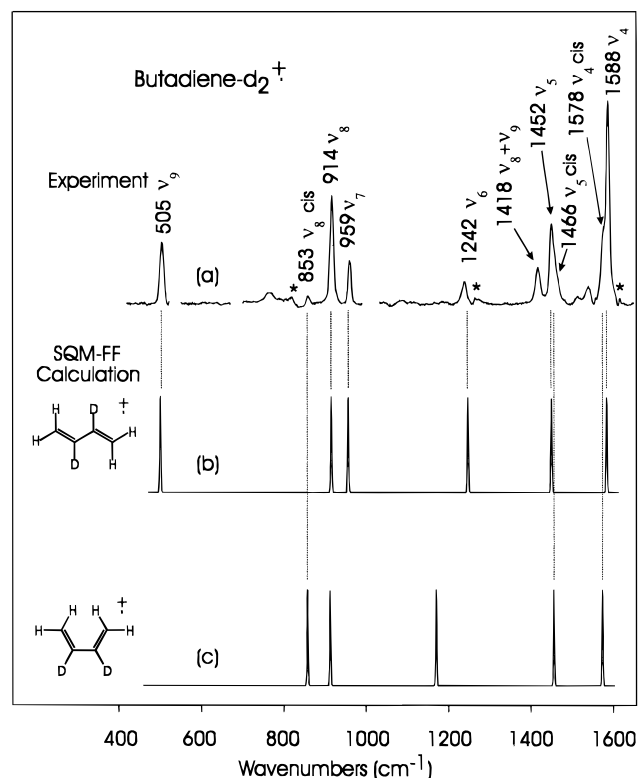
**Figure 1.** (a) Resonance Raman spectrum of BD<sup>•+</sup>-*d*<sub>0</sub> in a Freon glass at 77 K. Solvent and neutral BD bands have been subtracted, leaving only those of the radical cation which appear upon excitation at 550 nm where BD<sup>•+</sup> has its first absorption band. (b) Predicted positions of  $a_g$  fundamentals  $\nu_4$ – $\nu_9$  of *s-trans*-BD<sup>•+</sup>-*d*<sub>0</sub> from scaled B3LYP/6-31G\* force field; (c) Predicted positions of  $a_1$  fundamentals of *s-cis*-BD<sup>•+</sup>-*d*<sub>0</sub> from scaled B3LYP/6-31G\* force field. Assignments of the bands based on the force field calculations described in the text are indicated. Bands marked by asterisk are possible artifacts arising from the subtraction procedure of matrix bands.

## Results

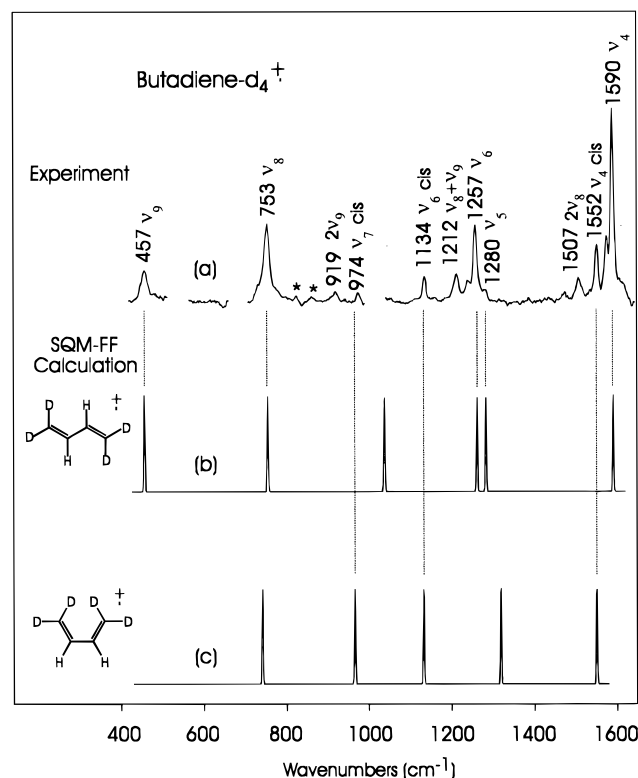
The RR spectra of the radical cations of BD-*d*<sub>0</sub>, BD-*d*<sub>2</sub>, BD-*d*<sub>4</sub>, and BD-*d*<sub>6</sub> are shown in Figures 1–4. In all spectra there are regions where the observation of RR bands of BD<sup>•+</sup> is rendered impossible due to strong Raman scattering of the solvent system. This concerns in particular the region around 1000 cm<sup>-1</sup> where the force field predicts  $\nu_6$  of BD<sup>•+</sup>-*d*<sub>6</sub> and  $\nu_7$  of BD<sup>•+</sup>-*d*<sub>4</sub>, respectively, which therefore escaped detection. The assignments in terms of fundamental vibrations or combination bands of *s-trans*- and *s-cis*-BD<sup>•+</sup> as they emerged from the SQM calculations are indicated above each peak.

Table 2 gives a complete summary of all observed and calculated IR- and RR-active fundamental frequencies of the four BD<sup>•+</sup> isotopomers as well as potential energy distributions (PED) in terms of the symmetry coordinates shown in Table 1, as determined with the present SQM force field. The optimized scaling factors for the 13 types of valence deformations are listed in the rightmost column of Table 1, and in Table 3 some important elements of the force constant matrix in internal coordinates are compared to those obtained previously for BD and BD<sup>•+</sup>.

As we have observed only few vibrations of *s-cis*-BD<sup>•+</sup> and these were predicted quite accurately by a B3LYP/6-31G\* force field for this rotamer which was scaled with the factors in Table 1, we refrained from a separate scaling procedure. Therefore, we list only the observed peak positions next to their predicted frequencies for this species (Table 4).



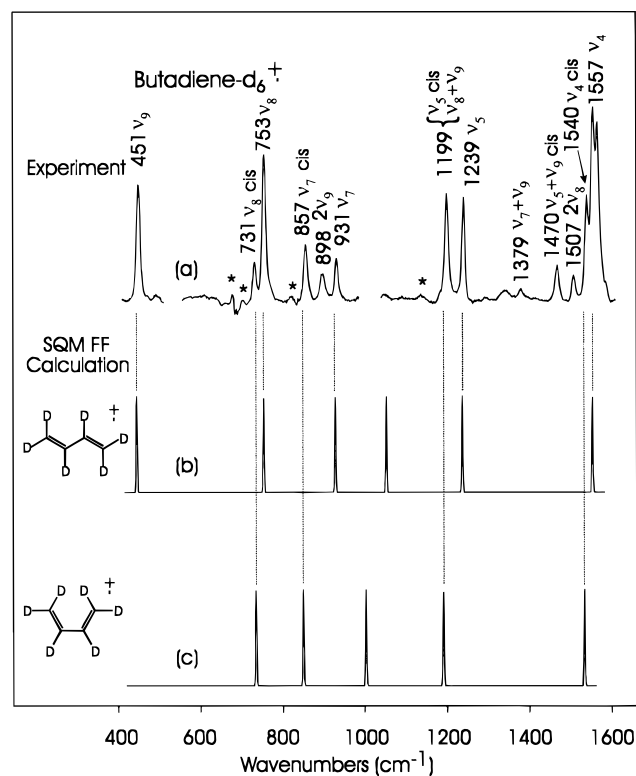
**Figure 2.** Resonance Raman spectrum of  $\text{BD}^{+\cdot}\text{-d}_2$  (a) and calculated totally symmetric fundamentals for *s-trans*- (b) and *s-cis*- $\text{BD}^{+\cdot}\text{-d}_2$  (c). See also caption to Figure 1.



**Figure 3.** Resonance Raman spectrum of  $\text{BD}^{+\cdot}\text{-d}_4$  (a) and calculated totally symmetric fundamentals for *s-trans*- (b) and *s-cis*- $\text{BD}^{+\cdot}\text{-d}_4$  (c). See also caption to Figure 1.

## Discussion

**Resonance Raman Spectra.** A general impression one gets from the RR spectra of the deuterated derivatives is that they contain more bands than that of  $\text{BD}^{+\cdot}\text{-d}_0$ . One of these is the low-frequency  $\nu_9$  fundamental that was not observed in the



**Figure 4.** Resonance Raman spectrum of  $\text{BD}^{+\cdot}\text{-d}_6$  (a) and calculated totally symmetric fundamentals for *s-trans*- (b) and *s-cis*- $\text{BD}^{+\cdot}\text{-d}_6$  (c). See also caption to Figure 1.

parent species<sup>3</sup> but occurs in the spectra of all deuterated derivatives. Apart from that, there are several more bands in the region 750–1000  $\text{cm}^{-1}$  and the region of the  $\nu_4$  C=C stretching fundamental (1500–1600  $\text{cm}^{-1}$ ) also appears to be richer in peaks. As will be shown below, some of these can be explained in terms of combinations or overtones of the  $\nu_7$ – $\nu_9$  fundamentals, whereas others occur rather precisely in places where fundamentals of the corresponding *s-cis* rotamers are expected.

With this in mind, we can proceed to discuss the assignment of the fundamentals in the RR spectra of the three radical cations. In the case of  $\text{BD}^{+\cdot}\text{-d}_2$ , the peaks at 1588, 1452, 1242, 959, 914, and 505  $\text{cm}^{-1}$  can easily be assigned to the  $\nu_4$ – $\nu_9$  fundamentals on the basis of the force field. In analogy with the parent  $\text{BD}^{+\cdot}\text{-d}_0$  the  $\nu_8 + \nu_9$  combination can be associated with the peak at 1418  $\text{cm}^{-1}$ . The slight shoulder on the high-energy side of  $\nu_5$  may be due to  $\nu_7 + \nu_9$  (expected at 1464  $\text{cm}^{-1}$ ) or due to  $\nu_5$  of the *s-cis* rotamer (predicted at 1456  $\text{cm}^{-1}$ ). This species manifests itself by the peak at 853  $\text{cm}^{-1}$  ( $\nu_8$ , predicted at 858  $\text{cm}^{-1}$ ) and by the low-energy shoulder on the 1588  $\text{cm}^{-1}$  peak ( $\nu_4$ , predicted at 1574  $\text{cm}^{-1}$ ). Finally, the small band at 1515  $\text{cm}^{-1}$  could possibly be assigned to  $3 \times \nu_9$  of the *s-trans* rotamer. This leaves only two bands, i.e., the peak at 1540  $\text{cm}^{-1}$  and the broad hump peaking at 755  $\text{cm}^{-1}$  which we cannot assign in terms of combination bands of *s-trans*- $\text{BD}^{+\cdot}\text{-d}_2$  or fundamentals of the *s-cis* rotamer.

In  $\text{BD}^{+\cdot}\text{-d}_4$  only the  $\nu_4$ ,  $\nu_8$ , and  $\nu_9$  fundamentals can be readily assigned to the peaks at 1590, 753, and 457  $\text{cm}^{-1}$  as their positions coincide very well with those predicted by B3LYP. Initially, we attempted to fit this force field by assigning the strong 1257  $\text{cm}^{-1}$  band to  $\nu_5$  and that at 1212  $\text{cm}^{-1}$  to  $\nu_6$ , but it turned out that no satisfactory solution could be found under these premises, both fundamentals being stubbornly predicted 20–30  $\text{cm}^{-1}$  too high. When these two were left out of the fitting procedure,  $\nu_6$  coincided with the 1257  $\text{cm}^{-1}$  band whereas

**TABLE 2: Comparison of Observed<sup>a</sup> and Calculated<sup>b</sup> IR and RR Frequencies for Four Isotopomers of Butadiene Radical Cation**

|                | BD- <i>d</i> <sub>0</sub> |                  |                 |   | BD- <i>d</i> <sub>6</sub>   |      |   |   | BD-1,1,4,4- <i>d</i> <sub>4</sub>                                   |      |   |   | BD-2,3- <i>d</i> <sub>2</sub>   |      |   |   |  |
|----------------|---------------------------|------------------|-----------------|---|---|------|---|---|---|------|---|---|---|------|---|---|--|
|                | obs                       | calc             | %I <sup>c</sup> | PED <sup>d</sup>                                      | obs   | calc | %I <sup>c</sup>                                       | PED <sup>d</sup>                                    | obs   | calc | %I <sup>c</sup>                                       | PED <sup>d</sup>                                      | obs   | calc | %I <sup>c</sup>   | PED <sup>d</sup>                                      |  |
| A <sub>g</sub> | $\nu_1$                   | 3136             |                 | 5 <sup>66</sup> , 4 <sup>32</sup>                     | 2341  |      | 5 <sup>59</sup> , 4 <sup>39</sup>                     |   | 3071  |      | 3 <sup>99</sup>                                       |   | 3136  |      | 5 <sup>67</sup> , 4 <sup>33</sup>                                     |   |  |
|                | $\nu_2$                   | 3071             |                 | 3 <sup>98</sup>                                       | 2282  |      | 3 <sup>91</sup>                                       |   | 2341  |      | 5 <sup>59</sup> , 4 <sup>39</sup>                     |   | 3032  |      | 4 <sup>67</sup> , 5 <sup>32</sup>                                     |   |  |
|                | $\nu_3$                   | 3032             |                 | 4 <sup>67</sup> , 5 <sup>33</sup>                     | 2209  |      | 4 <sup>56</sup> , 5 <sup>37</sup>                     |   | 2211  |      | 4 <sup>57</sup> , 5 <sup>38</sup>                     |   | 2281  |      | 3 <sup>94</sup>   |   |  |
|                | $\nu_4$                   | 1610             | 1612            |   | 2 <sup>39</sup> , 7 <sup>26</sup> , 1 <sup>25</sup> , 8 <sup>8</sup>  | 1557 | 1555  |   | 2 <sup>45</sup> , 1 <sup>36</sup> , 7 <sup>15</sup>                 | 1590 | 1591  |   | 2 <sup>35</sup> , 7 <sup>32</sup> , 1 <sup>29</sup>                   | 1588 | 1583  | 2 <sup>46</sup> , 1 <sup>27</sup> , 8 <sup>7/12</sup> |  |
|                | $\nu_5$                   | 1469             | 1464            |   | 8 <sup>76</sup> , 7 <sup>10</sup> , 1 <sup>10</sup>                   | 1239 | 1238  |   | 1 <sup>31</sup> , 2 <sup>6</sup> /8 <sup>18</sup> , 9 <sup>10</sup> | 1280 | 1283  |   | 2 <sup>34</sup> , 7 <sup>22</sup> , 8 <sup>16</sup> , 6 <sup>13</sup> | 1452 | 1449  | 8 <sup>74</sup> , 1 <sup>17</sup>                     |  |
|                | $\nu_6$                   | 1279             | 1285            |   | 6 <sup>27</sup> , 9 <sup>27</sup> , 1 <sup>21</sup> , 2 <sup>14</sup> | 1053 |   | 8 <sup>67</sup> , 6 <sup>14</sup> , 7 <sup>12</sup> | 1257  | 1262 |   | 1 <sup>41</sup> , 7 <sup>41</sup> , 6 <sup>12</sup>   | 1242  | 1247 | 9 <sup>33</sup> , 6 <sup>24</sup> , 2 <sup>20</sup> , 1 <sup>14</sup> |   |  |
|                | $\nu_7$                   | 1258             | 1259            |   | 7 <sup>62</sup> , 2 <sup>22</sup> , 1 <sup>12</sup>                   | 931  | 929   |   | 7 <sup>75</sup> , 8 <sup>10</sup> , 2 <sup>16</sup>                 | 1038 |   | 8 <sup>81</sup> , 6 <sup>10</sup>                     | 959   | 956  | 7 <sup>64</sup> , 1 <sup>19</sup> , 9 <sup>12</sup>                   |   |  |
|                | $\nu_8$                   | 927              | 928             |   | 9 <sup>58</sup> , 1 <sup>27</sup> , 2 <sup>12</sup>                   | 753  | 754   |   | 9 <sup>60</sup> , 1 <sup>20</sup> , 2 <sup>12</sup>                 | 753  | 755   |   | 9 <sup>62</sup> , 1 <sup>20</sup> , 2 <sup>11</sup>                   | 914  | 915   | 9 <sup>42</sup> , 7 <sup>23</sup> , 2 <sup>117</sup>  |  |
|                | $\nu_9$                   | 515 <sup>e</sup> | 515             |   | 6 <sup>73</sup> , 9 <sup>14</sup> , 2 <sup>8</sup>                    | 451  | 445   |   | 6 <sup>63</sup> , 9 <sup>26</sup>                                   | 457  | 457   |   | 6 <sup>63</sup> , 9 <sup>26</sup>                                     | 505  | 500   | 6 <sup>71</sup> , 9 <sup>14</sup>                     |  |
|                | A <sub>u</sub>            | $\nu_{10}$       | 1021            | 13  | 13 <sup>79</sup> , 14 <sup>16</sup>                                   | 830  | 7   | 13 <sup>82</sup> , 14 <sup>16</sup>                 |   | 996  | 995   | 26  | 14 <sup>61</sup> , 15 <sup>20</sup> , 6 <sup>17</sup>                 | 1016 | 1018  | 29  | 13 <sup>98</sup>                                     |
| $\nu_{11}$     |                           | 1001             | 1002            | 72  | 14 <sup>41</sup> , 13 <sup>15</sup> /16 <sup>20</sup>                 | 740  | 738   | 32  | 14 <sup>47</sup> , 15 <sup>16</sup> /19                             | 818  | 816   | 27  | 13 <sup>96</sup>  | 770  | 772   | 17  | 14 <sup>54</sup> 16 <sup>31</sup> , 15 <sup>15</sup> |
| $\nu_{12}$     |                           | 423              | 2               | 16 <sup>79</sup> , 14 <sup>15</sup>                   | 300   | 1    | 16 <sup>79</sup> , 14 <sup>15</sup> , 15 <sup>6</sup> |   | 304   | 1    | 16 <sup>82</sup> , 14 <sup>11</sup> , 15 <sup>6</sup> |   | 413   | 2    | 16 <sup>71</sup> , 14 <sup>22</sup> , 15 <sup>7</sup>                 |   |  |
| $\nu_{13}$     |                           | 184              | 5               | 15 <sup>60</sup> , 14 <sup>30</sup> , 16 <sup>8</sup> | 162   | 4    | 15 <sup>62</sup> , 14 <sup>26</sup> , 16 <sup>8</sup> |   | 168   | 4    | 15 <sup>58</sup> , 14 <sup>30</sup> , 16 <sup>9</sup> |   | 178   | 3    | 15 <sup>64</sup> , 14 <sup>26</sup> , 16 <sup>7</sup>                 |   |  |
| B <sub>g</sub> | $\nu_{14}$                | 1029             |                 | 10 <sup>74</sup> , 11 <sup>25</sup>                   | 870   |      | 10 <sup>50</sup> , 11 <sup>50</sup>                   |   | 958   |      | 11 <sup>81</sup> , 10 <sup>15</sup> , 12 <sup>4</sup> |   | 1016  |      | 10 <sup>91</sup> , 11-9   |   |  |
|                | $\nu_{15}$                | 907              |                 | 11 <sup>68</sup> , 10 <sup>23</sup> , 12 <sup>9</sup> | 710   |      | 10 <sup>50</sup> , 11 <sup>50</sup>                   |   | 767   |      | 10 <sup>86</sup> , 11 <sup>10</sup> , 12 <sup>4</sup> |   | 775   |      | 11 <sup>89</sup> , 10 <sup>6</sup>                                    |   |  |
|                | $\nu_{16}$                | 510              |                 | 12 <sup>90</sup> , 11 <sup>9</sup>                    | 384   |      | 12 <sup>96</sup>                                      |   | 402   |      | 12 <sup>91</sup> , 11 <sup>7</sup> , 10 <sup>2</sup>  |   | 500   |      | 12 <sup>95</sup>  |   |  |
| B <sub>u</sub> | $\nu_{17}$                | 3125             | 3136            | 15  | 20 <sup>66</sup> , 19 <sup>32</sup>                                   | 2358 | 2340  | 5   | 10 <sup>59</sup> , 19 <sup>39</sup>                                 | 3082 | 3080  | 4   | 18 <sup>99</sup>  | 3125 | 3136  | 9   | 20 <sup>67</sup> , 19 <sup>33</sup>                  |
|                | $\nu_{18}$                | 3074             | 3079            | 4   | 18 <sup>98</sup>  | 2276 | 2272  | 3   | 18 <sup>95</sup>  | 2253 | 2340  | 5   | 20 <sup>59</sup> , 19 <sup>40</sup>                                   | 3017 | 3030  | 12  | 19 <sup>67</sup> , 20 <sup>33</sup>                  |
|                | $\nu_{19}$                | 3026             | 3030            | 17  | 19 <sup>67</sup> , 20 <sup>32</sup>                                   | 2215 | 2205  | 4   | 19 <sup>56</sup> , 20 <sup>38</sup>                                 | 2218 | 2207  | 3   | 19 <sup>58</sup> , 20 <sup>38</sup>                                   | 2271 | 3   | 18 <sup>98</sup>                                      |  |
|                | $\nu_{20}$                | 1477             | 1487            | 26  | 23 <sup>77</sup> , 17 <sup>20</sup>                                   | 1319 | 1320  | 100   | 17 <sup>76</sup> , 23 <sup>16</sup> , 22 <sup>5</sup>               | 1347 | 1352  | 100   | 17 <sup>50</sup> , 22 <sup>38</sup> , 23 <sup>8</sup>                 | 1476 | 1484  | 14  | 23 <sup>81</sup> , 17 <sup>19</sup>                  |
|                | $\nu_{21}$                | 1330             | 1334            | 57  | 22 <sup>69</sup> , 17/23/24 <sup>10</sup>                             | 1047 | 1042  | 17  | 23 <sup>42</sup> , 22 <sup>41</sup> , 24 <sup>14</sup>              | 1268 | 1263  | 11  | 22 <sup>51</sup> , 17 <sup>33</sup> , 23 <sup>11</sup>                | 1266 | 1266  | 100   | 17, 23 <sup>13</sup> , 22 <sup>9</sup>               |
|                | $\nu_{22}$                | 1251             | 1248            | 100   | 17 <sup>78</sup> , 22 <sup>8</sup> , 23 <sup>8</sup>                  | 996  | 992   | 20  | 23 <sup>50</sup> , 22/24/17 <sup>16</sup>                           | 1022 | 1013  | 36  | 23 <sup>87</sup> , 17 <sup>12</sup>                                   | 1130 | 2   | 24 <sup>69</sup> , 22 <sup>20</sup> , 17 <sup>6</sup> |  |
|                | $\nu_{23}$                | 1006             | 1001            | 1   | 24 <sup>76</sup> , 22 <sup>22</sup>                                   | 750  | ≈0  | 24 <sup>59</sup> , 22 <sup>38</sup>                 |   | 818  | 0   | 24 <sup>82</sup> , 22 <sup>11</sup> , 21 <sup>7</sup> |   | 852  | 1   | 22 <sup>69</sup> , 24 <sup>30</sup>                   |  |
|                | $\nu_{24}$                | 294              | 1               | 21 <sup>92</sup> , 24 <sup>7</sup>                    | 248   | ≈0   | 21 <sup>87</sup> , 24 <sup>12</sup>                   |   | 255   | 1    | 21 <sup>87</sup> , 24 <sup>13</sup>                   |   | 284   | 1    | 21 <sup>92</sup> , 24 <sup>7</sup>                                    |   |  |
|                | rmsd <sup>f</sup>         |                  |                 |   |   |      |   |   |   |      |   |   |   |      |   |   |  |
|                | C-H/D                     |                  |                 | 7.37  |   |      |   | 12-36   |   |      |   | 10.32   |   |      |   | 12.14   |  |
| others         |                           |                  | 4.35            |   |   |      | 3.19  |   |   |      | 4.14  |   |   |      | 3.76  |   |  |
| total          |                           |                  | 5.15            |   |   |      | 6.75  |   |   |      | 6.17  |   |   |      | 6.06  |   |  |

<sup>a</sup> IR-frequencies from ref 1, RR frequencies from present work and ref 3. <sup>b</sup> Using the B3LYP SQM force field described in the text. <sup>c</sup> Relative IR intensity, normalized to most intense band (=100). <sup>d</sup> Potential energy distribution of each normal mode in terms of symmetry coordinates S<sub>1</sub>-S<sub>24</sub> (cf. Table 1 and ref 2), superscripts denote percentage contributions. <sup>e</sup> From analysis of combination bands (see text). <sup>f</sup> Root-mean-square difference between observed and calculated frequencies in cm<sup>-1</sup> for each isotopomer, subdivided according to C-H/C-D and other vibrations.

**TABLE 3: Diagonal Elements of the Force Constant Matrixes of BD and BD<sup>•+</sup>**

| type                    | BD <sup>•+</sup> <sup>b</sup> | BD <sup>•+</sup> <sup>c</sup> | BD <sup>d</sup> |
|-------------------------|-------------------------------|-------------------------------|-----------------|
| C-C stretch             | [6.35] <sup>e</sup>           | 6.49                          | 5.11            |
| C=C stretch             | 7.26                          | 6.85                          | 8.60            |
| C-H stretch (average)   | 5.15                          | 5.20                          | 5.10            |
| C-C-C bend              | [1.16] <sup>e</sup>           | 1.13                          | 1.11            |
| C-C-H bend              | 0.54                          | 0.54                          | 0.51            |
| CH <sub>2</sub> scissor | 0.45                          | 0.45                          | 0.45            |
| CH <sub>2</sub> rock    | 0.57                          | 0.55                          | 0.54            |
| CH <sub>2</sub> wag     | 0.28                          | 0.28                          | 0.24            |
| C-H wag                 | 0.27                          | 0.29                          | 0.28            |
| CH <sub>2</sub> twist   | 0.24                          | 0.22                          | 0.51            |
| C-C torsion             | 0.26                          | 0.23                          | 0.11            |

<sup>a</sup> Stretching force constants are in aJ/Å<sup>2</sup> (=mdyn/Å), those for angular deformations in aJ/rad<sup>2</sup> (=mdyn·Å/rad). <sup>b</sup> UMP2/6-31G\* force field scaled on the basis of IR frequencies alone<sup>1</sup>. <sup>c</sup> B3LYP/6-31G\* force field scaled on the basis of IR and RR frequencies. <sup>d</sup> Fully optimized force field for neutral. <sup>e</sup> Estimated, due to lack of spectroscopic data.

$\nu_5$  was predicted at 1283 cm<sup>-1</sup>. As the 1212 cm<sup>-1</sup> peak can be readily assigned to the  $\nu_8 + \nu_9$  combination and the shoulder at 1242 cm<sup>-1</sup> must be due to an impurity because its intensity varied between different experiments, we were forced to conclude that the  $\nu_5$  fundamental in *s-trans*-BD<sup>•+</sup>-*d*<sub>4</sub> gives rise only to a rather weak RR band, presumably the shoulder at ≈1280 cm<sup>-1</sup>. We can offer no explanation for this phenomenon, but we are confident that our assignment is correct, because we carefully examined all other possibilities and none could be brought into reasonable accord with the B3LYP force field.

With the above assignment, the peak at 1212 cm<sup>-1</sup> can be attributed to the  $\nu_8 + \nu_9$  combination (expected at 1210 cm<sup>-1</sup>) and that at 919 cm<sup>-1</sup> to 2 ×  $\nu_9$  (expected at 914 cm<sup>-1</sup>). The

**TABLE 4: Frequencies [cm<sup>-1</sup>] of the  $\nu_4$ - $\nu_8$  Fundamentals of *s-cis*-BD<sup>•+</sup> As Observed in the RR Spectra<sup>a</sup> and Predicted by the Scaled B3LYP Force Field<sup>b</sup>**

| mode    | BD <sup>•+</sup> - <i>d</i> <sub>0</sub> | BD <sup>•+</sup> - <i>d</i> <sub>2</sub> | BD <sup>•+</sup> - <i>d</i> <sub>4</sub> | BD <sup>•+</sup> - <i>d</i> <sub>6</sub> |
|---------|--|--|--|--|
| $\nu_4$ | 1583/1584                                | 1578/1574                                | 1552/1551                                | 1540/1535                                |
| $\nu_5$ | [1469]/1471                              | 1466/1456                                | -/1319                                   | 1199/1193                                |
| $\nu_6$ | -/1312                                   | -/1171                                   | 1134/1133                                | -/1004                                   |
| $\nu_7$ | 1080/1079                                | [914]/913                                | 974/966                                  | 857/851                                  |
| $\nu_8$ | -/919                                    | 853/858                                  | [740]/742                                | 731/735                                  |
| $\nu_9$ | -/307                                    | -/305                                    | -/267                                    | -/266                                    |

<sup>a</sup> Experimental numbers are to the left of the slash; numbers in brackets correspond to uncertain assignments. <sup>b</sup> Calculated numbers to the right of the slash; the scaling constants were taken from the optimized force field for the *s-trans* rotamer.

1507 cm<sup>-1</sup> band is probably due to 2 ×  $\nu_8$  (at 1506 cm<sup>-1</sup>), but it could also contain intensity from the  $\nu_7 + \nu_9$  combination, taking into account that  $\nu_7$  is predicted at 1038 cm<sup>-1</sup> (where it cannot be seen due to strong matrix signals). Finally, as in the case of the other isotopomers, the *s-cis* rotamer also appears to manifest itself in BD<sup>•+</sup>-*d*<sub>4</sub>, with bands at 974 cm<sup>-1</sup> ( $\nu_7$ , predicted at 966 cm<sup>-1</sup>), 1134 cm<sup>-1</sup> ( $\nu_6$  predicted at 1133 cm<sup>-1</sup>), and 1552 cm<sup>-1</sup> ( $\nu_4$  predicted at 1551 cm<sup>-1</sup>). Eventually, the low-energy shoulder at the 753 cm<sup>-1</sup> band could be due to  $\nu_8$  of the *s-cis* rotamer (predicted at 742 cm<sup>-1</sup>), but this assignment is less certain. A band at 1578 cm<sup>-1</sup> is yet unassigned. We believe that this could be due to Fermi resonance of the combination  $\nu_{20} + \nu_{24}$  (predicted at 1602 cm<sup>-1</sup>) with the  $\nu_4$  fundamental of the *s-trans* rotamer.

Finally, BD<sup>•+</sup>-*d*<sub>6</sub> has readily attributable fundamentals at 1557, 1239, 931, 753, and 451 cm<sup>-1</sup> (cf. Table 2) as well as overtones at 1507 cm<sup>-1</sup> (2 ×  $\nu_8$  expected at 1506 cm<sup>-1</sup>) and 898 cm<sup>-1</sup> (2 ×  $\nu_9$  expected at 902 cm<sup>-1</sup>) and combination bands at 1199 cm<sup>-1</sup> ( $\nu_8 + \nu_9$  expected at 1204 cm<sup>-1</sup>) and 1379 cm<sup>-1</sup> ( $\nu_7 + \nu_9$

expected at  $1382\text{ cm}^{-1}$ ). Unfortunately,  $\nu_6$  (predicted at  $1053\text{ cm}^{-1}$ , masked by matrix signals) cannot be observed, but if we assume that the prediction is correct, its combination with  $\nu_9$  (predicted at  $1504\text{ cm}^{-1}$ ) could contribute to the signal at  $1507\text{ cm}^{-1}$  which we assigned to  $2 \times \nu_8$ . Again, we find a number of bands which can be assigned to the *s-cis* rotamer of  $\text{BD}^{+}\text{-}d_6$ , i.e.,  $\nu_8$  at  $731\text{ cm}^{-1}$  (calcd  $735\text{ cm}^{-1}$ ),  $\nu_7$  at  $857\text{ cm}^{-1}$  (calcd  $851\text{ cm}^{-1}$ ), and  $\nu_4$  at  $1540\text{ cm}^{-1}$  (calcd  $1535\text{ cm}^{-1}$ ). In addition,  $\nu_5$  (calcd  $1193\text{ cm}^{-1}$ ) could well contribute to the intense  $1199\text{ cm}^{-1}$  peak which we assigned above to  $\nu_8 + \nu_9$  of the *s-trans* rotamer. This leaves the bands at  $1470$  and  $1566\text{ cm}^{-1}$  which we cannot assign to any combination bands of *s-trans*- $\text{BD}^{+}\text{-}d_6$  nor to any fundamentals of the *s-cis* rotamer. The  $1470\text{ cm}^{-1}$  peak could possibly have contributions from  $2 \times \nu_8$  (expected at  $1462\text{ cm}^{-1}$ ) and of  $\nu_5 + \nu_9$  (at  $1465\text{ cm}^{-1}$ ) of the *s-cis* rotamer, although one would then expect it to be less prominent. As in the case of  $\text{BD}^{+}\text{-}d_4$ , the  $1566\text{ cm}^{-1}$  band is tentatively explained by Fermi resonance of  $\nu_{20} + \nu_{24}$  (predicted at  $1567\text{ cm}^{-1}$ ) with  $\nu_4$  of *s-trans*.

**Force Field.** The force field that results from a fitting of the B3LYP/6-31G\* force constants in symmetrized internal coordinates on the basis of the above-discussed RR assignments and the previously observed IR frequencies<sup>1</sup> reproduces all 51 observed fundamental vibrations with a root-mean-square (rms) deviation of  $6.03\text{ cm}^{-1}$  ( $10.6\text{ cm}^{-1}$  for the 11 strongly anharmonic C–H/C–D stretches,  $3.92\text{ cm}^{-1}$  for the remaining 40 modes). Apart from the fact that the rms deviation has improved from the previous force field (which was not to be expected on inclusion of additional experimental data), it is more firmly rooted in experiment because many valence force constants which had been defined exclusively through their participation in antisymmetric (i.e., IR active) normal modes are now amenable to a more balanced description on the basis of the newly observed totally symmetric counterparts. Unfortunately this does not apply to the out-of-plane modes ( $b_g/a_u$ ) which could have benefitted considerably from additional experimental data. We are presently not in a position to carry out experiments that would allow us to fill this gap in our knowledge about this fundamental species.

With the above in mind we can proceed to examine the changes in the force field of  $\text{BD}^{+}$  as compared to its previous version<sup>1</sup> as well as to that of neutral  $\text{BD}^2$  (cf. Table 3). First we note that the central C–C stretching and C–C–C bending force constants that had previously only been estimated due to lack of experimental data are now rather firmly established. It turned out that the earlier estimate for the central C–C stretch had been rather good, but, more surprisingly, the terminal C=C stretch had been considerably overestimated. Inspection of the full force field reveals that this discrepancy is mainly due to a change in balance between the diagonal C=C stretching force constants  $f_2$  and  $f_3$  and the off-diagonal element  $f_{23}$  describing their interaction (in internal coordinates  $q_2$  and  $q_3$ ) which had been 0.747 in the previous scaled UMP2 force field<sup>1</sup> and is now nearly half,  $0.379\text{ aJ}/\text{\AA}^2$ . This permitted an increase of  $f_2$  and  $f_3$  without unduly affecting the calculated frequencies of the normal modes in which the corresponding symmetry coordinates  $S_2$  and  $S_{17}$  participate prominently. Interestingly, allowing the balance of  $f_2/f_3$  and  $f_{23}$  to change by scaling the force constants corresponding to  $S_2$  and  $S_{17}$  separately (which would have been meaningless in the previous IR study due to lack of observed modes containing  $S_2$ ) led to no change in the agreement with experiment in the case of the B3LYP force field. Conversely, doing the same with the UMP2 force field led to a dramatic improvement in the rms deviation, bringing it close to that achieved with the B3LYP force field, while  $f_2/f_3$  and  $f_{23}$  acquired

values very close to their B3LYP counterparts. It therefore appears that the off-diagonal element  $f_{23}$  had been wrong by a factor of nearly 2 in the UMP2 force field, a fact that did not reveal itself at the time due to the absence of totally symmetric vibrations. This finding has important repercussions to the application of the Pulay scaling procedure (where  $f_{ij}$  are scaled by factors corresponding to the geometric mean of those for  $f_i$  and  $f_j$ )<sup>7</sup> which relies on theoretical models giving reasonable estimates for the (otherwise not easily accessible) off-diagonal elements of the force constant matrixes. Apparently this condition is not always fulfilled even by MP2 force fields.

The remaining diagonal as well as the prominent off-diagonal force constants did not undergo any great changes from the previous study (the estimate for the C–C–C bending force constant had apparently also been quite good). It must be noted that the changes in the force constants for out-of-plane deformations (last four entries in Table 3) are not due to any new experimental data (no  $b_g$  fundamentals being observed in the RR spectra) but entirely due to the change in the quantum chemical force field which was scaled on the basis of the previous IR data alone. Interestingly, the B3LYP force field predicts force constants for twisting around the central and the terminal C–C bonds which are now nearly identical. This expresses itself also in a decrease of the difference  $\Delta r$  between the two C–C bond lengths in going from UMP2 ( $\Delta r = 2.4\text{ pm}$ ) to B3LYP ( $\Delta r = 2.0\text{ pm}$ ).

Nonwithstanding the above changes, the basic conclusions of the previous IR study remain entirely valid: (1) all in-plane bending force constants of BD are hardly affected by ionization; (2) the force constants for the C–H stretches and those for the out-of-plane C–H<sub>(2)</sub> wags increase by small but significant amounts and (c) the changes in the C–C stretching and twisting force constants nicely reflect the expectations based on removal of an electron from the  $\pi$ -HOMO of BD which is bonding along the terminal C=C bonds and antibonding along the central one. Especially these latter changes demonstrate clearly that a distinction between single and double bonds is meaningless in  $\text{BD}^{+}$ . This applies generally to polyene radical cations<sup>10</sup> except in the case of very long ones where polaron-type distortions of the framework become operative.<sup>11</sup>

## Summary

The resonance Raman (RR) spectra of four isotopomers of the radical cation of butadiene ( $\text{BD}^{+}$ ) have been observed and are assigned on the basis of a B3LYP/6-31G\* force field scaled according to the procedure proposed by Pulay et al.<sup>7</sup> In all cases the RR spectra show the occurrence of the *s-cis* rotamer of  $\text{BD}^{+}$  which had never been observed in previous studies. As in the case of the parent  $d_0$ -derivative,<sup>3</sup> only totally symmetric ( $a_g$ ) fundamentals, overtones, and combination bands are observed in the RR spectra, hence these experiments yield no new information on the out-of-plane force field of  $\text{BD}^{+}$ .

The second derivatives of the energy obtained from the B3LYP procedure form an excellent basis for fitting the corresponding force field in symmetrized internal coordinates to experimental data. Despite the fact that 22 new pieces of spectroscopic information from the RR spectra needed to be reproduced, the rms deviation between observed and calculated frequencies dropped by about 15% compared to the previous UMP2-based force field which had been scaled on the basis of the IR frequencies alone.<sup>1</sup> In fact, we found it impossible to achieve a satisfactory fit of the UMP2 force fields to both the IR and the RR frequencies, but we were able to show that this is mainly due to the fact that the off-diagonal element describing the interaction of the two terminal C=C bond stretches was

grossly overestimated by UMP2. Apart from that, the revised force field of  $\text{BD}^{+\bullet}$  has not changed significantly from that obtained previously and therefore the conclusions of the previous IR study<sup>1</sup> are confirmed.

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