

# Ab Initio Second-Order Møller-Plesset Calculation of the Vibrational Spectrum of Tetrahedrane

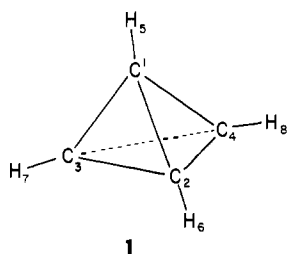
B. Andes Hess, Jr.,\* and L. J. Schaad\*

Contribution from the Department of Chemistry, Vanderbilt University, Nashville, Tennessee 37235. Received July 9, 1984

**Abstract:** The SCF vibrational spectra, including IR intensities, have been computed for tetrahedrane and tetrahedrane-*d*<sub>4</sub> with a 6-31G\* basis. Møller-Plesset second-order correlation corrections to the frequencies also have been computed.

There has been much recent interest in the C<sub>4</sub>H<sub>4</sub> potential surface as shown by the successful preparation of two long-sought isomers, cyclobutadiene<sup>1-3</sup> and methylenecyclopropene.<sup>4,5</sup> In the case of cyclobutadiene, theory<sup>6-12</sup> has played an important role in confirming its synthesis and structure.

One of the most interesting C<sub>4</sub>H<sub>4</sub> isomers, tetrahedrane (1), has so far eluded isolation although its tetra-*tert*-butyl derivative has been prepared and characterized by Maier.<sup>13</sup> Extensive calculations by Kollmar<sup>14</sup> have suggested that because of a high degree of strain as little as 10 kcal/mol may be required to sever a C-C bond in tetrahedrane which may therefore be isolable only at quite low temperatures. If this turns out to be the case, low-temperature IR and Raman spectroscopy are likely to be useful in the eventual characterization of this compound. We therefore report here an ab initio calculation of the vibrational frequencies and the IR intensities of tetrahedrane.



A 4-31G ab initio calculation of the vibrational frequencies together with an INDO estimate of IR intensities was reported as early as 1974 by Schulman and Venanzi.<sup>15</sup> However, our experience<sup>11,12,16</sup> indicates that inclusion of polarization functions and correlation energy greatly improves the agreement between theory and experiment. Calculations were therefore performed

(1) Lin, C. Y.; Krantz, A. *J. Chem. Soc., Chem. Commun.* **1972**, 1111-1112.

(2) Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.* **1973**, *95*, 614-617.

(3) Masamune, S.; Souto-Bachiller, F. A.; Machiguchi, T.; Bertie, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 4889-4891.

(4) Billups, W. E.; Lin, L.-J.; Casserly, E. W. *J. Am. Chem. Soc.* **1984**, *106*, 3698-3699.

(5) Staley, S. W.; Norden, T. D. *J. Am. Chem. Soc.* **1984**, *106*, 3699-3700.

(6) Borden, W. T.; Davidson, E. R.; Hart, R. *J. Am. Chem. Soc.* **1978**, *100*, 388-392.

(7) Jaffri, J. A.; Newton, M. D. *J. Am. Chem. Soc.* **1978**, *100*, 5012-5017.

(8) Kollmar, H.; Staemmler, V. *J. Am. Chem. Soc.* **1978**, *100*, 4304-4305.

(9) Schaad, L. J.; Hess, B. A., Jr.; Ewig, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 2281-2283.

(10) Schaad, L. J.; Hess, B. A., Jr.; Ewig, C. S. *J. Org. Chem.* **1982**, *47*, 2904-2906.

(11) Hess, B. A., Jr.; Čársky, P.; Schaad, L. J. *J. Am. Chem. Soc.* **1983**, *105*, 695-701.

(12) Hess, B. A., Jr.; Schaad, L. J.; Čársky, P. *Pure Appl. Chem.* **1983**, *55*, 255-260.

(13) Maier, G.; Pfiem, S.; Schaefer, U.; Matusch, R. *Angew. Chem.* **1978**, *90*, 552-553.

(14) Kollmar, H. *J. Am. Chem. Soc.* **1980**, *102*, 2617-2621.

(15) Schulman, J. M.; Venanzi, T. J. *J. Am. Chem. Soc.* **1974**, *96*, 4739-4746.

(16) Hess, B. A., Jr.; Schaad, L. J.; Polavarapu, P. *J. Am. Chem. Soc.* **1984**, *106*, 4348-4350.

**Table I.** Optimized Geometry of Tetrahedrane<sup>a</sup>

basis set	R <sub>C-C</sub>	R <sub>C-H</sub>	energy
4-31G <sup>b</sup>	1.482	1.054	-153.3414
DZ+P <sup>c</sup>	1.460	1.064	-153.4537
6-31G*	1.463	1.063	-153.5979
DZ+P/CEPA <sup>c</sup>	1.470		-154.0453
6-31G*/MP2	1.477	1.073	-154.1009

<sup>a</sup>Bond lengths in Å and energies in au. <sup>b</sup>Reference 15. <sup>c</sup>Reference 14.

**Table II.** Symmetry Coordinates<sup>a,b</sup>

species	coordinate
A <sub>1</sub>	S <sub>1</sub> = (1/6 <sup>1/2</sup> )(R <sub>12</sub> + R <sub>23</sub> + R <sub>13</sub> + R <sub>14</sub> + R <sub>24</sub> + R <sub>34</sub> ) S <sub>2</sub> = 1/2(R <sub>15</sub> + R <sub>26</sub> + R <sub>37</sub> + R <sub>48</sub> )
E	S <sub>3</sub> = [1/2(3 <sup>1/2</sup> )](2R <sub>12</sub> - R <sub>23</sub> - R <sub>13</sub> - R <sub>14</sub> - R <sub>24</sub> + 2R <sub>34</sub> ) S <sub>4</sub> = [1/2(6 <sup>1/2</sup> )](2A <sub>251</sub> - A <sub>362</sub> - A <sub>173</sub> - A <sub>184</sub> - A <sub>462</sub> - A <sub>273</sub> - A <sub>284</sub> - A <sub>451</sub> - A <sub>351</sub> + 2A <sub>384</sub> + 2A <sub>473</sub> + 2A <sub>162</sub> ) S <sub>3'</sub> = 1/2(R <sub>23</sub> - R <sub>13</sub> + R <sub>14</sub> - R <sub>24</sub> ) S <sub>4'</sub> = [1/2(2 <sup>1/2</sup> )](A <sub>362</sub> - A <sub>173</sub> + A <sub>184</sub> - A <sub>462</sub> + A <sub>273</sub> - A <sub>284</sub> + A <sub>451</sub> - A <sub>351</sub> )
T <sub>1</sub>	S <sub>5</sub> = [1/2(2 <sup>1/2</sup> )](A <sub>251</sub> + A <sub>173</sub> + A <sub>462</sub> - A <sub>284</sub> - A <sub>351</sub> + A <sub>384</sub> - A <sub>473</sub> - A <sub>162</sub> ) S <sub>5'</sub> = [1/2(2 <sup>1/2</sup> )](-A <sub>251</sub> - A <sub>362</sub> - A <sub>184</sub> + A <sub>273</sub> + A <sub>451</sub> + A <sub>384</sub> - A <sub>473</sub> + A <sub>162</sub> ) S <sub>5''</sub> = [1/2(2 <sup>1/2</sup> )](-A <sub>362</sub> - A <sub>173</sub> + A <sub>184</sub> + A <sub>462</sub> + A <sub>273</sub> - A <sub>284</sub> - A <sub>451</sub> + A <sub>351</sub> )
T <sub>2</sub>	S <sub>6</sub> = (1/2 <sup>1/2</sup> )(R <sub>23</sub> - R <sub>14</sub> ) S <sub>7</sub> = 1/2(R <sub>15</sub> + R <sub>48</sub> - R <sub>37</sub> - R <sub>26</sub> ) S <sub>8</sub> = [1/2(2 <sup>1/2</sup> )](A <sub>251</sub> + A <sub>384</sub> - A <sub>473</sub> - A <sub>162</sub> + A <sub>351</sub> + A <sub>284</sub> - A <sub>173</sub> - A <sub>462</sub> ) S <sub>6'</sub> = (1/2 <sup>1/2</sup> )(-R <sub>13</sub> + R <sub>24</sub> ) S <sub>7'</sub> = 1/2(-R <sub>36</sub> - R <sub>48</sub> + R <sub>37</sub> + R <sub>15</sub> ) S <sub>8'</sub> = [1/2(2 <sup>1/2</sup> )](-A <sub>362</sub> - A <sub>184</sub> + A <sub>273</sub> + A <sub>451</sub> + A <sub>251</sub> - A <sub>162</sub> - A <sub>384</sub> + A <sub>473</sub> ) S <sub>6''</sub> = (1/2 <sup>1/2</sup> )(-R <sub>12</sub> + R <sub>34</sub> ) S <sub>7''</sub> = 1/2(-R <sub>37</sub> + R <sub>26</sub> - R <sub>48</sub> + R <sub>15</sub> ) S <sub>8''</sub> = [1/2(2 <sup>1/2</sup> )](-A <sub>173</sub> + A <sub>462</sub> - A <sub>284</sub> + A <sub>351</sub> + A <sub>451</sub> - A <sub>273</sub> + A <sub>362</sub> - A <sub>184</sub> )

<sup>a</sup>The bond between atoms *i* and *j* is denoted by R<sub>ij</sub> and the angle formed by atoms *i*, *j*, and *k* with *j* at the vertex by A<sub>ijk</sub>. <sup>b</sup>Unprimed, primed, and doubly primed coordinates transform respectively like first, second, or third columns of the corresponding representation.

with 6-31G\*<sup>17</sup> and 6-31G\*/MP2<sup>18</sup> wave functions. Our ability to perform MP2 computations on a molecule of this size was greatly enhanced by the availability of an MP2 program written to take advantage of symmetry.<sup>19</sup>

Optimized geometries and energies are compared with several previous calculations in Table I. Kollmar<sup>8,14</sup> has found tetrahedrane to lie 27 kcal/mol above cyclobutadiene on the C<sub>4</sub>H<sub>4</sub> potential surface with a DZ+P basis set and 29 kcal/mol with inclusion of correlation. We find the same value at the SCF level

(17) Pople, J. A. In "Modern Theoretical Chemistry"; Schaefer, H. F., III, Ed.; Plenum Press: New York, 1977 p 1-27.

(18) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618-622.

(19) Čársky, P.; Hess, B. A., Jr.; Schaad, L. J. *J. Comput. Chem.* **1984**, *5*, 280-287.

**Table III.** Calculated Force Constants<sup>a</sup>

species	constant	SCF/6-31G*	MP2/6-31G*
A <sub>1</sub>	F <sub>11</sub>	4.898	4.391
	F <sub>22</sub>	6.778	6.387
E	F <sub>12</sub>	-0.042	-0.104
	F <sub>33</sub>	6.342	5.450
	F <sub>44</sub>	0.276	0.218
T <sub>1</sub>	F <sub>34</sub>	0.644	0.649
	F <sub>55</sub>	0.328	0.256
T <sub>2</sub>	F <sub>66</sub>	6.230	5.450
	F <sub>77</sub>	6.774	6.387
	F <sub>88</sub>	1.133	0.867
	F <sub>67</sub>	-0.153	-0.277
	F <sub>68</sub>	0.844	0.725
	F <sub>78</sub>	0.023	0.035

<sup>a</sup>Stretching force constants are in  $\text{m dyn } \text{Å}^{-1}$  and bending force constants in  $\text{m dyn } \text{Å} \text{ rad}^{-2}$ .

**Table IV.** Vibrational Frequencies of Tetrahedrane<sup>a</sup>

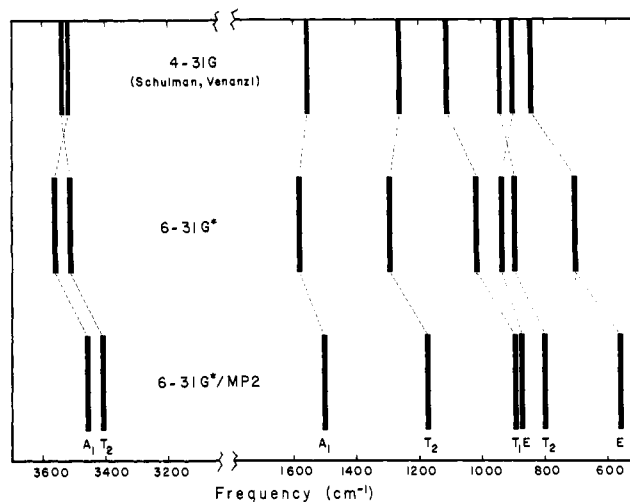
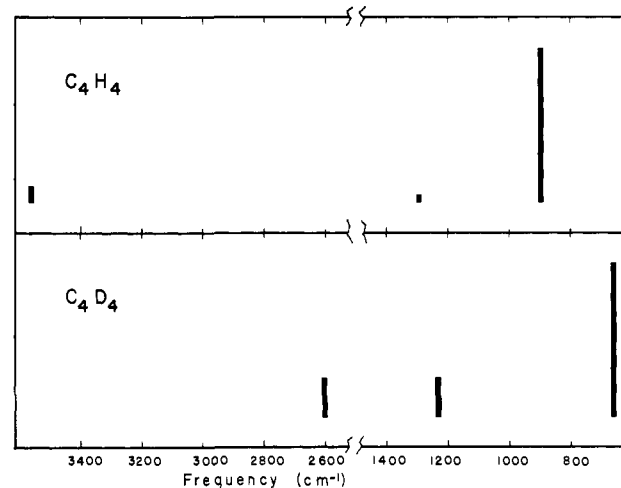
species	C <sub>4</sub> H <sub>4</sub>		C <sub>4</sub> D <sub>4</sub>	
	6-31G*	6-31G*/MP2	6-31G*	6-31G*/MP2
A <sub>1</sub>	1580	1494	1473	1393
	3560	3460	2701	2625
E	701	556	526	425
	934	878	880	813
T <sub>1</sub>	1015	888	814	713
T <sub>2</sub>	895 (1.00)	796	658 (1.00)	580
	1291 (0.05)	1172	1232 (0.26)	1131
	3513 (0.10)	3410	2600 (0.25)	2515

<sup>a</sup>Frequencies in  $\text{cm}^{-1}$ ; relative IR intensities given in parentheses.

(6-31G\*), but with MP2 this energy difference decreases to 23 kcal/mol (the disagreement may be due to the fact that Kollmar optimized only C-C bond distances in both molecules).

For the evaluation of force constants at the SCF level, the analytic gradient was computed for plus and minus distortions ( $0.01 \text{ Å}$  and  $3^\circ$ ) along each symmetry coordinate (Table II). However, for the computation of 6-31G\*/MP2 force constants both numerical first and second derivatives had to be calculated. Plus and minus distortions were made for the diagonal force constants and appropriate combination distortions for the off-diagonal force constants. The force constants that were obtained are given in Table III. Vibrational frequencies were computed with the Miyazawa version of Wilson's GF method.<sup>20</sup> For the IR-active bands (T<sub>2</sub>) derivatives of the dipole moment were obtained and used to compute IR intensities. Results are summarized in Table IV for tetrahedrane and its tetradeuterio derivative.

In Figure 1 are plotted tetrahedrane frequencies from the 4-31G, 6-31G\*, and 6-31G\*/MP2 computations. It is seen that there is a significant change in the computed pattern when polarization functions are added (6-31G\*) with the order of bands being interchanged in two cases. As was found for the vibrational

**Figure 1.** Theoretical vibrational frequencies of tetrahedrane.**Figure 2.** Theoretical (6-31G\*) IR spectra of tetrahedrane and tetradeuteriotetrahedrane. Relative intensities are shown by bar heights.

spectrum of cyclobutadiene, the main effect of correlation is to move all bands to lower frequency. Of the vibrations shown in Figure 1, only the T<sub>2</sub> modes are IR active; and Figure 2 shows 6-31G\* IR spectra (frequencies and intensities) for tetrahedrane and tetradeuteriotetrahedrane. In light of the excellent agreement found between the computed<sup>11</sup> and experimental<sup>3</sup> IR spectra of cyclobutadiene and methylenecyclopropene,<sup>4,21</sup> we anticipate that the computed spectra reported here will be useful in the eventual identification of tetrahedrane.

(20) Califano, S. "Vibrational States"; Wiley: New York, 1976; Chapter 4.

(21) Hess, B. A., Jr.; Michalska, D.; Schaad, L. J. *J. Am. Chem. Soc.*, in press.