The potential surface for the three methyl rotations in the tertiary-butyl cation, (CH₃)₃C⁺

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(Received 3 February 1997; accepted 9 June 1997)

The intricate symmetry of the potential energy surface for the three methyl rotation dimensions in the tertiary-butyl cation, (CH₃)₃C⁺, is examined with the presentation of analytic three-dimensional potential functions for the first time. The simplest function is a four-parameter model which is reminiscent of of a form commonly used in the studies of two-rotor systems. This function, arising purely from symmetry and proper Fourier series truncation, dictates the existence of four “canonical” stationary-point conformations, whose ab initio energies are sufficient to determine its parameter values. The simplicity of the surface leads to mirror-image relations concerning the normal mode curvatures at the canonical stationary points, and these relations are shown to be approximately valid on 33-dimensional and nonanalytic ab initio surfaces. A 14-parameter function is also developed, and values for its parameters were determined from fitting to ab initio energies and tested against normal mode frequencies at the canonical locations. Kinetic (inertial) terms are presented as well. To consider the neglected coupling of the pure torsional coordinates with other internal coordinates along the internal rotation pathways, total energy distribution (TED) analyses of ab initio harmonic force fields were performed, and contributions of from 5% to 40% from other internal coordinates were observed in the internal rotation normal modes at various stationary points. This suggests that further improvement of three-dimensional functions beyond those presented here may be of limited use without incorporation of bending potential terms.

[S0021-9606(97)02434-3]

I. INTRODUCTION

This paper addresses the form of three-internal-rotor potential functions for the tertiary-butyl cation. Studies of the potential coupling of two internal rotation modes in a molecule date back to the seminal work on acetone by Swalen and Costain¹ in 1959. For many of these systems, the potential surface is very well described by limited Fourier series potential functions such as²

\[ V(\alpha_1,\alpha_2) = A_{00}^{\alpha} + A_{10}^{\alpha} \cos[n_1 \alpha_1] + A_{11}^{\alpha} \cos[n_2 \alpha_2] 
+ A_{20}^{\alpha} \cos[2n_1 \alpha_1] + A_{21}^{\alpha} \cos[2n_2 \alpha_2] 
+ A_{11}^{\alpha} \sin[n_1 \alpha_1]\sin[n_2 \alpha_2] \]

and

\[ V(\alpha_1,\alpha_2) = A_{00}^\gamma + A_{10}^\gamma (\cos 3\alpha_1 + \cos 3\alpha_2) 
+ A_{11}^\gamma \cos 3\alpha_1 \cos 3\alpha_2 
- [A_{11}^\gamma] \sin 3\alpha_1 \sin 3\alpha_2, \]

where \( \alpha_1 \) and \( \alpha_2 \) are the torsional angles for each methyl group. The second form is specific to the commonly studied case of equivalent methyl rotors and \( C_{2v} \) frame.²⁻⁵ These potential functions are capable of quantitative reproduction of both thermodynamic and spectroscopic observations, particularly with the improved determination of their parameter values in recent years.⁶⁻¹¹ Extension to systems with three internal rotations appears not to have been made.

The tertiary-butyl cation, (CH₃)₃C⁺, plays an important role in the experimental gas-phase proton affinity scale¹²⁻¹⁴ because the proton affinity of isobutene, (CH₃)₂CCH₂, has been used as an important anchoring value. Unfortunately, the entropy change upon protonation of isobutene is considerably larger than those of protonations of most other small molecules, and has been difficult to quantify because of the lack of knowledge of the extent of coupling of the methyl rotations in both (CH₃)₂CCH₂ and particularly (CH₃)₃C⁺.²

The fluxional behavior of (CH₃)₃C⁺ consists of labile methyl internal rotation, with the energies of all methyl torsional positions lying within an 8-kJ mol⁻¹ potential energy range (vide infra), with further atomic scrambling requiring another 50 kJ mol⁻¹.¹⁵ Such a system is described by the \( G_{324} \) molecular symmetry group. This symmetry group has particularly prominent status, as it was a key paradigm [represented by trimethylboron, isoelectronic to (CH₃)₃C⁺] in the original paper of Longuet-Higgins¹⁶ on group theory for non-rigid molecules.

This paper examines the implications of \( G_{324} \) symmetry on the potential surface for the tertiary-butyl cation, and presents potential functions of differing accuracy, as well as some kinetic terms. The potential functions are fitted to conformation energies from ab initio calculations, and tested against ab initio potential curvatures.

II. THEORY

The general Fourier series expansion of the three-dimensional potential surface function can be written:
\[ V(\alpha_a, \alpha_b, \alpha_c) = \sum_{i,j,k=0}^{\infty} \left( A_{ijk}^{ccc} \cos[n_a \alpha_a] \cos[j_n \alpha_b] \cos[k_n \alpha_c] + A_{ijk}^{ccc} \sin[n_a \alpha_a] \cos[j_n \alpha_b] \cos[k_n \alpha_c] + A_{ijk}^{css} \cos[n_a \alpha_a] \sin[j_n \alpha_b] \cos[k_n \alpha_c] + A_{ijk}^{css} \sin[n_a \alpha_a] \sin[j_n \alpha_b] \cos[k_n \alpha_c] + A_{ijk}^{cs} \cos[n_a \alpha_a] \sin[j_n \alpha_b] \sin[k_n \alpha_c] + A_{ijk}^{cs} \sin[n_a \alpha_a] \sin[j_n \alpha_b] \sin[k_n \alpha_c] \right) \]

in the style of Smeyers and co-workers.\textsuperscript{7–11} The symmetry group \( G_{324} \) places several restrictions on the coefficients \( A \) and periodicities \( n \). Without recourse to the full \( G_{324} \) character table, we can determine these restrictions by "factorizing" \( G_{324} \):\textsuperscript{17}

\[ G_{324} = [C_3^a \otimes C_3^b \otimes C_3^c] \Lambda [D_{3h}] \]
\[ = [C_3^a \otimes C_3^b \otimes C_3^c] \Lambda [C_3^d M] \Lambda [F], \]

where \( \otimes \) and \( \Lambda \) indicate direct and semidirect products, respectively, and the operator groups are

\[ C_3^a = [E + (123) + (132)], \]
\[ C_3^b = [E + (456) + (465)], \]
\[ C_3^c = [E + (789) + (798)], \]
\[ C_3^d = [E + (abc) + (acb)], \]
\[ M = [E + (bc)], \]
\[ F = [E + V^*], \]

using Longuet-Higgins’ notation\textsuperscript{16} and Woodman’s \( V^* \) notation\textsuperscript{17}.

The superscripts \( a, b, c, d \) refer to carbon atoms and the numbers 1–9 to hydrogen atoms (Fig. 1), and we refer to the original papers for further explanation. Each operator group appearing in the complete factorization [Eq. (4)] places restrictions on the potential function [Eq. (3)], which are:

\[ C_3^a \Rightarrow V(\alpha_a, \alpha_b, \alpha_c) = V(\alpha_a \pm 2\pi/3, \alpha_b, \alpha_c) \]
\[ \Rightarrow n_a = 3, \]
\[ C_3^b \Rightarrow V(\alpha_a, \alpha_b, \alpha_c) = V(\alpha_a, \alpha_b \pm 2\pi/3, \alpha_c) \]
\[ \Rightarrow n_b = 3, \]
\[ C_3^c \Rightarrow V(\alpha_a, \alpha_b, \alpha_c) = V(\alpha_a, \alpha_b, \alpha_c \pm 2\pi/3) \]
\[ \Rightarrow n_c = 3, \]
\[ F \Rightarrow V(\alpha_a, \alpha_b, \alpha_c) = V(\alpha_a, \alpha_b, \alpha_c) \]
\[ \Rightarrow A_{ijk}^{ccc} = A_{ijk}^{csc} = A_{ijk}^{css} = A_{ijk}^{css} = 0, \]
\[ C_3^d \Rightarrow V(\alpha_a, \alpha_b, \alpha_c) = V(\alpha_c, \alpha_a, \alpha_b) = V(\alpha_b, \alpha_c, \alpha_a) \]
\[ \Rightarrow A_{ijk}^{cyx} = A_{ijk}^{yxz} = A_{ijk}^{xyz}, \]
\[ M \Rightarrow V(\alpha_a, \alpha_b, \alpha_c) = V(\alpha_a + \pi, \alpha_c + \pi, \alpha_b + \pi) \]
\[ \Rightarrow A_{ijk}^{xyz} = (-1)^{i+j+k} A_{ijk}^{xyz}. \]

Only the implications of \( F \) stated above are dependent on choice of origin, for which we assume the \( C_{3h} \) structure \( \text{rrr} \) (Fig. 1) to represent the \((0,0,0)\) position. If one assumes the \( C_{3h} \) position \( \text{uuu} \) to be the origin, then the implications would be that \( V(\alpha_1, \alpha_2, \alpha_3) = V(\pi - \alpha_1, \pi - \alpha_2, \pi - \alpha_3) \), and the roles of sines and cosines would be interchanged.

We shall discuss the resulting Fourier series truncated to differing orders of \((i + j + k)\). To zeroth and first order, the potential function is simply the constant \( A_{ccc}^{ccc} \), indicating free rotation. When one considers that first-order terms are present in cases like methanol and acetone (torsional barriers of \(3–5\) kJ mol\(^{-1}\)) but not in toluene or nitromethane (tor
sional barriers below 0.1 kJ mol$^{-1}$, one might immediately expect that methyl torsion barriers in (CH$_3$)$_3$C$^+$ should be near 0.1 kJ mol$^{-1}$. As we shall see, however, large second-order coupling terms vitiate the concept of single-roto
tional barriers and cause torsional hindrances which range from
toluene-like to methanol-like in magnitude.

The second-order expression is

$$
V(\alpha_a, \alpha_b, \alpha_c) = A_{110}^{ccc}(\cos 3\alpha_a + \cos 3\alpha_b + \cos 3\alpha_c)
+ \cos 3\alpha_a \cos 3\alpha_b + \cos 3\alpha_a \cos 3\alpha_c
+ \cos 3\alpha_b \cos 3\alpha_c + A_{110}^{ccc}(\sin 3\alpha_a \sin 3\alpha_b
+ \sin 3\alpha_a \sin 3\alpha_c + \sin 3\alpha_b \sin 3\alpha_c).
$$

(11)

The third-order expression introduces only two additional terms

$$
A_{211}^{ccc}(\cos 6\alpha_a \cos 3\alpha_b + \cos 6\alpha_b \cos 3\alpha_c
+ \cos 6\alpha_c \cos 3\alpha_a),
+ \cos 3\alpha_a \cos 3\alpha_b \cos 3\alpha_c
- \cos 3\alpha_a \cos 6\alpha_b)
$$

(12)

At fourth order, eight additional terms appear:

$$
A_{310}^{ccc}(\cos 12\alpha_a + \cos 12\alpha_b + \cos 12\alpha_c),
A_{310}^{ccc}(\cos 9\alpha_a \cos 3\alpha_b + \cos 9\alpha_b \cos 3\alpha_c + \cos 9\alpha_c \cos 3\alpha_a
+ \cos 3\alpha_a \cos 9\alpha_b + \cos 3\alpha_b \cos 9\alpha_c
+ \cos 3\alpha_c \cos 9\alpha_a),
$$

$$
A_{310}^{ccc}(\sin 9\alpha_a \sin 3\alpha_b + \sin 9\alpha_b \sin 3\alpha_c
+ \sin 9\alpha_c \sin 3\alpha_a
+ \sin 3\alpha_a \sin 9\alpha_b + \sin 3\alpha_b \sin 9\alpha_c
+ \sin 3\alpha_c \sin 9\alpha_a),
A_{220}^{ccc}(\cos 6\alpha_a \cos 6\alpha_b + \cos 6\alpha_b \cos 6\alpha_c
+ \cos 6\alpha_c \cos 6\alpha_a),
A_{220}^{ccc}(\sin 6\alpha_a \sin 6\alpha_b + \sin 6\alpha_b \sin 6\alpha_c
+ \sin 6\alpha_c \sin 6\alpha_a),
A_{211}^{ccc}(\cos 6\alpha_a \cos 3\alpha_b \cos 3\alpha_c
+ \cos 6\alpha_b \cos 3\alpha_c \cos 3\alpha_b
+ \cos 6\alpha_c \cos 3\alpha_a \cos 3\alpha_a),
A_{211}^{ccc}(\cos 6\alpha_a \sin 3\alpha_b \sin 3\alpha_c
+ \cos 6\alpha_b \sin 3\alpha_c \sin 3\alpha_b
+ \cos 6\alpha_c \sin 3\alpha_a \sin 3\alpha_a),
A_{211}^{ccc}(\sin 6\alpha_a \cos 3\alpha_b \sin 3\alpha_c
+ \sin 6\alpha_c \cos 3\alpha_a \sin 3\alpha_b
+ \sin 6\alpha_b \cos 3\alpha_a \sin 3\alpha_c
+ \sin 6\alpha_c \cos 3\alpha_b \sin 3\alpha_a
+ \sin 6\alpha_b \cos 3\alpha_a \sin 3\alpha_c).
$$

(13)

The second-order potential surface has four locations
that are stationary for arbitrary values of $A_{ij}^{ccc}$, and therefore we shall call the four corresponding ($\alpha_a, \alpha_b, \alpha_c$) stationary-
point conformations “canonical,” shown in Fig. 1: the $C_{3v}$
conformation (90°, 90°, 90°) = uuu (for up-up-up), the $C_{3h}$
conformation (0°, 0°, 0°) = rrr (for right-right-right), and two $C_2$
conformations (0°, 180°, 0°) = rrl (right-left-right) and
(90° + $\epsilon$, −90°, 90° − $\epsilon$) = udu (up-down-up). The udu st-
ationary point is unusual, because its location does not depend
on second-order $A_{ij}^{ccc}$ parameters (hence we call it a canoni-
cal stationary point; at second order $\epsilon = 0$), but does depend
on higher-order $A_{ij}^{ccc}$ parameters. (By ab initio calculations
below, $\epsilon$ is less than a degree on the true surface.) These
potential function forms also allow for other stationary points
which can be created by particular sets of $A_{ij}^{ccc}$ values;
the global minimum for (CH$_3$)$_3$C$^+$ is such a point, lying
quite near the udu stationary (saddle) point.

III. FITTING TO AB INITIO ENERGIES

We fitted and tested these potential functions with ab initio
data using the GAUSSIAN 92 suite of programs. Standard
levels of theory were employed, and core electrons were
held frozen in the correlation treatments. The correspon-
dences between the torsional parameters $\alpha$ and the individual dihedral
angles $\tau_{ccc,a}$ are taken to be

$$
\alpha_a = (1/6) \sum_j (\tau_{c_b c_c c_a H_j} + \tau_{c_b c_a c_c H_j} \pm 180°),
$$

(14)

$$
\alpha_b = (1/6) \sum_j (\tau_{c_c c_a c_b H_j} + \tau_{c_a c_b c_c H_j} \pm 180°),
$$

(15)

$$
\alpha_c = (1/6) \sum_j (\tau_{c_a c_b c_c H_j} + \tau_{c_b c_c c_a H_j} \pm 180°),
$$

(16)

where the $\tau$ values are defined between −180° and +180°.
The second $\tau$ terms [e.g., $\tau_{c_b c_c H_a}$ in Eq. (14)] will be
roughly +180° or −180° displaced from the leading $\tau$ terms
[e.g., $\tau_{c_b c_c H_a}$ in Eq. (14)], and hence the ±180° term
is inserted for appropriate averaging.

The first fitting was performed with the primitive model,
in which the bond lengths and angles were fixed arbitrarily at
r$_{CH}$ = 1.095 Å, r$_{CC}$ = 1.461 Å, $\theta_{CCC}$ = 120°, and
$\theta_{CCH}$ = 111°, with the methyl groups being individually $C_{3v}$ sym-
metric. For all nine symmetry-unique conformations in
which the methyl rotors could be in their right, up, left, or
down positions (e.g., 0°, 90°, 180°, or −90°, respectively),
MP2 energies with the 6-31G(d) basis set were computed.
These energies were observed to be fit very well (all within
0.15 kJ mol$^{-1}$) by the function truncated at second order [Eq.
(11), hereby designated $V^{(2)*}$] with $A^{ccc}_{110} = −1.24$ kJ mol$^{-1}$,
$A^{ccc}_{200} = 3.60$ kJ mol$^{-1}$, $A^{ccc}_{110}$, and $A^{ccc}_{200} = 0$. Since
$A^{ccc}_{200}$ will become important when relaxation is included,
one can conclude that the cos 6$\alpha$ terms are due primarily to
relaxation effects.

Moving on to fully relaxed models, we note that three of
the canonical conformations (uuu, rrr, and udu) were
studied by Sieber et al. who obtained fully relaxed MP2-
optimized structures with the 6-31G(d) basis set (and all
TABLE I. Ab initio values for inertial quantities (amu Å²) used in G matrices.

<table>
<thead>
<tr>
<th>Conformation</th>
<th>MP2/6-31G(d)</th>
<th>MP2/6-311G(d,p)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(I_i)</td>
<td>(A_{ijk})</td>
</tr>
<tr>
<td></td>
<td>(I_i)</td>
<td>(A_{ijk})</td>
</tr>
<tr>
<td>(rr)</td>
<td>3.031 85</td>
<td>0.080 17</td>
</tr>
<tr>
<td></td>
<td>3.040 85</td>
<td>0.080 74</td>
</tr>
<tr>
<td>(uu)</td>
<td>3.019 85</td>
<td>0.079 97</td>
</tr>
<tr>
<td></td>
<td>3.028 20</td>
<td>0.080 08</td>
</tr>
<tr>
<td>(du)</td>
<td>3.022 62</td>
<td>0.090 16</td>
</tr>
<tr>
<td></td>
<td>3.031 37</td>
<td>0.090 98</td>
</tr>
<tr>
<td>(ru)</td>
<td>3.022 67</td>
<td>0.083 14</td>
</tr>
<tr>
<td></td>
<td>3.030 99</td>
<td>0.083 62</td>
</tr>
<tr>
<td>(ud)</td>
<td>3.022 67</td>
<td>0.083 14</td>
</tr>
<tr>
<td></td>
<td>3.030 99</td>
<td>0.083 62</td>
</tr>
<tr>
<td>(rr)</td>
<td>3.031 66</td>
<td>0.084 12</td>
</tr>
<tr>
<td></td>
<td>3.040 77</td>
<td>0.084 67</td>
</tr>
<tr>
<td>(uu)</td>
<td>3.031 66</td>
<td>0.084 12</td>
</tr>
<tr>
<td></td>
<td>3.040 77</td>
<td>0.084 67</td>
</tr>
<tr>
<td>(du)</td>
<td>3.031 66</td>
<td>0.084 12</td>
</tr>
<tr>
<td></td>
<td>3.040 77</td>
<td>0.084 67</td>
</tr>
<tr>
<td>(ru)</td>
<td>3.032 70</td>
<td>0.087 08</td>
</tr>
<tr>
<td></td>
<td>3.041 88</td>
<td>0.087 99</td>
</tr>
<tr>
<td>(ud)</td>
<td>3.032 70</td>
<td>0.087 08</td>
</tr>
<tr>
<td></td>
<td>3.035 57</td>
<td>0.082 89</td>
</tr>
<tr>
<td>(Average)</td>
<td>3.027 09</td>
<td>0.084</td>
</tr>
<tr>
<td></td>
<td>3.036</td>
<td>0.084 41</td>
</tr>
</tbody>
</table>

The pertaining \(\tau_{CCCH}\) dihedral angles which would be 90° in the primitive model are 86.35° for \(\text{uuu}\) and 88.49°, \(-91.21°\), and 89.07° for \(\text{udu}\), with the 6-311G(d,p) basis.)

IV. TESTING AGAINST AB INITIO HARMONIC FREQUENCIES

We shall test the potential functions above by measuring their curvatures at the canonical stationary points. This was done by calculating the corresponding harmonic frequencies

| Table II. Ab initio energies [MP2/6-311G(d,p), kJ mol⁻¹] of various relaxed conformations.

<table>
<thead>
<tr>
<th>Conformation</th>
<th>(\tau_{C_1C_2C_3H_4})</th>
<th>(\tau_{C_1C_2C_3H_5})</th>
<th>(\tau_{C_1C_2C_3H_6})</th>
<th>(\alpha_a)</th>
<th>(\alpha_b)</th>
<th>(\alpha_c)</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>(rr)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.88</td>
</tr>
<tr>
<td>(uu)</td>
<td>86.35</td>
<td>86.35</td>
<td>86.35</td>
<td>90</td>
<td>90</td>
<td>90</td>
<td>6.95</td>
</tr>
<tr>
<td>(du)</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>0</td>
<td>180</td>
<td>0</td>
<td>7.34</td>
</tr>
<tr>
<td>(ru)</td>
<td>88.49</td>
<td>-91.21</td>
<td>89.07</td>
<td>90.47</td>
<td>-90</td>
<td>89.53</td>
<td>0.00</td>
</tr>
<tr>
<td>(rd)</td>
<td>90</td>
<td>0</td>
<td>90</td>
<td>93.62</td>
<td>6.61</td>
<td>92.49</td>
<td>3.29</td>
</tr>
<tr>
<td>(lu)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.26</td>
<td>91.82</td>
<td>2.28</td>
<td>2.89</td>
</tr>
<tr>
<td>(ld)</td>
<td>180</td>
<td>0</td>
<td>90</td>
<td>183.10</td>
<td>91.72</td>
<td>6.16</td>
<td></td>
</tr>
<tr>
<td>(cc)</td>
<td>45</td>
<td>45</td>
<td>45</td>
<td>49.32</td>
<td>49.32</td>
<td>49.32</td>
<td>2.57</td>
</tr>
<tr>
<td>(ck)</td>
<td>45</td>
<td>-45</td>
<td>45</td>
<td>49.77</td>
<td>-50.44</td>
<td>49.98</td>
<td>0.68</td>
</tr>
<tr>
<td>(cy)</td>
<td>45</td>
<td>-135</td>
<td>45</td>
<td>47.15</td>
<td>-132.89</td>
<td>48.58</td>
<td>4.91</td>
</tr>
<tr>
<td>(cx)</td>
<td>45</td>
<td>135</td>
<td>45</td>
<td>47.47</td>
<td>128.60</td>
<td>48.78</td>
<td>7.28</td>
</tr>
<tr>
<td>(cy)</td>
<td>45</td>
<td>-135</td>
<td>-45</td>
<td>48.79</td>
<td>-131.00</td>
<td>-50.50</td>
<td>5.44</td>
</tr>
<tr>
<td>(cx)</td>
<td>45</td>
<td>135</td>
<td>-45</td>
<td>49.41</td>
<td>130.72</td>
<td>-50.84</td>
<td>5.53</td>
</tr>
</tbody>
</table>

\(\text{a}\) Angles in degrees. See Eqs. (14)–(16) for definitions.

\(\text{b}\) Constrained during optimization.

\(\text{c}\) The ab initio global minimum lies at \((\alpha_a, \alpha_b, \alpha_c) = (85.45, -87.85, 86.34)\), with energy less than 0.001 kJ mol⁻¹ lower than that of \(\text{udu}\).
using the GF matrix method.\textsuperscript{21} The Mathematica program\textsuperscript{22} was employed extensively for this purpose. The harmonic frequencies are then tested by comparison to the directly computed, unapproximated MP2 values.

The elements of the kinetic $G$ matrix were derived in the manner of Swalen and Costain\textsuperscript{1} and found to be

$$G_{ij} = (I - \Lambda) / \left[ (I + \Lambda) (I - 2 \Lambda) \right],$$

$$G_{ij} = \Lambda / \left[ (I + \Lambda) (I - 2 \Lambda) \right],$$

where $I$ is the average moment of inertia of a methyl group reduced by the coupling with overall rotation, and $\Lambda$ is the average coupling term for two methyl groups.\textsuperscript{8,23} These two inertial quantities are taken as averages due to the minor (<0.5% of $I$) dependence on $\alpha_1$ as seen in Table I. In fact, since $\Lambda$ is only 3% of $I$ for (CH$_3$)$_3$C$^+$, the approximations $G_{ii} = 1/I$ and $G_{ij} = \Lambda / I^2$ were also tested, and the effect on the harmonic frequencies was less than 0.5 cm$^{-1}$. This was the form that was generally employed. We further tested the averaging approximation by employing

$$\begin{pmatrix}
1 / I_a & \Lambda_{ab} / I_a I_b & \Lambda_{ac} / I_a I_c \\
\Lambda_{ab} / I_a I_b & 1 / I_b & \Lambda_{bc} / I_b I_c \\
\Lambda_{ac} / I_a I_c & \Lambda_{bc} / I_b I_c & 1 / I_c
\end{pmatrix}$$

for the udu conformation, again reproducing the results of the previous two $G$ versions to within 0.5 cm$^{-1}$. We begin with the second-order function $V^{(2)}$. The force constant matrix $F$, containing elements $F_{ij} = \partial^2 V^{(2)} / \partial \phi_i \partial \phi_j$, is evaluated at each of the four positions of interest, producing:

$$\begin{pmatrix}
-36 A_{cccc}^{200} + 18 A_{issc}^{110} & 9 A_{sscc}^{110} & 9 A_{sccc}^{110} \\
9 A_{sscc}^{110} & -36 A_{cccc}^{200} + 18 A_{issc}^{110} & 9 A_{sccc}^{110} \\
9 A_{sscc}^{110} & 9 A_{sccc}^{110} & -36 A_{cccc}^{200} + 18 A_{issc}^{110}
\end{pmatrix}$$

for rrr, uuu, rlr, and udu, respectively. As opposed to the 3% ratio of $\Lambda$ to $I$ in the $G$ matrix, the ratio of $A_{sscc}^{110}$ or $A_{sccc}^{110}$ to $A_{cccc}^{200}$ is roughly 40%, allowing for no equivalent approximations.

Diagonalization of the matrix product of $F$ with $G$ gives the normal mode eigenvalues $\lambda_k$ which are converted to harmonic frequency wave numbers by $\omega_k = \sqrt{\lambda_k / (2 \pi c)}$ (c being the speed of light). These frequencies are listed in Table IV, together with the true MP2 harmonic frequencies computed analytically with both basis sets at the respective optimized stationary points. The agreement of the $V^{(2)}$ values with the true MP2 values is within 15 or 15i cm$^{-1}$ for 11 of 12 frequencies using the 6-31G(d) basis, and for 9 of 12 frequencies using the better 6-311G(d,p) data. With the better 6-311G(d,p) data, the two $V^{(2)}$ frequencies of lowest magnitude (the most sensitive ones) are unfortunately predicted to be real (27, 38 cm$^{-1}$) instead of imaginary (30i, 17i cm$^{-1}$), demonstrating qualitative error for $V^{(2)}$. The wide disparity of frequency magnitudes (from 17 to over 200 cm$^{-1}$) is indicative of not only severe coupling but of concerted motions of varying degrees of potential hindrance; for instance, the udu frequency at 17i cm$^{-1}$ [6-311G(d,p) basis] indicates that udu connects two minima via a very small barrier.

The most remarkable aspect of the $V^{(2)}$ potential is the symmetry of the curvatures at its canonical locations. Note that $A_{sscc}^{110}$ is approximately equal to $-A_{sscc}^{110}$ in Table III. If this were strictly true, then each element of the force constant matrix for uuu would be equal in magnitude and opposite in sign to its counterpart for rrr, and the same result would occur for udu versus rlr. This then leads to mirror-image harmonic frequencies. With the 6-31G(d) data in Table IV,
the true \textit{ab initio} frequencies display remarkable mirror-image character, except for the splitting of the magnitudes of the \{uuu, rrr\} pair at 1721,150 cm\(^{-1}\). In fact, even when \(A_{110}^{110}\) does not equal \(-A_{110}^{110}\) this particular splitting does not appear at second or even third order. With the 6-311G\((d,p)\) data, \(A_{110}^{110}\) and \(-A_{110}^{110}\) differ by a little more, and as a result the mirror-image nature becomes more approximate.

We move on to the fourth-order, 14-parameter potential function \(V^{(4)}\) to seek improvement in reproducing \textit{ab initio} frequencies, focusing only on 6-311G\((d,p)\) data. The resulting frequencies using the appropriate \(F\) matrices and the same \(G\) matrix are also shown in Table IV. Most frequencies are slightly better than those from the second-order function, but some are worse. The three most significant problems remaining in the \(V^{(4)}\) predictions are: the splitting of the third-order-degenerate magnitudes of the \{uuu, rrr\} pair (only split to 180i,178 cm\(^{-1}\) with \(V^{(4)}\), instead of 192i,145 from the \textit{ab initio} surface), the prediction of the 231-cm\(^{-1}\) udu frequency (261 cm\(^{-1}\) with \(V^{(4)}\)), and the prediction of the 171-cm\(^{-1}\) udu frequency (19 cm\(^{-1}\) with \(V^{(4)}\)). The last of these three should not be too surprising due to the magnified sensitivity of such low frequencies to parameter values, and although it incorrectly places the global minimum of \(V^{(4)}\) at the udu position, this should have little quantitative effect in application.

The remaining discrepancies with the true MP2/6-311G\((d,p)\) frequencies cannot be attributed to the 1/\(L\) and \(L/2\) approximation of the \(G\) matrix elements, since this was tested and shown to affect frequencies by less than 0.5 cm\(^{-1}\). One possible maleficence is deficiency in our fitting procedure, since our constraints for optimizations at nonstationary points were \(\pi\) dihedral angles and not \(\alpha\) ones, and since the function was fit to only a minimum number of points. Trial-and-error alteration of the parameter values was briefly attempted, with some improvement for frequency predictions; see again Tables III and IV for one alteration which includes adiabatically the zero-point vibrational energy (ZPVE) contributions from the higher-frequency modes, one can refit the four \(V^{(2)}\) parameters using canonical energies adjusted by half the sum of the 3\(N - 9 = 30\) higher harmonic frequencies. Using MP2/6-311G\((d,p)\) data, the contributions relative to the corrected near-minimum udu energy are (in kJ/mol): +0.46(rrr), +0.46(uuu), and +0.84(udu).

V. SUMMARY

The \(G_{324}\) symmetry group has been exploited in developing the Fourier expansion function for the three-dimensional potential surface for methyl internal rotations in the tertiary-butyl cation, \((\text{CH}_3)_3\text{C}^+\). A simple four-parameter functional form arises from the second-order Fourier series expansion, and this correctly predicts the four “canonial” stationary-point conformations. The simplicity of the surface itself leads to surprising mirror-image relations concerning the normal mode curvatures at these four positions, which are approximately valid when fitted to \textit{ab initio} energies and compared to analytic \textit{ab initio} harmonic frequencies. The fourth-order 14-parameter function was also developed, fitted, and examined, with minor improvements in predicting the true \textit{ab initio} frequencies at the canonical locations. These functions will be useful for the computation of properties, such as entropy or microwave transitions, which are dependent on these facile internal motions.

<table>
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<th>Conformation</th>
<th>Freq. (cm(^{-1}))</th>
<th>(\tau_{\text{CCCH}})</th>
<th>(\theta_{\text{IHCH}})</th>
<th>(\theta_{\text{CHCH}})</th>
<th>(\gamma_{\text{CCCH}})</th>
<th>(\tau_{\text{CCC}})</th>
<th>(R_{\text{CC}})</th>
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</tr>
</tbody>
</table>

\(^a\)The number of internal coordinates represented in each column are: 3 \(\tau_{\text{CCCH}}\), 6 \(\theta_{\text{IHCH}}\), 9 \(\theta_{\text{CHCH}}\), 2 \(\theta_{\text{CCC}}\), 1 \(\gamma_{\text{CCCH}}\) (umbrella or inversion mode), 3 \(R_{\text{CC}}\), and 9 \(R_{\text{CH}}\).
Total energy distribution analyses of the MP2/6-311G(d,p) harmonic force fields were presented, and bending and inversion coordinates were found to contribute from 5% to 13% to the methyl torsion normal modes at the uuu and udu positions, and 28% to 39% at the rrr and rlr positions. This suggests that further improvement of these potential functions might require incorporation of bending potential terms rather than higher-order Fourier series terms or more elaborate fitting procedures.

ACKNOWLEDGMENTS

P. R. Bunker and J. K. G. Watson are thanked for valuable discussions.

25 W. D. Allen, INTDER94, Stanford 1994 version. INTDER is a set of codes for performing general curvilinear transformations of coordinates and force constants, as well as harmonic frequency analyses.