The potential surface for the three methyl rotations in the tertiary-butyl cation, $(CH_3)_3C^+$

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The intricate symmetry of the potential energy surface for the three methyl rotation dimensions in the tertiary-butyl cation, $(CH_3)_3C^+$, 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 Costain[1] in 1959. For many of these systems, the potential surface is very well described by limited Fourier series potential functions such as[2]

$$V(\alpha_1, \alpha_2) = A_{00}^{cc} + A_{10}^{cc} \cos[n_1 \alpha_1] + A_{01}^{cc} \cos[n_2 \alpha_2]$$
$$+ A_{20}^{cc} \cos[2n_1 \alpha_1] + A_{02}^{cc} \cos[2n_2 \alpha_2]$$
$$+ A_{11}^{cc} \cos[n_1 \alpha_1] \cos[n_2 \alpha_2]$$
$$+ A_{11}^{ss} \sin[n_1 \alpha_1] \sin[n_2 \alpha_2] \tag{1}$$

and

$$V(\alpha_1, \alpha_2) = A_{00}^{cc} + A_{10}^{cc}(\cos 3\alpha_1 + \cos 3\alpha_2)$$
$$+ A_{11}^{cc} \cos 3\alpha_1 \cos 3\alpha_2$$
$$- |A_{11}^{cc}| \sin 3\alpha_1 \sin 3\alpha_2, \tag{2}$$

where α_1 and α_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, $(CH_3)_3C^+$, plays an important role in the experimental gas-phase proton affinity scale[12–14] because the proton affinity of isobutene, $(CH_3)_2CCH_2$, 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 $(CH_3)_2CCH_2$ and particularly $(CH_3)_3C^+$.[2]

The fluxional behavior of $(CH_3)_3C^+$ 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 $(CH_3)_3C^+$] in the original paper of Longuet-Higgins[16] on group theory for nonrigid 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:

$$V(\alpha_a,\alpha_b,\alpha_c)=\sum_{i,j,k=0}^{\infty} (A_{ijk}^{ccc}\cos[in_a\alpha_a]\cos[jn_b\alpha_b]\cos[kn_c\alpha_c]+A_{ijk}^{scc}\sin[in_a\alpha_a]\cos[jn_b\alpha_b]\cos[kn_c\alpha_c]$$
$$+A_{ijk}^{csc}\cos[in_a\alpha_a]\sin[jn_b\alpha_b]\cos[kn_c\alpha_c]+A_{ijk}^{ccs}\cos[in_a\alpha_a]\cos[jn_b\alpha_b]\sin[kn_c\alpha_c]$$
$$+A_{ijk}^{ssc}\sin[in_a\alpha_a]\sin[jn_b\alpha_b]\cos[kn_c\alpha_c]+A_{ijk}^{scs}\sin[in_a\alpha_a]\cos[jn_b\alpha_b]\sin[kn_c\alpha_c]$$
$$+A_{ijk}^{css}\cos[in_a\alpha_a]\sin[jn_b\alpha_b]\sin[kn_c\alpha_c]+A_{ijk}^{sss}\sin[in_a\alpha_a]\sin[jn_b\alpha_b]\sin[kn_c\alpha_c]) \tag{3}$$

in the style of Smeyers and co-workers.[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 ''factoring'' G_{324}:[17]

$$G_{324}=[C_3^a\otimes C_3^b\otimes C_3^c]\wedge[D_{3h}]$$
$$=[C_3^a\otimes C_3^b\otimes C_3^c]\wedge[[C_3^d\wedge M]\wedge[F]], \tag{4}$$

where $\otimes$ and Λ indicate direct and semidirect products, respectively, and the operator groups are

$$C_3^a=[E+(123)+(132)], \tag{5}$$
$$C_3^b=[E+(456)+(465)], \tag{6}$$
$$C_3^c=[E+(789)+(798)], \tag{7}$$
$$C_3^d=[E+(abc)+(acb)], \tag{8}$$
$$M=[E+(bc)], \tag{9}$$
$$F=[E+V^*], \tag{10}$$

using Longuet-Higgins' notation[16] and Woodman's V^*.[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:

$$C_3^a\Rightarrow V(\alpha_a,\alpha_b,\alpha_c)=V(\alpha_a\pm 2\pi/3,\alpha_b,\alpha_c)$$
$$\Rightarrow n_a=3,$$
$$C_3^b\Rightarrow V(\alpha_a,\alpha_b,\alpha_c)=V(\alpha_a,\alpha_b\pm 2\pi/3,\alpha_c)$$
$$\Rightarrow n_b=3,$$
$$C_3^c\Rightarrow V(\alpha_a,\alpha_b,\alpha_c)=V(\alpha_a,\alpha_b,\alpha_c\pm 2\pi/3)$$
$$\Rightarrow n_c=3,$$
$$F\Rightarrow V(\alpha_a,\alpha_b,\alpha_c)=V(-\alpha_a,-\alpha_b,-\alpha_c)$$
$$\Rightarrow A_{ijk}^{scc}=A_{ijk}^{csc}=A_{ijk}^{ccs}=A_{ijk}^{sss}=0,$$
$$C_3^d\Rightarrow V(\alpha_a,\alpha_b,\alpha_c)=V(\alpha_c,\alpha_a,\alpha_b)=V(\alpha_b,\alpha_c,\alpha_a)$$
$$\Rightarrow A_{ijk}^{xyz}=A_{jki}^{yzx}=A_{kij}^{zxy},$$
$$M\Rightarrow V(\alpha_a,\alpha_b,\alpha_c)=V(\alpha_a+\pi,\alpha_c+\pi,\alpha_b+\pi)$$
$$\Rightarrow A_{ijk}^{xyz}=(-1)^{i+j+k}A_{ikj}^{xzy}.$$

Only the implications of F stated above are dependent on choice of origin, for which we assume the C_{3h} structure **rrr** (Fig. 1) to represent the (0,0,0) position. If one assumes the C_{3v} position **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_{000}^{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
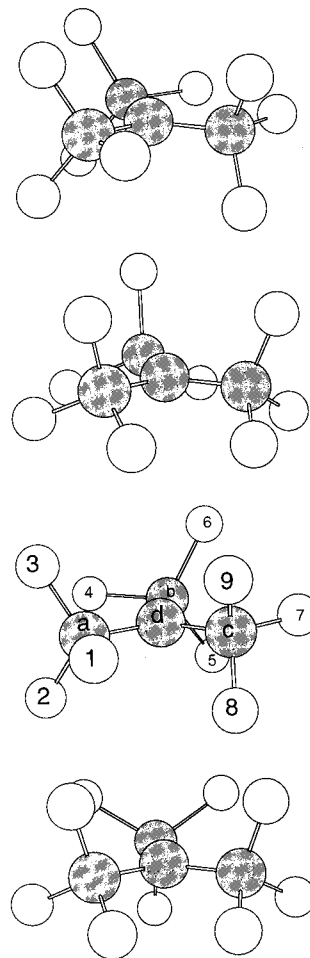

FIG. 1. The four canonical conformations of (CH$_3$)$_3$C$^+$. From top (high energy) to bottom (low energy): **rlr**, **uuu**, **rrr**, **udu**. Atomic labeling is demonstrated for **rrr**.

sional barriers below 0.1 kJ mol^{-1}),[18] 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-rotor barrier heights and cause torsional hindrances which range from toluenelike to methanol-like in magnitude.

The second-order expression is

$$V(\alpha_a,\alpha_b,\alpha_c) = A_{000}^{ccc} + A_{200}^{ccc}(\cos 6\alpha_a + \cos 6\alpha_b + \cos 6\alpha_c)$$
$$+ A_{110}^{ccc}(\cos 3\alpha_a \cos 3\alpha_b + \cos 3\alpha_a \cos 3\alpha_c$$
$$+ \cos 3\alpha_b \cos 3\alpha_c) + A_{110}^{ssc}(\sin 3\alpha_a \sin 3\alpha_b$$
$$+ \sin 3\alpha_a \sin 3\alpha_c + \sin 3\alpha_b \sin 3\alpha_c). \quad (11)$$

The third-order expression introduces only two additional terms

$$A_{210}^{ccc}(\cos 6\alpha_a \cos 3\alpha_b + \cos 6\alpha_b \cos 3\alpha_c$$
$$+ \cos 6\alpha_c \cos 3\alpha_a - \cos 3\alpha_a \cos 6\alpha_b - \cos 3\alpha_b \cos 6\alpha_c$$
$$- \cos 3\alpha_c \cos 6\alpha_a),$$
$$\quad (12)$$
$$A_{210}^{ssc}(\sin 6\alpha_a \sin 3\alpha_b + \sin 6\alpha_b \sin 3\alpha_c$$
$$+ \sin 6\alpha_a \sin 3\alpha_a - \sin 3\alpha_a \sin 6\alpha_b - \sin 3\alpha_b \sin 6\alpha_c$$
$$- \sin 3\alpha_c \sin 6\alpha_a).$$

At fourth order, eight additional terms appear:

$$A_{400}^{ccc}(\cos 12\alpha_a + \cos 12\alpha_b + \cos 12\alpha_c),$$
$$A_{310}^{ccc}(\cos 9\alpha_a \cos 3\alpha_b + \cos 9\alpha_b \cos 3\alpha_c + \cos 9\alpha_c \cos 3\alpha_a$$
$$+ \cos 3\alpha_a \cos 9\alpha_b + \cos 3\alpha_b \cos 9\alpha_c$$
$$+ \cos 3\alpha_c \cos 9\alpha_a),$$
$$A_{310}^{ssc}(\sin 9\alpha_a \sin 3\alpha_b + \sin 9\alpha_b \sin 3\alpha_c + \sin 9\alpha_c \sin 3\alpha_a$$
$$+ \sin 3\alpha_a \sin 9\alpha_b + \sin 3\alpha_b \sin 9\alpha_c + \sin 3\alpha_c \sin 9\alpha_a),$$
$$A_{220}^{ccc}(\cos 6\alpha_a \cos 6\alpha_b + \cos 6\alpha_b \cos 6\alpha_c$$
$$+ \cos 6\alpha_c \cos 6\alpha_a),$$
$$\quad (13)$$
$$A_{220}^{ssc}(\sin 6\alpha_a \sin 6\alpha_b + \sin 6\alpha_b \sin 6\alpha_c + \sin 6\alpha_c \sin 6\alpha_a),$$
$$A_{211}^{ccc}(\cos 6\alpha_a \cos 3\alpha_b \cos 3\alpha_c + \cos 6\alpha_c \cos 3\alpha_a \cos 3\alpha_b$$
$$+ \cos 6\alpha_b \cos 3\alpha_c \cos 3\alpha_a),$$
$$A_{211}^{css}(\cos 6\alpha_a \sin 3\alpha_b \sin 3\alpha_c + \cos 6\alpha_c \sin 3\alpha_a \sin 3\alpha_b$$
$$+ \cos 6\alpha_b \sin 3\alpha_c \sin 3\alpha_a),$$
$$A_{211}^{scs}(\sin 6\alpha_a \cos 3\alpha_b \sin 3\alpha_c + \sin 6\alpha_c \cos 3\alpha_a \sin 3\alpha_b$$
$$+ \sin 6\alpha_b \cos 3\alpha_c \sin 3\alpha_a$$
$$+ \sin 6\alpha_a \cos 3\alpha_c \sin 3\alpha_b + \sin 6\alpha_c \cos 3\alpha_b \sin 3\alpha_a$$
$$+ \sin 6\alpha_b \cos 3\alpha_a \sin 3\alpha_c).$$

The second-order potential surface has four locations that are stationary for arbitrary values of A_{ijk}^{xyz}, 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 $(90°,90°,90°) = \mathbf{uuu}$ (for up-up-up), the C_{3h} conformation $(0°,0°,0°) = \mathbf{rrr}$ (for right-right-right), and two C_s conformations $(0°,180°,0°) = \mathbf{rlr}$ (right-left-right) and $(90°+\epsilon,-90°,90°-\epsilon) = \mathbf{udu}$ (up-down-up). The $\mathbf{udu}$ stationary point is unusual, because its location does not depend on second-order A_{ijk}^{xyz} parameters (hence we call it a canonical stationary point; at second order $\epsilon = 0$), but does depend on higher-order A_{ijk}^{xyz} parameters. (By $ab\ initio$ calculations below, ϵ 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_{ijk}^{xyz} values; the global minimum for (CH$_3$)$_3$C$^+$ is such a point, lying quite near the $\mathbf{udu}$ 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.[19] Standard levels of theory were employed, and core electrons were held frozen in the correlation treatments. The correspondences between the torsional parameters α and the individual dihedral angles $\tau_{CCC_\alpha H_{\alpha i}}$ are taken to be

$$\alpha_a = (1/6)\sum_j^3 (\tau_{C_b C_d C_a H_{aj}} + \tau_{C_c C_d C_a H_{aj}} \pm 180°), \quad (14)$$

$$\alpha_b = (1/6)\sum_j^3 (\tau_{C_c C_d C_b H_{bj}} + \tau_{C_a C_d C_b H_{bj}} \pm 180°), \quad (15)$$

$$\alpha_c = (1/6)\sum_j^3 (\tau_{C_a C_d C_c H_{cj}} + \tau_{C_b C_d C_c H_{cj}} \pm 180°), \quad (16)$$

where the τ values are defined between $-180°$ and $+180°$. The second τ terms [e.g., $\tau_{C_c C_d C_a H_{aj}}$ in Eq. (14)] will be roughly $+180°$ or $-180°$ displaced from the leading τ terms [e.g., $\tau_{C_b C_d C_a H_{aj}}$ in Eq. (14)], and hence the $\pm 180°$ 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} symmetric. 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 $A_{110}^{ccc} = -1.24$ kJ mol^{-1}, $A_{000}^{ccc} = 3.60$ kJ mol^{-1}, $A_{110}^{ssc} = -A_{110}^{ccc}$, and $A_{200}^{ccc} = 0$. Since A_{200}^{ccc} will become important when relaxation is included, one can conclude that the cos 6α 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 $et\ al.$[15] 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 Å^2) used in G matrices.

Conformation	MP2/6-31G(d)		MP2/6-311G(d,p)	
	I_i	Λ_{jk}	I_i	Λ_{jk}
rlr	3.031 85	−0.080 17	3.040 85	−0.080 74
	3.019 85	−0.079 97	3.028 20	−0.080 08
	3.022 62	−0.090 16	3.031 37	−0.090 98
uuu	3.022 67	−0.083 14	3.030 99	−0.083 62
	3.022 67	−0.083 14	3.030 99	−0.083 62
	3.022 67	−0.083 14	3.030 99	−0.083 62
rrr	3.031 66	−0.084 12	3.040 77	−0.084 67
	3.031 66	−0.084 12	3.040 77	−0.084 67
	3.031 66	−0.084 12	3.040 77	−0.084 67
udu	3.027 09	−0.082 48	3.035 57	−0.082 89
	3.032 70	−0.087 08	3.041 88	−0.087 99
	3.027 09	−0.082 48	3.035 57	−0.082 89
Average	3.027	−0.084	3.036	−0.084

electrons correlated). They found that none of these three stationary points corresponded to minima, although the C_1 minimum they did find was indistinguishable in energy from their **udu** structure. We duplicated their MP2 fully relaxed optimizations with the 6-31G(d) basis (but with core electrons frozen) while adding the **rlr** conformation to the list, and then repeated the same calculations with the larger 6-311G(d,p) basis set. Correlation effects beyond MP2 on the structures of single-bond-saturated systems are known to be minor.[20]

Some comments about the resulting geometrical parameters are noteworthy. First, the differences due to the improved basis set are quite minor, with the largest effect being contractions of two degrees in certain θ_{CCH} values for the **udu** structure. (These structures are available on request.) Second, the four carbon atoms in the **uuu** and **udu** structures are, as expected, not quite coplanar, the central carbon being slightly displaced toward the bottom of the page in Fig. 1.

[The pertaining τ_{CCCH} dihedral angles which would be 90° in the primitive model are 86.35° for **uuu** and 88.49°, −91.21°, and 89.07° for **udu**, with the 6-311G(d,p) basis.] Third, the stationary point which we label **udu** is quite close to the second-order **udu** prediction, with $\epsilon < 1°$. Fourth, the moments of inertia for methyl rotations, which are presented in Table I (already reduced by the coupling with overall rotation), do not vary appreciably upon torsion, and nor do the kinetic coupling terms also listed.

Of more interest with these relaxed conformations are their energies. The relaxation has lowered the **udu** conformation energy to below that of **rrr**, which was the minimum using the primitive model. From the energies of the four canonical conformations, the four parameters of the second-order potential function ($V^{(2)}$) are uniquely defined. The resulting values for $[A_{000}^{ccc}, A_{200}^{ccc}, A_{110}^{ccc}, A_{110}^{ssc}]$ are $[2.970, 0.518, −1.415, 1.418]$ using 6-31G(d) energies and $[3.730, 0.665, −1.614, 1.738]$ using 6-311G(d,p) energies.

We also fitted the fourth-order, 14-parameter potential function (designated $V^{(4)}$), fitting analytically to the four canonical points above plus 10 more from restricted optimizations in C_1 symmetry. Note that these 10 optimizations were necessarily performed by constraining three $\tau_{CCC_\alpha H_{\alpha 1}}$ angles instead of the three α angles [see Eqs. (14)–(16)] due to algorithm limitations. The constrained $\tau_{CCC_\alpha H_{\alpha 1}}$ values and resulting α values and energies are shown in Table II. The **ccc** optimization resulted in a C_3 structure. The **rlu** and **lru** optimizations could have been confined to C_s symmetry, but this would not have removed the need to constrain $\tau_{CCC_\alpha H_{\alpha 1}}$ angles. The 14 fitted potential parameters appear in Table III.

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.[a]

Conformation	$\tau_{C_cC_dC_aH_{a1}}$	$\tau_{C_aC_dC_bH_{b1}}$	$\tau_{C_bC_dC_cH_{c1}}$	α_a	α_b	α_c	Energy[c]
rrr	0	0	0	0	0	0	0.88
uuu	86.35	86.35	86.35	90	90	90	6.95
rlr	0	180	0	0	180	0	7.34
udu	88.49	−91.21	89.07	90.47	−90	89.53	0.00
uru	90[b]	0[b]	90[b]	93.62	6.61	92.49	3.29
rur	0[b]	90[b]	0[b]	4.26	91.82	2.28	2.09
rlu	0[b]	180[b]	90[b]	3.67	183.10	91.72	6.16
lru	180[b]	0[b]	90[b]	180.02	4.00	91.10	5.46
ccc	45[b]	45[b]	45[b]	49.32	49.32	49.32	2.57
ckc	45[b]	−45[b]	45[b]	49.77	−50.44	49.98	0.68
cyc	45[b]	−135[b]	45[b]	47.15	−132.89	48.58	4.91
cxc	45[b]	135[b]	45[b]	47.47	128.60	48.78	7.28
cyk	45[b]	−135[b]	−45[b]	48.79	−131.00	−50.50	5.44
cxk	45[b]	135[b]	−45[b]	49.41	130.72	−50.84	5.53

[a]Angles in degrees. See Eqs. (14)–(16) for definitions.
[b]Constrained during optimization.
[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 **udu**.

TABLE III. Parameter values (kJ mol^{-1}) for potential functions for methyl internal rotation in $(CH_3)_3C^+$.

	MP2/6-31G(d)		MP2/6-311G(d,p)		
	$V^{(2)}$ (primitive)	$V^{(2)}$	$V^{(2)}$	$V^{(4)}$	$V^{(4)}$ (adjusted)
A_{000}^{ccc}	3.60	2.970	3.730	3.843	3.843
A_{200}^{ccc}	0	0.518	0.665	0.664	0.664
A_{110}^{ccc}	−1.24	−1.415	−1.615	−1.644	−1.644
A_{110}^{ssc}	1.24	1.418	1.738	1.712	1.712
A_{210}^{ccc}	0	0	0	−0.061	−0.061
A_{210}^{ssc}	0	0	0	0.044	0.044
A_{400}^{ccc}	0	0	0	0.006	0.006
A_{310}^{ccc}	0	0	0	0.023	0.01
A_{310}^{ssc}	0	0	0	−0.042	−0.042
A_{220}^{ccc}	0	0	0	−0.043	−0.01
A_{220}^{ssc}	0	0	0	0.053	−0.05
A_{211}^{ccc}	0	0	0	−0.018	0.
A_{211}^{ssc}	0	0	0	0.060	0.060
A_{211}^{scs}	0	0	0	0.001	0.001

TABLE IV. Harmonic frequencies (cm^{-1}) for methyl torsions.

	MP2/6-31G(d)ω_i		MP2/6-311G(d,p)ω_i			
Conformation	$V^{(2)}$	ab initio	$V^{(2)}$	$V^{(4)}$	$V^{(4)}$ (adj.)	ab initio
rlr	215 i	208 i	236 i	220 i	236 i	227 i
	173 i	169 i	194 i	189 i	184 i	188 i
	34	33	27	20 i	45 i	30 i
uuu	169 i	172 i	179 i	180 i	200 i	192 i
	75	77	83	69	74	77
	75	77	83	69	74	77
rrr	169	150	179	178	156	145
	76 i	71 i	100 i	102 i	88 i	98 i
	76 i	71 i	100 i	102 i	88 i	98 i
udu	215	210	238	261	250	231
	173	169	192	190	192	184
	33 i	31 i	38	19	33 i	17 i

using the GF matrix method.[21] The Mathematica program[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[1] and found to be

$$G_{ii} = (I - \Lambda)/[(I+\Lambda)(I-2\Lambda)], \tag{17}$$

$$G_{ij} = \Lambda/[(I+\Lambda)(I-2\Lambda)], \tag{18}$$

where I is the average moment of inertia of a methyl group reduced by the coupling with overall rotation, and Λ is the average coupling term for two methyl groups.[8,23] These two inertial quantities are taken as averages due to the minor ($<0.5\%$ of I) dependence on α_i as seen in Table I. In fact, since Λ is only 3% of I for $(CH_3)_3C^+$, 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

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

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 $F_{ij} = \partial V^2/\partial \alpha_i \partial \alpha_j$, is evaluated at each of the four positions of interest, producing:

$$\begin{pmatrix} -36A_{200}^{ccc}-18A_{110}^{ccc} & 9A_{110}^{ssc} & 9A_{110}^{ssc} \\ 9A_{110}^{ssc} & -36A_{200}^{ccc}-18A_{110}^{ccc} & 9A_{110}^{ssc} \\ 9A_{110}^{ssc} & 9A_{110}^{ssc} & -36A_{200}^{ccc}-18A_{110}^{ccc} \end{pmatrix},$$

$$\begin{pmatrix} 36A_{200}^{ccc}-18A_{110}^{ssc} & 9A_{110}^{ccc} & 9A_{110}^{ccc} \\ 9A_{110}^{ccc} & 36A_{200}^{ccc}-18A_{110}^{ssc} & 9A_{110}^{ccc} \\ 9A_{110}^{ccc} & 9A_{110}^{ccc} & 36A_{200}^{ccc}-18A_{110}^{ssc} \end{pmatrix},$$

$$\begin{pmatrix} -36A_{200}^{ccc} & -9A_{110}^{ssc} & 9A_{110}^{ssc} \\ -9A_{110}^{ssc} & -36A_{200}^{ccc}+18A_{110}^{ccc} & -9A_{110}^{ssc} \\ 9A_{110}^{ssc} & -9A_{110}^{ssc} & -36A_{200}^{ccc} \end{pmatrix},$$

$$\begin{pmatrix} 36A_{200}^{ccc} & -9A_{110}^{ccc} & 9A_{110}^{ccc} \\ -9A_{110}^{ccc} & 36A_{200}^{ccc}+18A_{110}^{ssc} & -9A_{110}^{ccc} \\ 9A_{110}^{ccc} & -9A_{110}^{ccc} & 36A_{200}^{ccc} \end{pmatrix}$$

for **rrr**, **uuu**, **rlr**, and **udu**, respectively. As opposed to the 3% ratio of Λ to I in the G matrix, the ratio of A_{110}^{ssc} or A_{110}^{ccc} to A_{200}^{ccc} is roughly 40%, allowing for no equivalent approximations.

Diagonalization of the matrix product of F with G gives the normal mode eigenvalues λ_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_{110}^{ssc} is approximately equal to $-A_{110}^{ccc}$ 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 correspondent 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 *ab initio* frequencies display remarkable mirror-image character, except for the splitting of the magnitudes of the {**uuu**, **rrr**} pair at {172i,150} cm^{-1}. In fact, even when A_{110}^{ssc} does not equal $-A_{110}^{ccc}$, this particular splitting does not appear at second or even third order. With the 6-311G(d,p) data, A_{110}^{ssc} and $-A_{110}^{ccc}$ 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 *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 *ab initio* surface), the prediction of the 231-cm^{-1} **udu** frequency (261 cm^{-1} with $V^{(4)}$), and the prediction of the 17i-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 $1/I$ and Λ/I^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 τ dihedral angles and not α 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 produces all harmonic frequencies to within 20 cm^{-1} of the true MP2/6-311G(d,p) values. A second possibility, however, is that the remaining disagreement is due to the neglect of potential (and kinetic) coupling with other internal coordinates, which we now address.

One means of quantifying the coupling to other internal coordinates is with total energy distribution (TED) analyses of harmonic force fields.[24–26] The energy distribution of normal mode k among the internal coordinates i can be determined as

$$[\text{TED}]_i^k = 100 L_{ik}[L^{-1}]_{ki}, \tag{19}$$

where the L matrix is derived from the fully dimensional F and G matrices.[26] Using the INTDER program,[27] TED analyses were performed with a common internal coordinate set at each of the four canonical stationary points, and the results are summarized in Table V. These analyses suggest that the internal rotations are roughly 10% coupled to intramethyl motions, and are further coupled from 0% to 20% to methyl wagging modes, depending on their torsional position. Cou-

TABLE V. Total energy distributions for torsional modes, as obtained from the MP2/6-311G(d,p) harmonic force fields.[a]

Conformation	Freq. (cm^{-1})	τ_{CCCH}	θ_{HCH}	θ_{CCH}	θ_{CCC}	γ_{CCCC}	R_{CC}	R_{CH}
rlr	227 i	69	13	18	0	0	0	0
	188 i	72	11	17	0	0	0	0
	30 i	66	10	18	0	6	0	0
uuu	192 i	113	−11	−2	0	0	0	0
	77	110	−9	−2	1	0	0	0
	77	110	−9	−2	1	0	0	0
rrr	145	60	10	20	0	9	0	0
	98 i	69	11	19	0	0	0	0
	98 i	69	11	19	0	0	0	0
udu	231	105	−8	0	3	0	0	0
	184	106	−8	0	2	0	0	0
	17 i	112	−10	−2	0	0	0	0

[a]The number of internal coordinates represented in each column are: 3 τ_{CCCH}, 6 θ_{HCH}, 9 θ_{CCH}, 2 θ_{CCC}, 1 γ_{CCCC} (umbrella or inversion mode), 3 R_{CC}, and 9 R_{CH}.

pling to the skeletal umbrella mode was found to be significant (5%–10%) in only two of the 12 cases. Based on this data, it would seem that the varying degrees of coupling with angular coordinates might preclude substantial improvement upon the $V^{(4)}$ potential function (or its parameter values given in Table III) by other purely torsional potential functions. This deficiency in $V^{(4)}$ is not serious for thermodynamic computations but its effect upon spectroscopic predictions might prove to be of future concern.

Finally, if one wished to use an effective potential function which included 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 $3N-9=30$ 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(**rlr**).

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, $(CH_3)_3C^+$. A simple four-parameter functional form arises from the second-order Fourier series expansion, and this correctly predicts the four ''canonical'' 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 *ab initio* energies and compared to analytic *ab initio* harmonic frequencies. The fourth-order 14-parameter function was also developed, fitted, and examined, with minor improvements in predicting the true *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.

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

[1] J. D. Swalen and C. C. Costain, J. Chem. Phys. **31**, 1562 (1959).

[2] A. L. L. East and L. Radom, J. Chem. Phys. **106**, 6655 (1997).

[3] J. R. Hoyland, J. Chem. Phys. **49**, 1908 (1968).

[4] D. M. Grant, R. J. Pugmire, R. C. Livingston, K. A. Strong, H. L. McMurry, and R. M. Brugger, J. Chem. Phys. **52**, 4424 (1970).

[5] P. Groner, G. A. Guirgis, and J. R. Durig, J. Chem. Phys. **86**, 565 (1987).

[6] T. Kundu, S. N. Thakur, and L. Goodman, J. Chem. Phys. **97**, 5410 (1992).

[7] D. C. Moule, Y. G. Smeyers, M. L. Senent, D. J. Clouthier, J. Karolczak, and R. H. Judge, J. Chem. Phys. **95**, 3137 (1991).

[8] Y. G. Smeyers, M. L. Senent, V. Botella, and D. C. Moule, J. Chem. Phys. **98**, 2754 (1993).

[9] M. L. Senent, D. C. Moule, Y. G. Smeyers, A. Toro-Labbé, and F. J. Peñalver, J. Mol. Spectrosc. **164**, 66 (1994).

[10] M. L. Senent, D. C. Moule, and Y. G. Smeyers, J. Chem. Phys. **102**, 5952 (1995).

[11] M. L. Senent and Y. G. Smeyers, J. Chem. Phys. **105**, 2789 (1996).

[12] M. Mautner and L. W. Sieck, J. Am. Chem. Soc. **113**, 4448 (1991).

[13] B. J. Smith and L. Radom, J. Am. Chem. Soc. **115**, 4885 (1993).

[14] J. E. Szulejko and T. B. McMahon, J. Am. Chem. Soc. **115**, 7839 (1993).

[15] S. Sieber, P. Buzek, P. v. R. Schleyer, W. Koch, and J. W. M. Carneiro, J. Am. Chem. Soc. **115**, 259 (1993).

[16] H. C. Longuet-Higgins, Mol. Phys. **6**, 445 (1963).

[17] C. M. Woodman, Mol. Phys. **19**, 753 (1970).

[18] W. Gordy and R. L. Cook, *Microwave Molecular Spectra* (Wiley-Interscience, New York, 1970).

[19] M. J. Frisch, G. W. Trucks, M. Head-Gordon, P. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Johnson, H. B. Schlegel, M. A. Robb, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, GAUSSIAN 92, Gaussian Inc., Pittsburgh, PA, 1992.

[20] A. Chung-Phillips and K. A. Jebber, J. Chem. Phys. **102**, 7080 (1995).

[21] E. B. Wilson, Jr., J. C. Delius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

[22] S. Wolfram, *The Mathematica Book*, 3rd ed. (Wolfram Media/Cambridge University Press, Cambridge, 1996).

[23] K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. **10**, 428 (1942).

[24] P. Pulay and F. Török, Acta Chim. Acad. Sci. Hungary **44**, 287 (1965).

[25] F. Keresztury and G. Jalsovszky, J. Mol. Struct. **10**, 304 (1971).

[26] W. D. Allen, A. G. Császár, and D. A. Horner, J. Am. Chem. Soc. **114**, 6834 (1992).

[27] 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.