

The structure of nalkanes: High precision *ab initio* calculation and relation to vibrational spectra

A. L. Aljibury, R. G. Snyder, Herbert L. Strauss, and Krishnan Raghavachari

Citation: *The Journal of Chemical Physics* **84**, 6872 (1986); doi: 10.1063/1.450691

View online: <http://dx.doi.org/10.1063/1.450691>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/84/12?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

Photodissociation dynamics of water in the second absorption band. II. *Ab initio* calculation of the absorption spectra for H₂O and D₂O and dynamical interpretation of “diffuse vibrational” structures
J. Chem. Phys. **90**, 7150 (1989); 10.1063/1.456680

Structure, vibrational spectra, and IR intensities of polyenes from *ab initio* SCF calculations
J. Chem. Phys. **88**, 1003 (1988); 10.1063/1.454266

Calculated B/A parameters for nalkane liquids
J. Acoust. Soc. Am. **82**, 614 (1987); 10.1121/1.395409

Isolated C–H stretching vibrations of nalkanes: Assignments and relation to structure
J. Chem. Phys. **81**, 5352 (1984); 10.1063/1.447677

Consistent Force Field for Calculations of Conformations, Vibrational Spectra, and Enthalpies of Cycloalkane and nAlkane Molecules
J. Chem. Phys. **49**, 5116 (1968); 10.1063/1.1670007



The structure of *n*-alkanes: High precision *ab initio* calculation and relation to vibrational spectra

A. L. Aljibury,^{a)} R. G. Snyder, and Herbert L. Strauss

Department of Chemistry, University of California, Berkeley, California 94720

Krishnan Raghavachari

AT & T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 10 December 1985; accepted 3 March 1986)

Detailed geometries and deuterium-isolated CH stretching frequencies are calculated for several different conformers of small *n*-alkanes at a number of levels of *ab initio* theory. The results of the calculations are carefully compared to experiment. The calculated frequencies fit a linear correlation to the calculated bond lengths with a mean absolute error of about 3 cm^{-1} . The experimental frequencies fit this correlation more closely. Notable deviations from the correlation occur for the crowded C–H bonds that exist in *gauche* conformers. The changes in geometry on rotating a methyl group in propane are calculated and compared with experimental results on frequency shifts for *n*-alkane methyl groups.

I. INTRODUCTION

The properties of the simple hydrocarbons have always been of interest since their structure and bonding serve as prototypes for much of carbon-based chemistry. Vibrational studies of deuterium-isolated C–H stretching modes provide high accuracy data that discriminates among various C–H bonds.^{1–5} This data can provide insight into structural detail and in the case of the *n*-alkanes enables us to make uniquely sensitive tests on the accuracy of *ab initio* calculations.

Deuterium isolated C–H stretching modes have proved to be remarkably local—that is, the frequency of each such mode correlates directly with the properties of the particular C–H bond from which it arises. It is therefore meaningful to compare observed isolated C–H stretching frequencies with properties of the C–H bond derived from theory.^{1–3} Recently, we have measured the gas phase Raman spectra of a series of simple alkanes in the C–H stretching region and assigned the deuterium isolated C–H stretching vibrations for a variety of conformers.⁴ This was accomplished by examining deuterated molecules which contained only one C–H bond, in either a specific or a random position. With a few exceptions, which are discussed below, the C–H frequencies were found to correlate linearly with calculated *ab initio* bond lengths to a precision of about 1 cm^{-1} in frequency or, equivalently to a precision of 10^{-4} Å in bond length. It is this high precision that provides a unique opportunity to assess the accuracy of *ab initio* calculations.

The meaningfulness of such a high order of precision in the calculated structural parameters is not apparent from the literature. For example, it has been noted that when the absolute values of the C–H bond lengths calculated at the 4-21G level are compared with the experimental values of C–H bond lengths for saturated hydrocarbons there are systematic discrepancies of the order of 0.01 Å .⁶ The magnitude of the discrepancy remains about the same for small mole-

cules, even for calculations at the 6-31G* level.⁷ Attempts to calculate frequencies directly yield even worse agreement with experiment: At either the 3-21G or 6-31G* level frequencies are too high by an average of about 200 cm^{-1} .⁸

Empirical correlations between calculated and experimental properties can be quite precise, however, and are widely used for this reason.^{1,2,4,5,8} The excellent correlation with observed frequencies within a given group of homologous molecules indicates that the calculated differences in structure can be meaningful even though the absolute values of the bond lengths are not. Furthermore, the C–H frequencies of *n*-alkanes are observed to fall in clusters that are regularly spaced with an average separation of $14.5 \pm 1\text{ cm}^{-1}$. The clustering of frequencies (and also, we note, of calculated C–H bond lengths) is a further manifestation of the fact that the isolated C–H stretching frequencies are determined by the structure of the *n*-alkane in the immediate vicinity of the C–H bond.⁴

To obtain structural and frequency information at the required high precision, we have calculated *ab initio* geometries for the various conformations of small *n*-alkanes using Hartree–Fock calculations with a 4-31G basis set.^{9(a)} More extensive calculations including the determination of the harmonic force constants and vibrational frequencies were also carried out with the slightly larger 6-31G basis set.^{9(b)}

The excellent correlation between calculated and experimental geometries and frequencies demonstrated here suggests that relatively simple calculations of bond lengths will provide predictions of frequencies. This is particularly useful in situations that are not directly accessible by experiment. An example is the variation in the geometry of a methyl group as a function of torsion angle. We will discuss this example and will compare the available, albeit indirect, data⁵ to the results of the calculation.

We first present the results of the *n*-alkane structure and frequency calculations using the various basis sets and compare these results to the experimental data. We then present the results for the methyl group, and finally we provide a brief discussion and summary.

^{a)} On leave from the University of Baghdad, Baghdad, Iraq.

II. RESULTS

A. Detailed geometry

The set of calculations with the 4-31G basis set,^{9(a)} which is the smaller, was done with the GAUSSIAN-78 and GAUSSIAN-80 programs at the Hartree-Fock level of theory. The optimizations were carried out until the residual forces were less than 10^{-4} mdyn, and this provided a geometry that had converged to 10^{-4} Å in the bond lengths and 10^{-3} rad in the bond angles. The detailed geometries of methane, ethane, propane, *n*-butane (both *trans* and *gauche*), *n*-pentane (*trans-trans*), isobutane, and neopentane are presented in Table I. (The geometry of propane as a function of torsional angle was also calculated and will be presented later in the paper.)

The calculated results are in good agreement with experiment for all geometrical parameters. The C-H and C-C bond lengths are, as expected, one to two hundredths of an angstrom less than the experimental values.¹¹⁻¹⁵ However, the calculated HCH angles are close to the experimental values to within a tenth of a degree both for ethane¹⁶ and for all such angles in propane.¹³ The calculated CCC angle in *gauche*-butane is about 1° larger than in *trans*-butane, in agreement with the electron-diffraction results.¹⁷

A discussion of the variation of the C-H bond lengths and of their correlation with the experimental frequencies may be found in our previous publication.⁴ Here, we simply note that the other geometrical features, C-C bond lengths and interbond angles show remarkable constancy among the all *trans n*-alkanes.

For *gauche n*-butane, there is a complication since not all the calculated C-H bond lengths correlate with our experimental frequencies. The difficulty involves the op_g^* C-H bond, which is the out-of-plane methyl group bond involved

in the closest nonbonding interaction. Such bonds are referred to as "crowded" C-H bonds in the following discussion. The geometry reported in Table I is that obtained by letting the calculated geometry optimize in the usual way. This leads to a CCCC dihedral angle of 65.2° and a bond length of 1.0826 Å, a value that does not remotely correlate with any observed isolated C-H frequency.⁴ If, however, the torsional angle is *constrained* to be 67.3°, a value closer to experimentally measured values,^{14,18} a C-H bond length of 1.0836 Å is found. This value is in accord with the experimental correlation.⁴ This problem is considered in more detail in the next section.

B. Calculated bond length vs calculated frequency

A larger basis set, 6-31G,^{9(b)} was used in a second set of calculations in which both geometries and frequencies were determined. Again, the geometries were computed precisely under criteria that carefully controlled the convergence. Consequently, all the calculated frequencies are believed to have a precision of about 1 cm^{-1} . The C-H bond lengths and the calculated harmonic frequencies (discussed further below) are listed in Table II for most of the molecules in Table I. In addition, similar calculations were performed for *trans-gauche n*-pentane, but these results are not listed in Table II. The basis sets are different for Table I and Table II, and this results in a small uniform shift in the calculated bond lengths: The 6-31G values are uniformly larger by about 0.001 Å.¹⁹

To test the effect of higher levels of *ab initio* theory, further calculations were carried out on butane. The results are shown in Table III. Both the C-H bond lengths and the CCCC dihedral angle are listed. The calculated parameters in Table III are for the following basis sets:

TABLE I. Optimized geometry and energies of alkanes (C_1 - C_5) at the 4-31G level.

Molecule	r_{C-H} (Å)	HCH°	HCC°	r_{C-C} (Å)	CCC	E_{min} (a.u.)
CH ₄	1.0810	109.4 ₇				- 40.139 77
C ₂ H ₆	1.0835	107.7 ₂	111.1 ₆	1.528 ₈		- 79.115 60
C ₃ H ₈	1.0835 ip ^a	107.7 ₈ ^b	111.2 ₆ ^b			- 118.092 81
	CH ₃	107.9 ₀ ^b	111.0 ₀ ^b			
T-C ₄ H ₁₀	CH ₂	106.4 ₁	109.4 ₃	1.529 ₈	112.6 ₃	- 157.071 59
	CH ₃	107.7 ₅	111.2 ₅			
	CH ₂	107.8 ₆	111.0 ₆	1.529 ₃ ^α		
	CH ₃	106.2 ₅	109.4 ₅	1.530 ₅ ^β	112.9 ₄	
G-C ₄ H ₁₀	CH ₂	107.4 ₀	110.8 ₆			- 157.070 16 ^c
	CH ₃	107.7 ₅	111.8 ₀			
	CH ₂	106.3 ₈	108.8 ₄	1.530 ₉		
	CH ₃	107.7 ₅	111.2 ₅	1.535 ₁	114.1 ₀	
TT-C ₅ H ₁₂	CH ₂	106.4 ₁	109.2 ₂	1.529 ₆ ^α	112.8 ₇	- 196.049 29
	CH ₃	107.9 ₆	110.7 ₂	1.530 ₇ ^β	113.3 ₀	
	α-CH ₂	106.4 ₁	109.2 ₂			
	β-CH ₂	106.4 ₁	109.2 ₂			
iso-C ₄ H ₁₀	CH ₂	107.7 ₅	111.2 ₅			- 157.072 6
	CH ₃	107.9 ₆	110.7 ₂			
neo-C ₅ H ₁₂	CH	107.7 ₅	111.1 ₅	1.532 ₅	110.9 ₁	- 196.051 38
	CH ₂	107.7 ₅	111.1 ₅	1.537 ₀	109.4 ₉	

^a Abbreviations: ip, in plane; op, out-of-plane, see the text for op_g^* .

^b The first HCH angle is ip-op, the second is op-op, similarly the first HCC angle is with the ip HC, the second with the op HC.

^c The *trans-gauche* difference in E_{min} is 0.001 43 a.u. = 0.90 kcal/mol.

TABLE II. Geometries and isolated C–H stretching frequencies of *n*-alkanes calculated at the HF/6-31G level.

Molecule	$r_{\text{C-H}} (\text{\AA})$	Isolated frequency (cm^{-1})		Frequency shifts (cm^{-1}) ^b		Δ	$\Delta - 5$
		Theory	Expt	Theory	Expt		
CH ₄	1.0821	3271	2992
C ₂ H ₆	1.0844	3232	2953	39	39	0	-5
C ₃ H ₈	CH ₃	1.0845 ip ^a	3232	2950	39	42	-2
		1.0854 op ^a	3223	2937	48	55	2
T-C ₄ H ₁₀	CH ₂	1.0864	3199	2920	72	72	-5
	CH ₃	1.0845 ip ^a	3232	2949	39	43	-1
		1.0853 op ^a	3223	2936	48	56	3
		1.0873	3189	2907	82	85	-2
G-C ₄ H ₁₀	CH ₃	1.0846 ip ^a	3230	2949	41	43	-3
		1.0838 op ^{a*}	3241	2949	30	43	8
		1.0856 op ^a	3219	2933	52	59	2
	CH ₂	1.0867 ip ^a	3194	2917	77	75	-7
TT-C ₅ H ₁₂		1.0875 op ^a	3188	2903	83	89	1
	CH ₃	1.0845 ip ^a	3232	2949	39	43	-1
		1.0853 op ^a	3223	2936	48	56	3
	α -CH ₂	1.0873	3190	2906	81	86	0
	β -CH ₂	1.0883	3180	2892	91	100	4

^a Abbreviations: ip, in plane; op, out-of-plane; see the text for op^{*}.

^b Shift relative to CH₄.

Column 1: The 6-31G basis set (as in Table II).

Column 2: A polarized 6-31G* basis,²⁰ which was chosen to investigate the effect of using a larger basis set.

Column 3: A 6-31G basis set in which electron correlation is included by means of second-order Møller–Plesset perturbation theory (MP2).^{21,22}

Again there is a nearly uniform difference between the bond length calculated by different methods. We note that the calculated dihedral angle in *gauche* *n*-butane remains remarkably constant at about $65.5 \pm 0.4^\circ$ (Tables I and III) at all the different levels of theory. The op^{*} C–H bond length will be discussed further below.

Vibrational frequencies were determined with the optimized geometries. First, complete harmonic force fields were evaluated by means of analytical second derivative techniques,^{8(a)} and then the vibrational problem was solved for each appropriate isotopically substituted molecules to

yield the deuterium-isolated C–H frequencies. These frequencies are listed in Table II. As expected,^{8(b)} the absolute calculated frequencies are too high by about 10%, but the computed frequency shifts relative to methane are comparable to experiment (Table II). (In what follows, “frequency shift” will refer to downward shift of frequency from the isolated C–H stretching frequency of methane.) As before, we carried out some calculations at a higher level of theory¹⁰ to determine the effect on the frequencies. We note, however, that improving the level of the *ab initio* theory can worsen the absolute agreement between theory and experiment, although usually the differences are still systematic. For example, the calculated values of the frequency shifts for *n*-alkanes with the polarized 6-31G* basis set are about 10% smaller than the 6-31G values in Table II.¹⁰

To determine the degree of localization of the isotopically isolated C–H stretching modes, we compare the C–H frequencies derived from a complete normal coordinate calculation with those calculated on the assumption that the molecule is a two particle system, i.e., a hydrogen atom attached to a rigid framework. If the framework is given a mass of 12 amu (the mass of a single carbon atom), it is found that the frequencies, which are listed in Table IV, have values that are uniformly about 12 cm^{-1} higher than those calculated for the entire nonrigid molecule. The uniform shift of the calculated two-particle frequencies is solely due to a mass effect, since, if a mass of 13.3 amu is assigned to the framework, the two-particle frequencies are all within 1 cm^{-1} of the C–H frequencies of the nonrigid molecule. This clearly shows that all the isolated C–H stretching frequencies are local in nature. Because the vibration is nearly pure C–H stretching, the effect of interaction force constants is negligible. Thus the magnitudes of the frequencies are governed by the corresponding diagonal force constants.

Figure 1 illustrates the same point. If the diagonal stretching force constants for the various C–H bonds are

TABLE III. Calculated geometrical parameters for *n*-butane calculated at different levels of theory.

Conformer	Parameter ^b	HF/6-31G	HF/6-31G*	MP2/6-31G
Trans	CH ₃ -ip ^a	1.0845	1.0857	1.0990
	-op ^a	1.0853	1.0864	1.0998
Gauche	CH ₂ -	1.0873	1.0881	1.1028
	CH ₃ -ip ^a	1.0846	1.0857	1.0991
	-op ^{a*}	1.0838	1.0850	1.0985
	-op ^a	1.0856	1.0868	1.1002
	CH ₂ - ip ^a	1.0867	1.0873	1.1021
	-op ^a	1.0875	1.0883	1.1029
	Dihedral angle	65.9°	65.9°	65.4°

^a Abbreviations: ip, in plane; op, out-of-plane; see the text for op^{*}.

^b Bond lengths in Å and dihedral angles in degrees.

TABLE IV. Force constants and the corresponding isolated frequencies for the various C-H bonds in *n*-alkanes calculated at the HF/6-31G level.

Molecule	Hydrogen	Force constant (mdyn Å ⁻¹)	Frequency ^b (cm ⁻¹) effective diatomic mass	
			$m_c = 12.0$	$m_c = 13.3$
CH ₄		5.906	3283	3271
C ₂ H ₆		5.766	3244	3232
C ₃ H ₈	CH ₃ -ip ^a	5.766	3244	3232
	-op ^a	5.734	3235	3223
	CH ₂	5.646	3210	3198
<i>T</i> -C ₄ H ₁₀	CH ₃ -ip ^a	5.766	3245	3232
	-op ^a	5.735	3236	3223
	CH ₂	5.614	3201	3189
<i>G</i> -C ₄ H ₁₀	CH ₃ -ip ^a	5.760	3243	3231
	-op ^{a*}	5.801	3254	3242
	-op ^a	5.723	3232	3220
	CH ₂ -ip ^a	5.631	3206	3194
	-op ^a	5.609	3200	3188
<i>TT</i> -C ₅ H ₁₂	CH ₃ -ip ^a	5.765	3244	3232
	-op ^a	5.735	3236	3224
	α -CH ₂	5.615	3202	3190
	β -CH ₂	5.582	3192	3180

^a Abbreviations: ip, in plane; op, out-of-plane; see the text for op^{a*}.

^b Calculated as a diatom C-H with the effective mass of the carbon as m_c .

plotted against the corresponding isolated frequencies, a nearly perfect straight line is obtained.

1. Bond length/frequencies

We now consider the bond length frequency correlations. In Fig. 2 the calculated C-H bond lengths from Table II are plotted against the corresponding experimentally determined isolated C-H frequencies. *Trans-gauche n*-pentane has been included to provide additional data points, particularly for the crowded C-H bonds. The correlation between these two quantities is excellent and very similar to

that found in our previous work,⁴ except for the points associated with crowded C-H bonds. In Ref. 4, we plotted the values of the C-H bond lengths obtained from the calculation in which the dihedral angle was constrained (see Sec. II A). However, here in Fig. 2, the results from the unconstrained calculations are plotted and hence the deviations. The points for the crowded C-H bonds are indicated by arrows.

Table III shows that the use of higher levels of *ab initio* theory does not cause the anomalous bond lengths calculated for the crowded C-H bonds to become appreciably less

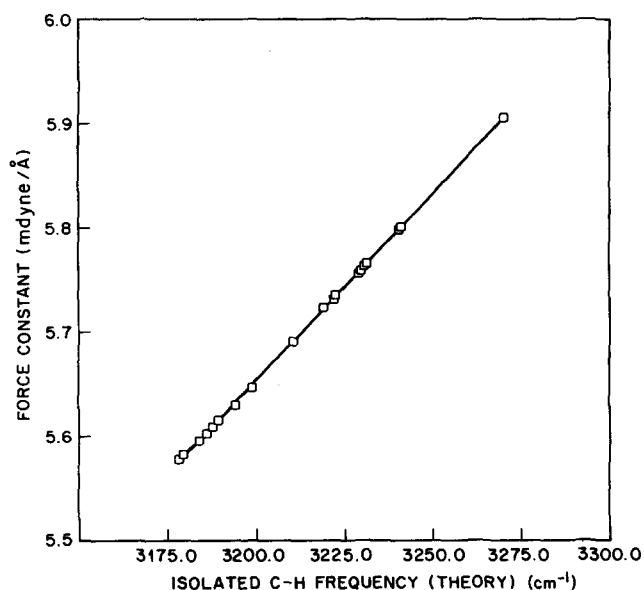


FIG. 1. The calculated force constants, K_{CH} in mdyn/Å, vs the calculated deuterium-isolated CH frequencies, ν_{CH}^D in cm⁻¹.

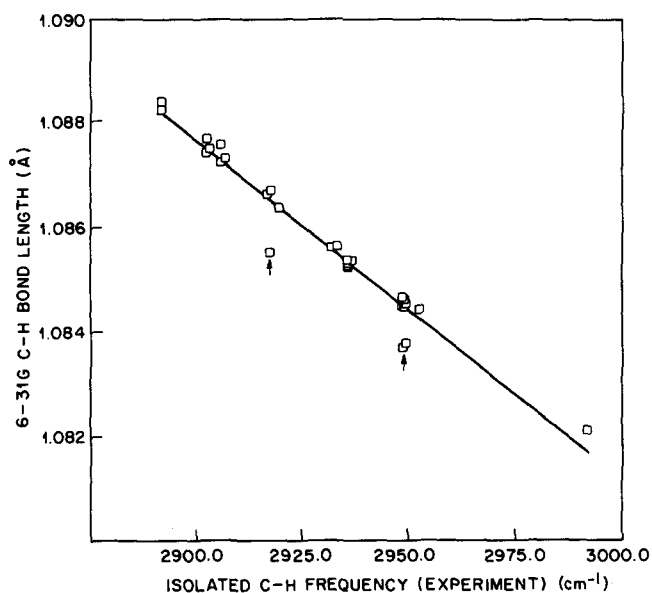


FIG. 2. The calculated C-H bond lengths in Å vs the experimental isolated frequencies in cm⁻¹. The arrows indicate data points for the crowded C-H bonds designated op^{a*} in the text.

anomalous. Nor is the CCCC dihedral angle of *n*-butane much changed: Its calculated value varies between the narrow limits 65.4° and 65.9° . The calculated values of the dihedral angle can be compared to the values obtained from non-vibrational experiments in order to provide an independent assessment of the agreement between theory and experiment. The early electron diffraction work¹⁴ yielded a higher value, $67.5 \pm 1.1^\circ$, and as mentioned earlier, a constrained calculation with the dihedral angle set at 67.3° , which is near this experimental value, yielded bond lengths consistent with the established correlation. However, newer experimental results²³ provide even higher values of the angle, $72.4 \pm 4.8^\circ$ and $70.5 \pm 4.5^\circ$. These values barely overlap the *ab initio* values for this angle. Clearly it is of much interest to resolve this significant difference between experiment and theory. Comparison of the relative values of the bond lengths for the ip (in plane) and op_g^* methyl hydrogens in *gauche*-butane (which have been assigned from experiment⁴ to the same isolated C-H stretching frequency) shows that all three levels of theory give similar results, viz. the bond length for the op_g^* hydrogen is 0.0007 ± 0.0001 Å shorter than that of the ip hydrogen.

In summary, the *ab initio* values of the dihedral angle of *n*-butane are in approximate agreement with the various experimental values. The calculated values of the bond lengths for all the *n*-alkanes fit a bond length experimental-isolated frequency correlation nearly exactly except for the crowded C-H bonds.

We now examine the correlation between bond lengths and isolated frequencies for the case where the values of *both* are calculated and find quite a different situation. These two quantities are plotted against each other in Fig. 3. As mentioned earlier, the isolated frequencies and bond lengths have been calculated in a manner to insure that there is no residual, purely numerical error in the points plotted in Fig.

3. Surprisingly, the correlation is not as good as that in Fig. 2. A quantitative comparison of the goodness of fit between these plots was made on the basis of the R^2 coefficient computed for a straight line fit of the data in Table II. (The op_g^* point in the table was omitted.) For bond lengths vs experimental frequencies (Fig. 2), $R^2 = 0.9968$; for bond lengths vs calculated frequencies (Fig. 3) $R^2 = 0.985$. The difference between the two correlations, the one using experimental frequencies and the other using calculated frequencies, will, of course, also be evident if the two sets of frequencies are plotted against one another as shown in Fig. 4.

Similar results can also be seen in Table II. If we compare the frequency shifts between theory and experiment (Δ indicates the difference between the shifts), the largest errors (~ 13 – 15 cm^{-1}) are found for the crowded pair of C-H bonds of *gauche* *n*-butane and for the crowded C-H bonds of *trans-gauche* *n*-pentane (not listed in Table II). But there are also errors of the order of 7 – 8 cm^{-1} in the case of CH_3 - op bonds and 8 – 9 cm^{-1} in the case of the pentane β - CH_2 bonds. Thus when we use calculated frequencies we find a range of errors rather than the near perfect fit with (a few) exceptions that was found when we plotted bond length against experimental frequency.

Closer scrutiny of the deviation Δ between the theoretical and experimental frequency shifts in Table II shows that there is a significant systematic error. The calculated values for Δ are, in most cases, smaller than the experimental values. If all the shifts calculated from theory are uniformly increased by 5 cm^{-1} and then compared with experimental values, the resulting errors (indicated by $\Delta - 5$ in Table II) have both positive and negative signs. The mean absolute deviation between theory and experiment is now about 3 cm^{-1} (corresponding to a mean error in the relative bond lengths of about 0.0002 Å) and this represents the random component of the error in the calculations after correcting for the systematic underestimations. The crowded bond in

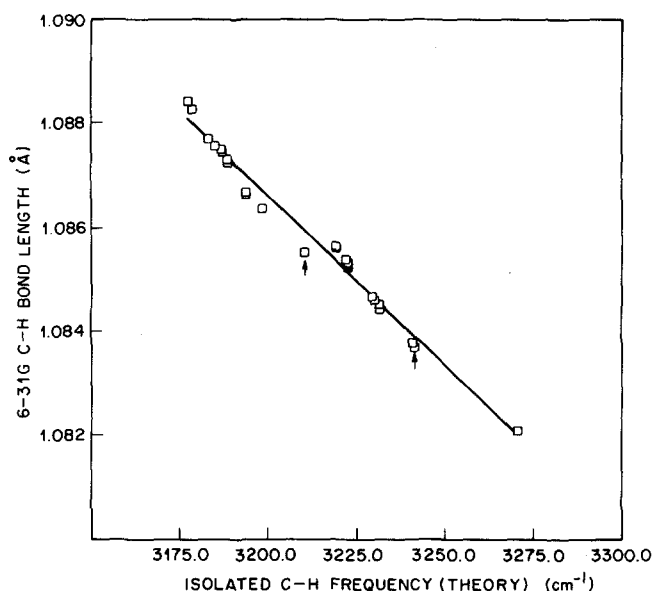


FIG. 3. The calculated C-H bond lengths vs the calculated isolated C-H frequencies in cm^{-1} . As in Fig. 2, the arrows point to the op_g^* frequencies. Note that in addition to the op_g^* data points, a number of other points deviate significantly from the correlation.

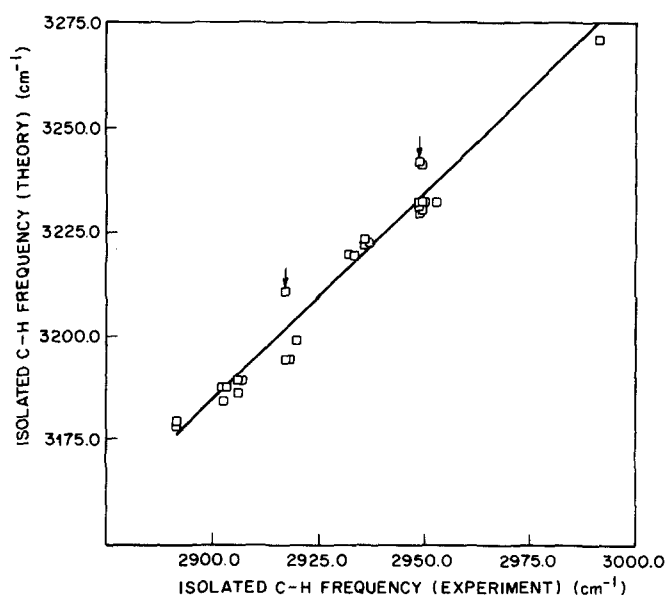


FIG. 4. The calculated isolated C-H frequencies vs the experimental frequencies, both in cm^{-1} . The arrows point to the op_g^* points.

gauche-butane still has the largest error (8 cm⁻¹) but this deviation does not stand out, since it is compatible with a distribution of errors having a mean value of ≈ 3 cm⁻¹.

C. Rotation of the methyl group

Table V indicates how the energy and bond lengths in propane vary with the rotation of one of the methyl groups. These results are for the 4-31G basis set. Only points between 0° and 60° need be calculated, since the properties of the molecule are exactly the same at an angle ψ and 120°- ψ , and of course, these repeat every 120°.

The energy variation can be made explicit by expressing it in a Fourier series. We obtain (in a.u.)

$$E(\psi) = -118.091\,253\,75 - 25\,452.92 \times 10^{-7} \cos 3\psi \\ - 75 \times 10^{-7} \cos 6\psi + 2.92 \times 10^{-7} \cos 9\psi \\ - 37.5 \times 10^{-7} \cos 12\psi. \quad (1)$$

This gives a threefold barrier of 3.19 kcal/mol, very close to the value of 3.3 kcal/mol for the rotation of one methyl group obtained from an analysis of the microwave data for propane.²⁴ The sixfold term is about ten calories, a reasonable magnitude,²⁵ and the ninefold term is smaller still. The 12-fold term is larger, but points calculated at more closely spaced values of ψ are needed to obtain an accurate 12-fold term. In the present calculation all the accumulated numerical error is probably in this term.

As the methyl group rotates, so does the in-plane hydrogen until, at a ψ of 120°, it becomes an out-of-plane hydrogen. Therefore the angle dependence of all three bond lengths can be written in one formula, which in angstroms, is

$$r_{ip} = 1.0835 - 4.7 \times 10^{-4} \cos \psi - 0.9 \times 10^{-4} \cos 2\psi \\ + 4.4 \times 10^{-4} \cos 3\psi + 0.3 \times 10^{-4} \cos 4\psi \\ - 0.5 \times 10^{-4} \cos 5\psi + \dots \quad (2)$$

Note the slow convergence of this series. The symmetry of the molecule requires only that the series contain cosine terms (not just threefold terms). The bond length changes are small—not much bigger than the error in the calculations,

and so it is possible that a more accurate calculation of the bond lengths would lead to a Fourier expansion with more obviously converging terms. The out-of-plane bond lengths can be obtained from Eq. (2) by adding or subtracting 120° from ψ . The variation of all three bond lengths with angle is shown in Fig. 5. The methyl group bond lengths change dramatically. All three C-H bond lengths initially *decrease* on rotation away from their equilibrium positions. From our bond length—frequency correlation we find that the change in bond length of about 10^{-3} Å corresponds to an increase in frequency of about 16 cm⁻¹. This is in accord with the results of our vibrational studies of methyl group rotation in *n*-alkanes which show that the experimental CH ip-CH op splitting is about 10 cm⁻¹ and that the CH frequencies increase on rotation. A more detailed analysis of the effect of the rotation on the vibrational spectrum will be required to make the comparison with experiment more quantitative.

The largest change in any bond length is for the C-C bond adjoining the rotating methyl. It increases by 0.013 Å in going to the eclipsed conformation. Unfortunately there is no direct way to check this value. However, it is qualitatively in accord with the calculated values of the derivatives of the internal rotation barrier of ethane with respect to the C-C bond length.²⁶ Indeed such calculations also indicate a decrease in the C-H bond length with torsion about the C-C bond.

As expected, much smaller C-H bond length changes are found in the methyl group at the other end of the molecule.

III. DISCUSSION AND CONCLUSIONS

As we have already noted in the Introduction, the values of *ab initio* calculated structural parameters and vibrational frequencies do not compare well in an absolute way with those from the experiment. However, the high level of precision that can be obtained in these calculations can be exploited through the *correlation* of calculated and experimental quantities within a homologous group of molecules. The criterion for usefulness is thus shifted away from one of agree-

TABLE V. The structural effect of rotating the methyl group in propane.

Bond length		$\psi = 0^\circ$	$\psi = 15^\circ$	$\psi = 30^\circ$	$\psi = 45^\circ$	$\psi = 60^\circ$
Rotating CH ₃ ^a	C-H _{ip}	1.083 5 Å	1.083 4	1.083 2	1.082 9	1.082 9
	C-H _{op}	1.084 3	1.084 2	1.083 7	1.083 2	1.083 0
	C-H _{op}	1.084 3	1.084 2	1.083 9	1.083 7	1.083 6
α_{C-C}		1.529 ₈	1.531 1	1.536 7	1.542 0	1.543 2
Rigid CH ₃ ^a	C-H _{ip}	1.083 5	1.083 6	1.083 7	1.083 7	1.083 7
	C-H _{op}	1.084 3	1.084 5	1.084 7	1.084 4	1.084 3
	C-H _{op}	1.084 3	1.084 1	1.083 8	1.083 9	1.084 1
β_{C-C}		1.529 8	1.530 8	1.530 7	1.531 8	1.531 0
CH ₂	C-H _{ψ_+} ^c	1.085 5	1.085 4	1.085 2	1.084 6	1.084 3
	C-H _{ψ_-}	1.085 5	1.085 1	1.084 3	1.084 1	1.084 2
E_{min} a.u.		-118.093 81	-118.093 05	-118.091 25	-118.089 45	-118.088 72

^a The "rotating" CH₃ is the one which is at the angle ψ ; the CH₃ at the other end is referred to as "rigid."

^b ψ is the dihedral angle between the C-C-H_{ip} and the C-C-C plane.

^c C-H _{ψ_+} is the methylene C-H bond which lies in the direction of increasing torsional angle ψ .

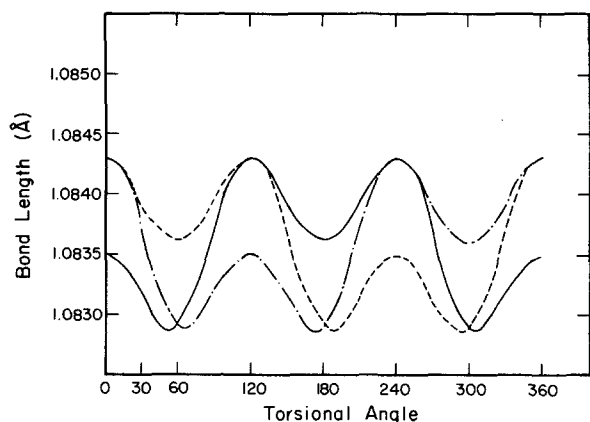


FIG. 5. The calculated variation in the C-H bond lengths in Å of a methyl group of propane as a function of the torsional angle. The variation is periodic and the three hydrogens exchange positions as the methyl group rotates. The variation in bond length of 10^{-3} Å corresponds to a frequency shift of about 16 cm^{-1} (Fig. 2). The full line follows the length of the CH bond that starts out in-plane at zero degrees, the dashed and dot-dashed lines follow the two initially out-of-plane CH bonds.

ment among absolute magnitudes to one of correlation. The failure to obtain agreement comes from a number of well defined sources. Experimentally determined structural parameters rarely lend themselves to simple interpretation. Of relevance to our discussion are the existence of many different kinds of "effective" bond lengths, each appropriate to the experimental method used. None of these effective values can easily be reduced to a value that can be compared directly to the computed bond length with an accuracy that approaches 10^{-4} Å. A similar situation exists for experimental vibrational frequencies. These should, in principle, be corrected for a myriad of anharmonic effects and then reduced to harmonic valence frequencies by solving the normal coordinate problem. Fortunately, the deuterium isolated C-H stretching modes are localized to such a degree that their frequencies accurately reflect the subtle distinctions among alkane C-H bonds so that the (unmanageable) corrections are not needed.

Correlations between bond lengths and frequencies have been known for a long time (cf. "Badger's rule").²⁷ What distinguishes the correlation that we have demonstrated is its extraordinary precision $1\text{ cm}^{-1} \cong 1 \times 10^{-4}$ Å albeit, only over a set of similar molecules (Fig. 2). As we have noted, however, even the correlation for the *n*-alkanes is not completely free of complications, namely from the crowded C-H bonds. It is somewhat disappointing, then, that the correlation between the calculated frequencies and the calculated bond lengths (Fig. 3), and likewise between the *calculated* frequencies and the *observed* frequencies is not as good (Fig. 4). It is also disappointing that the calculated frequencies do not arrange themselves into the clusters spaced by $14.5 \pm 1\text{ cm}^{-1}$ such as are observed in the experiments. However, these shortcomings are the result of quite small errors, since careful consideration of the calculated frequency shifts indicates a mean absolute error of only $\approx 3\text{ cm}^{-1}$.

The excellent correlation between bond length and observed frequencies provides a way to determine vibrational frequencies in experimentally inaccessible situations. An example is our determination of the bond lengths and prediction of the frequency shifts for the C-H stretching vibrations of a methyl group as a function of internal rotation angle. The results agree qualitatively with experiment, although a more quantitative comparison will require a more detailed treatment of the internal rotation motion.⁵

ACKNOWLEDGMENTS

We are pleased to acknowledge support by grants to RGS and HLS by the National Science Foundation (Grant No. CHE-83-16674) and the National Institutes of Health (Grant No. GM 27690).

¹D. C. McKean, Q. Rev. 7, 399 (1978).

²D. C. McKean, J. E. Boggs, and L. Schäfer, J. Mol. Struct. **116**, 313 (1984).

³K. Raghavachari, J. Chem. Phys. **81**, 2717 (1984).

⁴R. G. Snyder, A. L. Aljibury, H. L. Strauss, H. L. Casal, K. M. Gough, and W. J. Murphy, J. Chem. Phys. **81**, 5352 (1984).

⁵R. A. MacPhail, R. G. Snyder, and H. L. Strauss, J. Chem. Phys. **82**, 1118 (1982).

⁶(a) L. Schäfer, C. Van Alsenoy, and J. N. Scarsdale, J. Mol. Struct. **86**, 349 (1982); L. Schäfer, *ibid.* **100**, 51 (1983); (b) C. E. Blom, P. J. Slingerland, and C. Altona, Mol. Phys. **31**, 1359 (1976).

⁷D. J. DeFrees, B. A. Levi, S. K. Pollack, W. J. Hehre, J. S. Binkley, and J. A. Pople, J. Am. Chem. Soc. **101**, 4085 (1979); J. A. Pople, in *Applications of Electronic Structure Theory*, edited by H. F. Schaefer III (Plenum, New York, 1977), Chap. 1.

⁸(a) J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, Int. J. Quantum Chem. Symp. **13**, 225 (1979); (b) J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. DeFrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, and W. J. Hehre, *ibid.* **15**, 269 (1981).

⁹(a) R. Ditchfield, W. J. Hehre, and J. A. Pople, J. Chem. Phys. **54**, 724 (1971); (b) W. J. Hehre, R. Ditchfield, and J. A. Pople, *ibid.* **56**, 2257 (1972).

¹⁰K. Raghavachari, J. Chem. Phys. **81**, 1383 (1984).

¹¹D. C. McKean, J. L. Duncan, and L. Batt, Spectrochim. Acta Part A **29**, 1037 (1973).

¹²D. R. Lide, Jr., J. Chem. Phys. **33**, 1514 (1960).

¹³T. Iijima, Bull. Chem. Soc. Jpn. **45**, 1291 (1972).

¹⁴K. Kuchitsu, Bull. Chem. Soc. Jpn. **32**, 748 (1959).

¹⁵W. F. Bradford, S. Fitzwater, and L. S. Bartell, J. Mol. Struct. **38**, 185 (1977).

¹⁶D. E. Shaw, D. W. Lepard, and H. L. Welsh, J. Chem. Phys. **42**, 3736 (1965).

¹⁷L. S. Bartell and A. D. Kohl, J. Chem. Phys. **39**, 3097 (1963).

¹⁸P. B. Woller and E. W. Garbisch, J. Am. Chem. Soc. **94**, 5310 (1972).

¹⁹We also tried a 4-21G basis set. However, this basis set did not lead to different bond lengths for the in-plane and out-of-plane C-H bonds of the methyl group. Calculations in methyl groups reported in Ref. 2 show differences among methyl bond lengths for 4-21G calculations but these are much smaller than for 4-31G or 6-31G calculations.

²⁰P. C. Hariharan and J. A. Pople, Chem. Phys. Lett. **16**, 217 (1972).

²¹C. Möller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).

²²J. S. Binkley and J. A. Pople, Int. J. Quantum Chem. **9**, 229 (1975).

²³R. K. Heenan and L. S. Bartell, J. Chem. Phys. **78**, 1270 (1983).

²⁴J. R. Hoyland, J. Chem. Phys. **49**, 1908 (1968).

²⁵Known sixfold barriers have about this value—for example, the methyl barriers in *p*-fluorotoluene, 13.8 cal/mol; nitromethane, 6.0 cal/mol, methyl boron difluoride, 13.8 cal/mol. J. E. Wollrab, *Rotational Spectra and Molecular Structure* (Academic, New York, 1967).

²⁶B. Kirtman, W. E. Palke, and C. S. Weig, J. Chem. Phys. **64**, 1883 (1976).

²⁷R. M. Badger, J. Chem. Phys. **2**, 128 (1934).