# GAS PHASE INFRARED CONTOUR SIMULATION OF ISOLATED C-H STRETCHES IN BUTANE-d,

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# ABSTRACT

n-Butane-d, was synthesized with the hydrogen atom located in one of the methyl groupings. Both C-H stretches of the *trans* conformer and two of the three C-H stretches of the gauche conformer were assigned to transitions observed in the gas phase infrared spectrum, using the harmonic rigid rotor approximation. The simulation lends support to the more recent literature values of the *trans-gauche* relative populations. The assignments agree with those obtained by other authors using different techniques, and, when compared to  $\nu_{CH}^{is}$  values in propane, lead to  $\gamma$  substitution effects of methyl which are very small, except perhaps on the opg (out-of-plane gauche) bond, where steric interaction is likely.

#### INTRODUCTION

For some time, isolated C—H stretches have been used as a sensitive probe of C—H bonding properties (1) and it is therefore natural that both bonding properties and conformational characteristics of n-alkanes should be investigated using this technique. Results reported for propane [2], where matters are straightforward due to the lack of conformational isomerism, have indicated a noticeable difference in bonding between in-plane and out-of-plane C—H bonds in the methyl groups and between methyl and methylene C—H bonds.

The next n-alkane, n-butane, is the lowest of the series capable of exhibiting gauche and trans isomerism, and has been proven at room temperature in the gas phase to exist as a mixture of both [3-6]. Although all of these studies indicate the trans form to be the more stable, the relative populations through the years have oscillated somewhat, with the more recent studies converging on 64-68% trans [5, 6]. None of the gas phase electron diffrac-

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tion studies [3, 4, 6] was able to distinguish more than one type of C-H bond in the molecule, owing to the smaller accuracy inherent to this technique. In view of the results obtained for propane [2] but also in view of, for instance, the ab-initio results on n-alkanes by Schäfer et al. [7], it was judged necessary to tackle the n-butane problem with isolated C-H stretches.

In this study we report results on butane- $d_9$ , with the C-H bond located in the methyl grouping. Although efforts have been made towards the synthesis of the derivative having a methylene C-H bond, we have not been able to isolate this compound.

Very often important information can be obtained from a quantitative study of the infrared gas contours of the stretches, but the conformer complication for the present compound makes necessary the use of a more quantitative approach. Therefore the observed gas phase contours were simulated using rigid asymmetric top calculations which eventually allowed identification of the observed C—H transitions.

After completion of the simulations discussed in this paper, a study on isolated C-H stretches in n-alkanes studied by gas phase Raman spectroscopy by R. G. Snyder et al. [8] has appeared. Their assignments, based on a correlation of ab-initio bond lengths with isolated C-H frequencies, will be compared with our results below. To facilitate this, we will use Snyder's notation [8] for distinguishing methyl protons, i.e.  $ip_t$  (in-plane) and  $op_t$  for the *trans* conformer, and  $ip_g$ ,  $op_g$  and  $op_g^*$  for the *gauche* conformer.

# EXPERIMENTAL

Principal axis coordinates and rotational constants were calculated from the geometry in Table 1. The pure-type transitions were calculated in the harmonic rigid rotor approximation at 293.16 K, using a slit of  $0.5 \text{ cm}^{-1}$ , at  $0.1 \text{ cm}^{-1}$  interval and a limiting value of J equal to 120.

Because of their weak dependence on rotational constants, pure A, B and

## **TABLE** 1

Butane geometry<sup>a</sup>

v(C-C)	153.5	
$\nu$ (CD <sub>a</sub> ) methyl <sup>b</sup>	109.6	
$\nu(C-D_s)$ methyl	109.45	
$\nu(C-D)$ methylene	109.8	
$\alpha(CCC)$	113.0	
$\alpha$ (DCD) methyl	108.0	
$\alpha(CCD)$ methyl	111.0	
$\alpha$ (DCD) methylene	106.0	
$\alpha(CCD)$ methylene	109.4	
$\tau$ (gauche) <sup>c</sup>	65	

<sup>a</sup>Distances in pm, angles in degrees. <sup>b</sup>C—H distances were systematically 0.2 pm longer. <sup>c</sup>Measured from the *cis* position.

C transitions for *trans* and *gauche* conformers were calculated for butane- $d_{10}$  and used for each of the respective *trans* and *gauche*  $d_9$  derivatives. This approximation is further justified by the approximate nature of the molecular geometry in Table 1. As a test, the A contour was calculated for the *trans*- $d_9$ -derivative with the C—H bond in the C<sub>s</sub>-plane: across the contour derivations from the corresponding  $d_{10}$  contour were within the line thickness of the pen used for the plots.

The high characteristicity of the isolated C-H stretches implies the assumption of  $\partial \vec{\mu}/\partial Q$  along the C-H bond to be quite accurate. The  $\partial \vec{\mu}/\partial Q$ 's were calculated in the appropriate d<sub>9</sub>-principal coordinate systems and are shown in Table 2. Using these, the hybrid  $\nu$ (C-H) contours were calculated in the usual way (9). Theoretical hybrids used to simulate a particular PQR feature were convolved with a slit function such that the experimental Q branch FWHH was reproduced. For the present molecule Lorentzian slit functions were found to give the better results.

The experimental spectrum was recorded on a Nicolet 7199 FTIR spectrometer at a resolution of  $0.12 \text{ cm}^{-1}$ , the output being digitised at a frequency interval of  $0.06 \text{ cm}^{-1}$ . Since for comparison purposes it is advantageous that both experimental and calculated spectra are digitized at the same interval, the experimental spectrum was interpolated using cubic splines. Because the relative intensity of Q versus P and R branches is an important characteristic of the contour, care was taken in the interpolation not to influence the relative intensity of the sharp 2950.0 cm<sup>-1</sup> Q branch.

The sample of  $CHD_2CD_2CD_2CD_3$  was prepared from a commercial sample of  $CD_3CD_2CD_2CD_3Br$  (Merck, Sharp and Dohme, 99.6% D) by treating the corresponding Grignard compound with H<sub>2</sub>O, and passing the product through a trap cooled to  $-96^{\circ}C$ .

# RESULTS

The C—H stretching region of the gas phase IR spectrum of methyl C—H n-butane-d<sub>9</sub> is compared in Fig. 1 with the corresponding region of methyl C—H propane-d<sub>7</sub>. The frequency correspondance of the dominant Q branch in the C<sub>4</sub> with the corresponding transition in the C<sub>3</sub> derivative is striking: this would immediately suggest that the absorption at 2950 cm<sup>-1</sup> in n-butane-d<sub>9</sub> is due to the *trans* conformer. Because of its higher relative intensity, we

## TABLE 2

Direction cosines for isolated C-H stretches in butane-d,

Conformer	<b>cos</b> α	cos β	$\cos \gamma$
ip <sub>t</sub>	-0.70589	0.70832	0.00
opt	-0.11441	-0.52642	-0.84249
op*	-0.44941	-0.85457	-0.26026
opg	0.10921	0.03037	0.99355
ipg	0.89969	0.01646	-0.43622



Fig. 1. Vapour phase infrared spectrum of the C-H stretching region of  $CD_3CD_2CHD_2$  (top spectrum) and  $CD_3(CD_2)_2CHD_2$  (lower spectrum, resolution, 0.12 cm<sup>-1</sup>).



Fig. 2. Comparison of experimental contours of the most intense C-H transition with hybrid contours of individual conformers. E, experimental spectrum, conformers identified as in text.

first turned our attention to simulating this absorption. In Fig. 2 the experimental contour of the 2950 cm<sup>-1</sup> absorption is compared, by equating maximum intensities, with the contour of each of the five possible hybrids.

Clearly none of the individual hybrids satisfactorily simulates the experimental contour, which shows that a second transition must be present, accidentally degenerate with the first. The deviations between experiment and calculation are important for every case of Fig. 2, from which is clear that both transitions must contribute considerable intensity. This excludes the  $op_g^*$ ,  $op_g$  and  $op_t$  hybrids from being present as, in the case of an important contribution, their pecularities would stand out in the experimental contour. On the other hand, both  $ip_{g}$  and  $ip_{t}$  contours have P and R contours similar to the experimental ones. The R branch of the  $ip_t$  higher and the R branch of the ipg contour lower in intensity than experiment suggests that agreement would improve by combining these contours. The result is shown in Fig. 3 where linear combination with increasing ipg content are compared with experiment. It is clear that optimum agreement is obtained in the immediate vicinity of 0.75 ip<sub>t</sub> + 0.25 ip<sub>s</sub>. It may be remarked that some discrepancy remains in the region between Q and R branch. Usually such deviations indicate that the convolution reproducing the Q branch width was performed using a poor slit function, i.e. that the latter does not represent the frequency distribution of excited state transitions that gives rise to the observed width of the Q branch. For the present case however the deviation disappears when the transition of 2933.8 cm<sup>-1</sup> is included in the simulation, so that the agreement in fact is better than apparent from Fig. 2(d). This result not only shows that the ip C-H stretches of both gauche and trans conformers absorb at 2950.0 cm<sup>-1</sup>, but at the same time proves that gauche



Fig. 3. Comparison of the high frequency side of the most intense experimental C—H transition with combinations of  $ip_t$  and  $ip_g$  hybrids. (a)  $ip_t$ ; (b) 0.9  $ip_t + 0.1$   $ip_g$ ; (c) 0.8  $ip_t + 0.2$   $ip_g$ ; (d) 0.75  $ip_t + 0.25$   $ip_g$ ; (e) 0.7  $ip_t + 0.3$   $ip_g$ ; (f) 0.6  $ip_t + 0.4$   $ip_g$ ; (g) 0.5  $ip_t + 0.5$   $ip_g$ ; (h) 0.4  $ip_t + 0.6$   $ip_g$ ; (i) 0.3  $ip_t + 0.7$   $ip_g$ ; (j)  $ip_g$ .

and *trans* conformers coexist at room temperature. If one assumes that in the gas phase for C—H bonds in closely analogous environments the extinction coefficients cannot be too different, the intensity ratio  $ip_t/ip_g$  in Fig. 2(d) is a measure of the relative population of the conformers. The ratio 75/25 here obtained then confirms the above-mentioned literature values.

The next step is the inclusion in the simulation of a transition positioned at 2937 cm<sup>-1</sup>. Assuming that this feature is not a Fermi resonance with the 2950 cm<sup>-1</sup> transitions, three candidates, or combinations of them, remain. The result of adding a transition of 2937.0 cm<sup>-1</sup> with intensity such that the relative intensity of the Q branch is reproduced, is shown in Fig. 4, for each of the possible assignments. It is immediately obvious that good agreement is obtained by using the opt hybrid. Improvement might be expected from linear combinations of opg and opg<sup>\*</sup>: however, although the region between 2937.0 and 2950.0 cm<sup>-1</sup> can be somewhat improved, the deviations in the low frequency region remain quite pronounced, so it must be concluded that the 2937 cm<sup>-1</sup> transition must be assigned to the opt hybrid.

With one Q branch remaining, at 2933.8 cm<sup>-1</sup>, attempts were made to simulate this band as a mixture of the two remaining hybrids, e.g.  $op_g$  and  $op_g^*$ . One such attempt, using the above assignments of the two high frequency bands, is shown in Fig. 5(a), with Fig. 5(b) comparing the experiment with the low frequency transition simulated with the  $op_g$  hybrid alone. Although it would be difficult to judge between the two assignments from



Fig. 4. Comparison of simulation with experiment for the upper two transitions. Highest frequency transition, 0.75 ip<sub>t</sub> + 0.25 ip<sub>g</sub>; lower transition (a)  $op_t$ ; (b)  $op_g^*$ ; (c)  $op_g$ .

the deviations that remain in the low frequency region of the absorption complex, it is clear from Fig. 5 that admixture of the  $op_g^*$  hybrid definitely worsens the agreement in the region between the upper Q branches. Therefore the assignment of the 2933.8 cm<sup>-1</sup> transition to the  $op_g$  C—H stretching alone is preferred.

All clearly observable Q branches in the experimental spectrum have now been accounted for, while the stretching in the op<sup>\*</sup><sub>g</sub> C—H bond remains unassigned. Some deviation between experiment and calculation remains, as observed above, on the low frequency side of the absorption region considered. In this region a weak feature is observed near 2904 cm<sup>-1</sup>, which might indicate the presence of a weak, broad Q branch. Its frequency, however, appears too much separated from the other transitions to be considered as due to the op<sup>\*</sup><sub>g</sub> H-atom.

As there is no obvious reason why the extinction coefficients for  $op_g^*$ and  $op_g$  stretches should dramatically differ, the absence of a separate Qbranch assignable to  $op_g^*$  shows that the latter must appear accidentally degenerate, either under the 2950.0 or the 2937.0 cm<sup>-1</sup> transition, and remain undetected because of its small relative intensity.

### DISCUSSION

Because they have been arrived at by quite different methods, it is interesting to compare our results with those of R. G. Snyder et al. [8]. At the



Fig. 5. Comparison of complete simulation with experiment. High frequency transition 0.75 ip<sub>t</sub> + 0.25 ip<sub>g</sub>; middle transition,  $op_t$ . (a) Lower transition, 0.5  $op_g + 0.5 op_g^*$ ; (b) lower transition,  $op_g$ .

outset it may be remarked that the motivation for the choice of Raman spectroscopy by these authors, i.e. narrower bands in comparison with infrared contours, is contradicted by our own experiment: this is especially clear for the 2933.8 cm<sup>-1</sup> Q branch which in IR shows a well-defined maximum but is observed in Raman as a shoulder only.

The Raman study observes, for the simpler n-alkanes, a high correlation between observed isolated C—H stretch and corresponding bond length as calculated from unconstrained ab-initio calculations at the 4-31G level. This relation consequently is used to assign C—H stretches to bands observed for the more complicated molecules such as n-butane with its two conformers, thereby implying validity of the relation, the proof of which is one of the aims of the study.

In spite of this liability to bias, the assignments of  $ip_t$ ,  $op_t$ ,  $ip_g$  and  $op_g$ C—H stretches agree with ours. The perdeuterated n-butane sample also contained some methylene C—H so these stretches could be identified at 2918, 2907 and 2903.5 cm<sup>-1</sup>. The weak maximum observed in our spectrum at 2904 cm<sup>-1</sup> thus can be assigned to methylenic C—H bonds present as an impurity, while, although not identifiable by the presence of observable Qbranches, the methylenic transitions at 2918 and 2907 cm<sup>-1</sup> presumably contribute to the deviation, which is apparent from Fig. 5, between the observed and calculated spectrum in this region.

The  $op_g^*$  stretch was assigned in the Raman spectrum from an ab-initio calculation in which the dihedral angle defining the *gauche* conformer had to be constrained, at 2950 cm<sup>-1</sup>. This assignment at least is not contradicted by our results.

The chemical meaning of our results is as follows. The virtual identity between the ip<sub>t</sub> (2950.0) and op<sub>t</sub> (2937.0 cm<sup>-1</sup>) frequencies found here in butane, and those found earlier in the methyl group of propane (2950 and 2916 cm<sup>-1</sup>) [1] suggests that the  $\beta$  effect of the CH<sub>2</sub> group in propane is identical to the  $\beta$  effect of the methyl in propane, and that the  $\gamma$  effect of the remote methyl in the *trans* conformer of butane is negligible. This seems reasonable on physical grounds, as does the lack of influence of the remote methyl group in the *gauche* conformer on the in-plane CH bond ( $\nu_{ip}$  = 2950 cm<sup>-1</sup>). The  $\gamma$  effect of methyl on the op<sub>g</sub> bond (2933.8 cm<sup>-1</sup>) is also small. However, if the op<sub>g</sub><sup>\*</sup> bond indeed gives a band at 2950 cm<sup>-1</sup>, the  $\gamma$ effect of +16 cm<sup>-1</sup> (2950 - 2934 cm<sup>-1</sup>), equal in magnitude to the  $\beta$  effect of CH<sub>2</sub> or CH<sub>3</sub>, would certainly suggest a marked steric influence, which again is not unexpected.

# CONCLUSION

The simulation of the C-H stretching region of n-butane d<sub>9</sub> is remarkably accurate, which apart from the other approximations involved, is due not only to the harmonic nature of the present C-H stretch modes, but also to the extreme accuracy of the  $\partial \vec{\mu} / \partial Q$  approximation. The former is a consequence of the relatively high stability of the C-H bond, which minimizes anharmonicity effects, and of the absence in the C-H stretching region of overtone or combination levels that tend to give coriolis coupling with the C-H fundamentals. The accuracy of the dipole change vector approximation is a consequence of the unique properties of the isolated C-H bonds, which for instance is reflected also in the correlation of the stretching frequencies with experimental bond lengths [1].

The  $\nu_{CH}^{is}$  values derived indicate that the  $\gamma$  substitution effects of a methyl group are very small except possibly for the opg bond of the gauche conformer, where steric effects may be important.

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