

See discussions, stats, and author profiles for this publication at:
<https://www.researchgate.net/publication/223611749>

The far infrared spectrum, ab initio calculations and conformational energy differences of 1-butene

ARTICLE *in* JOURNAL OF MOLECULAR STRUCTURE · OCTOBER 2000

Impact Factor: 1.6 · DOI: 10.1016/S0022-2860(00)00572-X

CITATIONS

34

READS

5

4 AUTHORS, INCLUDING:



Gamil A. Guirgis

College of Charleston

341 PUBLICATIONS 2,690 CITATIONS

SEE PROFILE

The far infrared spectrum, ab initio calculations and conformational energy differences of 1-butene

S. Bell^a, B.R. Drew^{b,1}, G.A. Guirgis^{b,2}, J.R. Durig^{b,*}

^aDepartment of Chemistry, University of Dundee, Dundee DD1 4HN, Scotland, UK

^bDepartment of Chemistry, University of Missouri-Kansas City, Kansas City, MO 64110-24990 USA

Received 31 January 2000; accepted 17 April 2000

Abstract

The far infrared spectra of 1-butene, $\text{CH}_2=\text{CHCH}_2\text{CH}_3$, and the d_3 species $\text{CH}_2=\text{CHCH}_2\text{CD}_3$ have been recorded from 50 to 360 cm^{-1} at a resolution of 0.10 cm^{-1} . The geometrical structures and vibrational frequencies of the *cis*(synplanar) and *gauche*(anticlinal) conformers have been determined by ab initio calculations in order to calculate torsional constants and to aid in assignments of the far infrared bands. A wide range of basis sets and ab initio theoretical methods up to MP4 have been used in order to predict the *cis*–*gauche* conformational energy difference. The fundamental and a few other methyl torsional transitions have been observed for both the *cis* and *gauche* conformers for both isotopic species and threefold barriers to internal rotation of $1680 \pm 15\text{ cm}^{-1}$ ($4.80 \pm 0.04\text{ kcal/mol}$) for the *cis* rotamer and $1150 \pm 50\text{ cm}^{-1}$ ($3.29 \pm 0.14\text{ kcal/mol}$) for the *gauche* conformer have been determined. The methyl barrier for the *cis* conformer is much higher than that derived from the microwave splittings. The potential energy function for asymmetric torsion has been redetermined from which values of the *cis* to *gauche* barrier of $835 \pm 48\text{ cm}^{-1}$ ($2.39 \pm 0.14\text{ kcal/mol}$), and the *gauche* to *gauche* barrier of $615 \pm 51\text{ cm}^{-1}$ ($1.76 \pm 0.15\text{ kcal/mol}$) have been obtained. The *cis*–*gauche* enthalpy difference has been determined to be $73 \pm 6\text{ cm}^{-1}$ ($209 \pm 17\text{ cal/mol}$) in krypton and $64 \pm 10\text{ cm}^{-1}$ ($183 \pm 29\text{ cal/mol}$) in xenon with the *cis* conformer as the more stable form from the variable temperature studies of the infrared spectra ($3500\text{--}400\text{ cm}^{-1}$). These experimental and theoretical results are compared with the corresponding quantities of some similar molecules. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: 1-Butene; Far infrared spectrum; Conformational energy; Ab initio calculations

1. Introduction

This study of the far infrared spectrum of 1-butene represents the next step along the homologous series

from 1-propene whose far infrared spectrum has been reported [1] and which exhibits methyl torsional transitions. In contrast to 1-propene, 1-butene has two internal rotors and is the simplest alkene able to possess conformational isomers due to hindered rotation about the middle C–C bond. Indications of the existence of two conformers have been found over many years in spectroscopic studies of various types, including infrared/Raman, NMR and microwave spectroscopy. The initial infrared studies [2,3] indicated that two conformers existed but were not able to determine positively the dihedral angles or

* Corresponding author. Tel.: +1-816-235-1136; fax: +1-816-235-5191.

E-mail address: durigj@umkc.edu (J.R. Durig).

¹ Taken in part from the dissertation of B. R. Drew, which will be submitted to the Department of Chemistry in partial fulfillment of the Ph.D. degree.

² Permanent address: Analytical R & D Department, ICD Division, Bayer Corp., Bushy Park Plant, Charleston, SC 29411.

identify which conformer has the lower energy. The NMR investigations [4,5] gave evidence that the isomerism was synplanar/anticlinal or *cis* to *gauche* (CCCC dihedral angles of 0° and approximately 120°) with the *cis* conformer having the lower energy. From a study [6] of the microwave spectrum, which included measurement of the temperature dependence of rotational line intensities, an estimate was made of the *cis* to *gauche* energy difference with the *gauche* conformer being the rotamer with lower energy by 53 cm^{-1} . This very thorough microwave work also included a determination of the structural parameters of the *cis* conformer and a partial determination of the *gauche* conformer structural parameters.

The far infrared spectrum of 1-butene at 0.25 cm^{-1} resolution was reported and an analysis was previously presented by one of us [7]. It included a presentation of the results of a variable temperature study of what appeared to be conformer pairs in the Raman spectrum of liquid 1-butene. From this study it was determined that the *cis* conformer was lower by 77 cm^{-1} in the liquid phase. An estimate of the energy obtained from the potential energy function fitted to the torsional data in the gas phase gave an enthalpy value of 26 cm^{-1} , again with the *cis* rotamer lower in energy. A recent infrared and Raman study [8] has determined, from the conformer pairs in the mid-infrared spectrum of the gas, that the *cis* conformer has a lower energy by 73 cm^{-1} .

Among the subsequent microwave studies, one was concerned with the effect of centrifugal distortion [9], but although it proceeded to a re-evaluation of the rotational constants, neither did it provide any re-evaluation of the structural parameters of 1-butene nor did it provide any information on the conformational isomerism and the energy difference between the conformers. The microwave spectra of a large number of mono- and di-deuterated species were obtained in another study [10] but the rotational constants of the d_3 species of interest in the present study were not determined. A further report of microwave spectroscopy results [11] was concerned with isotopic labeling but in spite of interest being directed towards structural details such as the dihedral angles involving the methylene and methyl hydrogens, it does not provide any further insight about asymmetric or methyl torsional energies. The interpretation of the far infrared spectrum of 1-butene is closely concerned

with the energy difference between the two conformers and the focus of the present study. The results of the earlier microwave study [6] are therefore most relevant to the present study and, additionally, in that study the barriers to methyl torsion of both the *cis* and *gauche* conformers, were determined.

The molecule propanal is structurally similar and isoelectronic with 1-butene and it also exhibits *cis* to *gauche* conformational isomerism, but by contrast it has a large energy difference between the conformers. Recently the far infrared spectrum has been re-examined [12] with the aid of a number of ab initio calculations of geometrical structures, vibrational frequencies and conformational energy differences. The energy separation between the two rotational conformers is 370 cm^{-1} . A second molecule exhibiting the *cis* and *gauche* conformations is 1,2-pentadiene (ethyl allene) and its far infrared spectrum has also been reported recently [13]. It is much more similar to the situation in 1-butene as it possesses an asymmetric rotor (ethyl) adjacent to a C=C double bond and has a small conformational energy difference.

It has been found in both of these studies that the *cis*–*gauche* conformational energy difference calculated by the ab initio methods is rather sensitive to basis set type and size and also to the method of calculation or “level of theory” employed. For propanal, some amount of convergence towards the preferred experimental conformational energy difference appears to have been reached with the second order Moller–Plesset method and large basis sets. The results of some ab initio calculations for 1-butene, up to MP3/6-31G(d), have been reported [14], and although the calculations reported herein confirm these results, a higher quality of calculation is required. Hence, calculations up to MP2/6-311++G(3df,3pd) were employed so that the predicted conformational energy difference between the *cis* and *gauche* conformers would converge towards the experimentally determined value. In view of the extent of disagreement between the conformational energy differences calculated and those reported from a variety of experimental methods, a variable temperature spectroscopic investigation of 1-butene was performed. The results of this experimental and theoretical study are reported within.

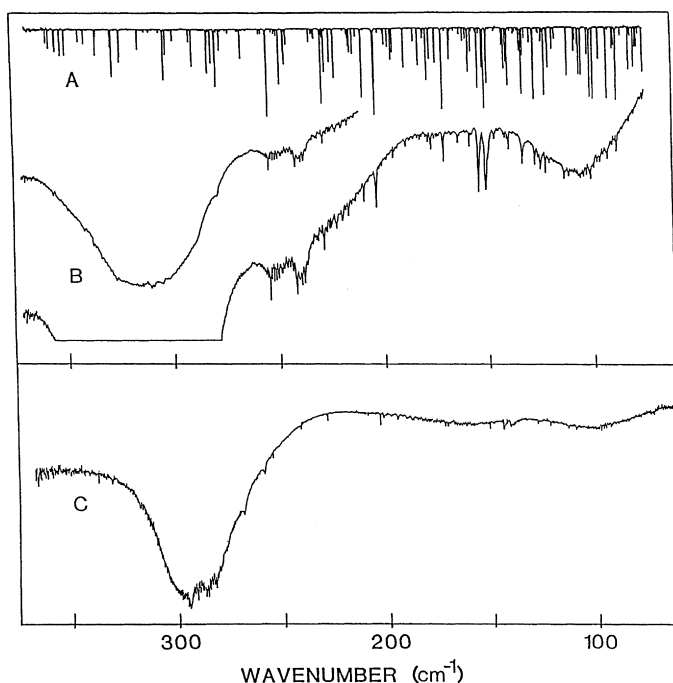


Fig. 1. Far infrared spectra of 1-butene: (A) water reference spectrum; (B) the spectrum of normal 1-butene (d_0) at low and high pressure; and (C) the spectrum of 1-butene- d_3 ($CH_2=CHCH_2CD_3$) at low pressure.

2. Experimental

A lecture bottle of 1-butene was purchased from Matheson Gas Products, East Rutherford, NJ and was used in recording the far infrared spectrum after drying over molecular sieves. The sample of 1-butene- d_3 , $CH_2=CHCH_2CD_3$, was obtained from Merck Chemical Co.

The far infrared spectra of the gases were recorded with a Nicolet model 200 SXV interferometer equipped with a vacuum bench and a liquid helium cooled Ge bolometer containing a wedged sapphire filter and polyethylene windows. Interferograms were recorded 256 times at a resolution of 0.10 cm^{-1} with a $6.25\text{ }\mu\text{m}$ Mylar beamsplitter and transformed with a boxcar truncation function.

A 1-m cell fitted with polyethylene windows was employed, but since the absorption intensity of 1-butene in the far infrared is very small, a high pressure of gas was used in spite of the path length employed. Representative spectra of both species are shown in Fig. 1. For the high pressure trace of the spectrum of 1-butene- d_0 , the pressure in the cell was 700 mmHg,

but the peaks near 150 cm^{-1} still show only a 10% decrease in transmittance. The amount of sample of 1-butene- d_3 allowed only a total pressure of 100 mmHg.

The mid-infrared spectra of the sample, dissolved in liquified xenon and krypton as a function of temperature, were recorded on a Bruker model IFS-66 Fourier transform interferometer equipped with a Globar source, Ge/KBr beamsplitter and a DTGS detector. The temperature studies, ranging from -55 to -100°C for xenon and -105 to -150°C for krypton, were performed in a specially designed cryostat cell that consisted of a 4 cm pathlength copper cell with wedged silicon windows sealed to the cell with indium gaskets. The cell is cooled by boiling liquid nitrogen and is monitored with two Pt thermoresistors. The complete cell is attached to a pressure manifold to allow for the filling and evacuation of the cell. Once the cell is cooled to the desired temperature, a small amount of the sample is condensed into the cell. The cell is then pressurized with the noble gas, which immediately starts condensing in the cell, allowing the compound to dissolve. For each temperature investigated, 100 interferograms were recorded at

1.0 cm⁻¹ resolution, averaged and transformed with a boxcar truncation function.

3. Ab initio calculations

Most of the electronic structure calculations were made with the GAUSSIAN 94 program [15]. Many calculations were made at the restricted Hartree–Fock level (given as HF) or using the Møller–Plesset method to second order (MP2) but a few calculations were made using higher orders (MP3, MP4). Since large basis set effects are seen, a range of calculations was made with the conventional split-valence 6-31G basis augmented by various amounts of polarization functions and diffuse functions. Almost as many calculations were made with the double-zeta DZ basis set of Dunning [16] and also by adding larger polarization functions. Finally, the most extended fundamental sp basis set used was the triple split valence basis set with the double plus version of Møller–Plesset, which was extended with three sets of five d-type and one set of seven f-type polarization functions on the carbon atoms and three sets of three p-type and one set of five d-type polarization functions on the hydrogen atoms, as well as adding diffuse functions to both types of atoms.

For some basis sets and calculation methods, the geometric structure was fully optimized for all conformers, but geometric structure parameters are reported only for *cis* and *gauche* conformers obtained from only a few of the methods employed. Only for the *cis* (Cs, which stands for *cis* staggered) and antiperiplanar (Ts *trans* staggered, which is a transition state) structures was the molecule constrained to C_s symmetry in order to distinguish between A' and A'' vibrations for the frequency calculations.

The energy of the *cis* conformer is given in Table 1 as a total electronic energy in E_h as an indication of the accuracy of calculation but other conformers and/or barriers are given as an energy difference in cm⁻¹. For almost all levels of theory and all basis sets, the *gauche* has lower energy than the *cis* rotamer and its energy is therefore given as *negative* in Table 1. The energy of the *gauche* to *gauche* transition state and the barrier between the *cis* to *gauche* conformation were also calculated for a number of ab initio levels and basis sets.

The energy of the *cis* form with the methyl eclipsed, labeled Ce, and the *gauche* form with the methyl eclipsed, labeled Ge, are given for only a few ab initio methods as the methyl torsional barriers are usually easily calculated and agree well experimentally even at the HF level. The agreement in the methyl barrier for the *cis* conformer is less satisfactory as it is a little higher for MP2 than for the HF calculations.

Concerning the barriers for asymmetric torsion, the *gauche* to *gauche* transition state barrier is in good agreement between the experimental values and between the Møller–Plesset calculations to any order. Many of the ab initio *gauche*–*cis* energy differences are negative in agreement with one of the experimental studies but in disagreement with the other experimental studies. Additionally, the magnitude of the energy difference is always larger by all ab initio methods in comparison with the microwave value, but decreases to 100 cm⁻¹ and below as the method of calculation improves. The exception to this is on adding diffuse functions although adding diffuse functions to a molecule with no electronegative atoms without triple-zeta basis and more polarization functions is not a good practice. Indeed it requires a triple-split basis set and extra d and p functions for the energy difference to be reduced again. It seems, however, that with the fundamental DZ basis set and polarization functions there is often a more rapid convergence towards the experimental energy difference with less computational effort [16,17]. For example, 6-311+G(2d,p) indicates that 200 basis functions were employed, but TZ(2d,p) indicates 176 functions and DZ(2d,p) indicates that only 128 functions were utilized.

A second problem concerning the asymmetric torsion is the disagreement between the methods in the calculation of the *cis* to *gauche* barrier height, Bs in Table 1. The microwave spectrum does not provide a value for this parameter but all the ab initio methods give a barrier of almost the same as the energy at the *gauche* to *gauche* transition state marked Ts. It should be noted that the energy differences are relative to the *cis* conformer in Table 1, i.e. the *gauche* to *gauche* barrier height is greater than the value in the table by the magnitude of the *gauche* to *cis* energy difference. In the previous far infrared work [7], in order to fit the *cis* torsional data a much higher *cis* to *gauche* barrier was required.

Table 1

Ab initio energies for 1-butene and energy differences between conformers

	Energy ^a	Energy differences ^b				
	Cs	Gs	Bs	Ts	Ce	Ge
HF/3-21G	5.241943481	−289.72	523.08	461.89	1458.91	1149.69
HF/6-31G	6.045475450	−234.40	593.68	468.56	1404.67	1115.97
HF/6-31G(d)	6.104979610	−242.22	645.11	530.23		
HF/6-31G(d,p) ^c	6.117129005	−231.48				
MP2/6-31G(d)	6.620402478	−173.68	598.06	630.94	1553.97	1185.27
MP2/6-31G(d,p) ^c	6.685141410	−160.60				
MP3/6-31G(d,p) ^c	6.72871538	−108.28				
MP4/6-31G(d,p) ^c	6.75425169	−135.32				
MP2/6-31+G(d)	6.629176382	−260.67				
MP2/6-311+G(d,p) ^c	6.741188099	−184.35				
MP2/6-311+G(d,d,p) ^c	6.770832888	−93.64	707.97	706.61		
HF/DZ	6.061077936	−226.48	621.67	404.21	1353.54	1112.06
HF/DZ(d)	6.125098809	−238.47	673.71	481.99		
HF/DZ(d,p) ^d	6.138867176	−223.35	704.78	594.16		
MP2/DZ(d)	6.628565020	−153.61	593.70	597.02	1500.87	1110.91
MP2/DZ+(d) ^d	6.636053991	−240.32				
MP2/DZ(d,p) ^d	6.696611541	−123.74	617.97	626.43		
MP3/DZ(d,p) ^d	6.74292926	−87.33	620.41	606.04		
MP4/DZ(d,p) ^d	6.76630899	−111.54	599.79	594.16		
MP2/DZ(d,d,p) ^d	6.728142538	−68.41	697.39	613.67	1449.95	1130.02
MP2/TZ(d,d,p) ^d	6.778892410	−106.80				
Expt. MW ^e	0	−52.5	?	605	1396	1105
Expt. IR/Raman ^f	0	25.9	1114	591	1320	1120

^a Energy of the *cis* conformer given as $-(E + 150)E_h$. All MP2/MP3/MP4 calculations are frozen core. Geometries are fully optimized unless indicated.

^b Conformation labeling: C = *cis*, G = *gauche*, T = *trans*, B = barrier between *cis* and *gauche*, s = staggered methyl, and e = eclipsed methyl. ΔE in cm^{-1} is given relative to Cs except for Ge which is relative to Gs.

^c At geometries of MP2/6-31Gdp.

^d At geometries of MP2/DZd.

^e Ref. [6].

^f Ref. [7].

Although a large number of structures have been optimized, only a few sets of geometrical parameters are given in Tables 2 and 3. The meaning of the internal coordinate labels can be understood from the labeling in Fig. 2. It is evident that rotational constants obtained from geometrical structures calculated at the MP2 level with d polarization functions give good agreement with the microwave rotational constants. Geometries calculated at the HF level given in Tables 2 and 3 show that the C=C bond and all C–H bonds are too short. The latter situation is important for the calculation of torsional constants as bond lengths, which are too short, lead to a low methyl top moment I_τ and to a high F number for

methyl torsion. As found before [12,13], the MP2/6-31G(d) calculations provide a little better agreement with the microwave rotational constants for the *cis* form than those from the MP2/DZ(d) calculation. For *gauche* 1-butene as for *gauche* propanal [13], the torsional angle τ obtained from the MP2/6-31G(d) calculations is smaller relative to the angle obtained from the microwave data but if set to the microwave value of 119.9° the rotational constants are $A = 22550$, $B = 4164$ and $C = 4065$ MHz, in very good agreement with the experimental constants.

The 6-31G(d) geometrical structures are employed in the calculation of the kinetic constants for both the methyl and asymmetrical (ethyl) torsions. The

Table 2

Geometrical parameters (bond lengths in Å, angles in degrees, rotational constants in MHz, I_r in amu Å², and F in cm⁻¹) for *cis* 1-butene obtained from ab initio calculations and microwave spectra

Parameter	Coordinate	RHF/6-31G(d)	MP2/6-31G(d)	MP2/6-311++G(d,p)	MP2/6-311+G(2d,2p)	MP2/6-311+G(2df,2pd)	MP2/6-311++G(3df,3pd)	Expt. r_e -like MW ^a	Expt. r_o -adjusted A&M ^b
C ₁ C ₂	<i>R</i>	1.3191	1.3375	1.3410	1.3350	1.3320	1.3324	1.335	1.336 ± 0.008
C ₂ C ₃	<i>S</i>	1.5079	1.5024	1.5040	1.5001	1.4951	1.4947	1.501	1.507 ± 0.010
C ₃ C ₄	<i>T</i>	1.5263	1.5225	1.5244	1.5205	1.5161	1.5157	1.530	1.536 ± 0.006
C ₁ C ₂ C ₃	<i>φ</i>	127.20	126.21	125.97	125.79	125.90	125.92	126.1	126.7 ± 0.4
C ₂ C ₃ C ₄	<i>θ</i>	115.86	115.16	115.16	114.90	114.94	114.89	114.5	114.8 ± 0.5
C ₁ C ₂ C ₃ C ₄	<i>τ</i>	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C ₁ H ₁	<i>r</i> ₁	1.0752	1.0844	1.0848	1.0783	1.0794	1.0801	1.092	1.090
C ₁ H ₂	<i>r</i> ₂	1.0756	1.0848	1.0848	1.0780	1.0790	1.0801	1.093	1.090
C ₂ H ₃	<i>r</i> ₃	1.0794	1.0900	1.0899	1.0830	1.0837	1.0852	1.091	1.090
C ₃ H _{4,5}	<i>r</i> _{4,5}	1.0888	1.0980	1.0975	1.0904	1.0920	1.0926	1.093	1.095
C ₄ H ₆	<i>r</i> ₆	1.0851	1.0930	1.0929	1.0856	1.0871	1.0878	1.094	1.095
C ₄ H _{7,8}	<i>r</i> _{7,8}	1.0852	1.0931	1.0934	1.0866	1.0880	1.0885	1.096	1.095
C ₂ C ₁ H ₁	<i>ξ</i> ₁	122.74	122.47	122.10	121.90	121.97	121.94	121.1	120.5
C ₂ C ₁ H ₂	<i>ξ</i> ₂	121.05	121.06	120.73	120.78	120.81	120.80	119.8	120.5
C ₁ C ₂ H ₃	<i>ψ</i>	118.26	118.39	118.36	118.23	118.23	118.30	119.0	118.2 ± 1.1
C ₂ C ₃ H _{4,5}	<i>δ</i> _{4,5}	108.19	108.48	108.22	108.38	108.37	108.35	109.0	108.6
C ₄ C ₃ H _{4,5}	<i>γ</i> _{4,5}	109.37	109.51	109.62	109.66	109.77	109.73	109.1	109.3
H ₁ C ₃ H ₅	<i>ε</i>	105.34	105.22	105.57	105.43	105.16	105.35	105.7	105.3
C ₃ C ₄ H ₆	<i>β</i> ₆	110.32	110.56	110.47	110.69	110.76	110.61	111.0	110.4 ± 0.7
C ₃ C ₄ H _{7,8}	<i>β</i> _{7,8}	111.38	111.12	111.11	111.15	111.18	111.13	111.3	110.4 ± 0.7
H ₆ C ₄ H ₇	<i>α</i> ₇	107.80	107.94	107.99	107.91	107.88	107.92	108.0	108.5
H ₆ C ₄ H ₈	<i>α</i> ₈	107.80	107.94	107.99	107.91	107.88	107.92	108.0	108.5
H ₇ C ₄ H ₈	<i>α</i> ₆	108.02	108.03	108.04	107.88	107.80	108.00	107.0	107.7
C ₂ C ₃ C ₄ H ₆	<i>φ</i> ₆	180.0	180.0	180.0	180.0	180.0	180.0	180.0	180.0
<i>Rotational constants</i>									
<i>A</i>		15673.32	15327.78	15273.73	15356.81	15413.92	15408.24	15302.54	
<i>B</i>		5518.72	5611.02	5611.46	5675.09	5696.83	5700.00	5574.92	
<i>C</i>		4294.12	4326.17	4322.64	4363.45	4381.19	4383.44	4303.14	
<i>κ</i>		-0.7848	-0.7664	-0.7646	-0.7614	-0.7615	-0.7612	-0.7688	
<i>I_r</i>		3.1018	3.1512	3.1539	3.1094	3.1158	3.1228	3.154	
<i>F</i>		5.7312	5.6374	5.6324	5.7098	5.6998	5.6877	5.6310	

^a Assumptions: CH(at C=C) = 1.090 Å; CH(at C-C) = 1.095 Å. H₁ and H₂ are symmetric to the C₁C₂ band in the C₁C₂C₃ plane. The bisecting line <H₄C₃H₅ coincides with the bisecting line of <C₂C₃C₄. The H₆, H₇ and H₈ atom are located symmetric to the C₃C₄ bond.

^b This study combining ab initio predictions (MP2/6-311++G(d,p)) with reported microwave rotational constants Ref. [6].

Table 3

Geometrical parameters (bond lengths in Å, angles in degrees, rotational constants in MHz, I , in amu Å², F in cm⁻¹, and ΔH in cm⁻¹) for *gauche* 1-butene obtained from ab initio calculations and microwave spectra

Parameter	Coordinate	RHF/6-31G(d)	MP2/6-31G(d)	MP2/6-311+G(d,p)	MP2/6-311+G(2df,2pd)	MP2/6-311++G(3df,3pd)	Expt. r_o -like MW ^a	Expt. r_o -adjusted A&M ^b
C ₁ C ₂	<i>R</i>	1.3187	1.3372	1.3347	1.3317	1.3320	1.342 ± 0.009	1.341
C ₂ C ₃	<i>S</i>	1.5050	1.4983	1.4960	1.4915	1.4908	1.493 ± 0.008	1.495
C ₃ C ₄	<i>T</i>	1.5323	1.5295	1.5285	1.5244	1.5244	1.536 ± 0.012	1.538
C ₁ C ₂ C ₃	ϕ	125.40	124.69	124.49	124.80	124.77	125.4 ± 0.2	125.0
C ₂ C ₃ C ₄	θ	112.49	111.98	111.79	111.79	111.61	112.1 ± 0.2	112.0
C ₁ C ₂ C ₃ C ₄	τ	119.71	117.76	117.50	117.93	116.13	119.9 ± 0.3	119.9
C ₁ H ₁	<i>r</i> ₁	1.0771	1.0864	1.0867	1.0812	1.0819	1.090	1.087
C ₁ H ₂	<i>r</i> ₂	1.0757	1.0848	1.0849	1.0791	1.0801	1.090	1.085
C ₂ H ₃	<i>r</i> ₃	1.0800	1.0906	1.0907	1.0847	1.0861	1.090	1.091
C ₃ H ₄	<i>r</i> ₄	1.0859	1.0958	1.0954	1.0883	1.0904	1.095	1.095
C ₃ H ₅	<i>r</i> ₅	1.0884	1.0974	1.0969	1.0913	1.0917	1.095	1.097
C ₄ H ₆	<i>r</i> ₆	1.0855	1.0936	1.0936	1.0861	1.0882	1.095	1.094
C ₄ H ₇	<i>r</i> ₇	1.0852	1.0930	1.0934	1.0877	1.0882	1.095	1.093
C ₄ H ₈	<i>r</i> ₈	1.0862	1.0939	1.0941	1.0884	1.0890	1.095	1.094
C ₂ C ₁ H ₁	ξ_1	121.84	121.42	121.05	120.97	120.98	120.5	121.3
C ₂ C ₁ H ₂	ξ_2	121.71	121.85	121.51	121.52	121.50	120.5	121.8
C ₁ C ₂ H ₃	ψ	118.91	119.10	119.04	118.78	118.82	117.1 ± 1.3	119.3
C ₂ C ₃ H ₄	δ_4	109.58	109.33	109.29	109.37	109.48	109.7	109.2
C ₂ C ₃ H ₅	δ_5	109.11	109.55	109.39	109.42	109.44	109.7	109.3
C ₄ C ₃ H ₄	γ_4	109.84	109.94	109.97	110.14	110.06	109.7	109.5
C ₄ C ₃ H ₅	γ_5	108.93	109.16	109.18	109.08	109.05	109.7	109.5
H ₄ C ₃ H ₅	ϵ	106.72	106.74	107.10	106.88	107.10	105.7 ± 0.7	107.2
C ₃ C ₄ H ₆	β_6	110.95	111.20	111.18	111.35	111.21	110.3 ± 0.8	111.1
C ₃ C ₄ H ₇	β_7	110.89	110.52	110.45	110.62	110.52	110.3 ± 0.8	110.4
C ₃ C ₄ H ₈	β_8	111.15	110.91	110.79	110.82	110.81	110.3 ± 0.8	110.7
H ₆ C ₄ H ₇	α_7	108.16	108.29	108.37	108.29	108.38	108.6	108.8
H ₆ C ₄ H ₈	α_8	107.75	107.91	108.02	107.93	107.95	108.6	107.7
H ₇ C ₄ H ₈	α_6	107.80	107.89	107.92	107.60	107.85	108.6	108.0
C ₂ C ₃ C ₄ H ₆	ϕ_6	178.58	178.93	179.01	178.35	178.26	180.0	179.0
<i>Rotational constants</i>								
<i>A</i>		22911.93	22265.65	22341.16	22455.92	22146.47	22557.33	
<i>B</i>		4164.44	4185.29	4209.47	4225.31	4244.55	4156.28	
<i>C</i>		4065.29	4097.63	4120.06	4132.84	4158.25	4056.21	
κ		-0.9895	-0.9904	-0.9902	-0.9899	-0.9904	-0.9892	
<i>I_r</i>		3.1058	3.1561	3.1603	3.1213	3.1285	3.154	
<i>F</i>		5.9918	5.8800	5.9505	5.9433	5.9166	5.9005	
ΔE (cm ⁻¹) ^c		242	172	39	22	30	53	

^a Ref. [6]. Assumptions: CH(at C=C) = 1.090 Å; CH(at C-C) = 1.095 Å. H₁ and H₂ are symmetric to the C₁C₂ band in the C₁C₂C₃ plane. The bisecting line <H₄C₃H₅ coincides with the bisecting line of <C₂C₃C₄. The H₆, H₇ and H₈ atom are located symmetric to the C₃C₄ bond.

^b This study combining ab initio predictions (MP2/6-311++G(d,p)) with reported microwave rotational constants Ref. [6].

^c Difference in energy of the *cis* conformer and *gauche* conformer with the *gauche* conformer, the more stable rotamer.

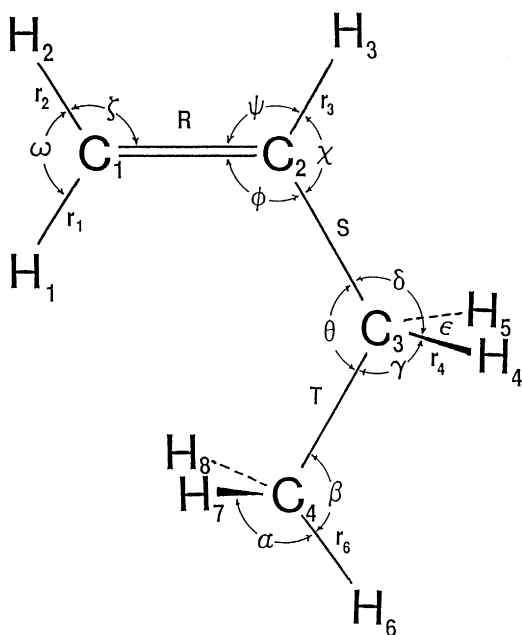


Fig. 2. The structure of the *cis* conformer of 1-butene with internal coordinate labels.

constants for the methyl torsion of the d_0 species are given in Tables 2 and 3. With the torsional angle of the *gauche* conformer corrected to 119.9° , the methyl torsional constant F is 5.8891 cm^{-1} . The torsional constants for the asymmetrical torsion are obtained as an F series

$$F(\tau) = F_0 + \sum_i F_i \cos i\tau$$

with a flexible model employing both the *cis* and *gauche* geometrical structures assuming them to be small periodic functions of the torsional angle of the general type:

$$B(\tau) = a + b \cos \tau + c \sin \tau.$$

The torsional constants for the d_3 isotopomer are also required in this study and are obtained from the same structural parameters as the normal species with the appropriate mass changes. The methyl torsion constants for d_3 are $F = 2.9594 \text{ cm}^{-1}$ for the *cis* form and $F = 3.2074 \text{ cm}^{-1}$ for the *gauche* form with the dihedral angle adjusted to 119.9° .

4. Analysis and discussion

Vibrational wavenumbers. The vibrational wavenumbers of both the *cis* and *gauche* conformers have been calculated by the ab initio second derivative methods to aid in the identification of bands in the far infrared spectrum. The mid-infrared spectra of normal 1-butene in the gas, liquid and solid phases have been reported [2,3,7,8] along with the Raman spectrum of the liquid phase. Assignments have been made for most of the vibrational modes of both the *cis* and *gauche* conformers. The comparison with the previous assignment of the observed infrared and Raman frequencies is incidental to this study and is not exhaustive. However, since both infrared and Raman intensities are calculated from the dipole derivatives at the MP2 level and from polarizability derivatives at the HF level, these are provided as being related to the discussion on assignments of the vibrational wavenumbers.

Vibrational wavenumbers obtained by the ab initio calculation are mostly higher than the observed fundamental wavenumbers and are usually adjusted by scaling force constants in internal coordinates. A full normal coordinate analysis is therefore necessary in order to carry out this scaling. The definitions of symmetry coordinates are given in Table 4 of which 34 are employed in terms of the internal coordinates shown in Fig. 2 and in Tables 2 and 3. For the *cis* conformer, the calculated wavenumbers are given in Table 5. There are 19 A' modes and 11 A'' modes and the wavenumbers are labeled ν_1 – ν_{30} in the symmetry order. It can be seen that the wavenumbers obtained at the MP2 level are much nearer to the observed than those obtained at the HF level and although both require scaling, the scale factors for MP2 are closer to unity. In fact, a scale factor of 0.9 was used for all vibrational modes except for the C–H stretches, which were given a factor of 0.88 and the skeletal bending and torsional modes which were not scaled, i.e. 1.0. The wavenumbers of the fundamentals for the *gauche* conformer are listed in Table 6 and these are labeled ν_1 – ν_{30} as for the *cis* conformer so that the coordinate definitions are unaltered although the symmetry symbols no longer apply.

For both conformers, the potential energy distributions and infrared intensities given in Tables 5 and 6 are from the MP2 force constant calculations with the

Table 4
Symmetry coordinates for vibrations of *cis* 1-butene

Species	Description	Coordinate
A'	=CH ₂ antisymmetric stretch	$S_1 = r_1 - r_2$
	=CH ₂ symmetric stretch	$S_2 = r_1 + r_2$
	CH ₃ antisymmetric stretch	$S_3 = 2r_6 - r_7 - r_8$
	=CH stretch	$S_4 = r_3$
	CH ₃ symmetric stretch	$S_5 = r_6 + r_7 + r_8$
	> CH ₂ symmetric stretch	$S_6 = r_4 + r_5$
	C=C stretch	$S_7 = R$
	CH ₃ antisymmetric deformation	$S_8 = 2\alpha_6 - \alpha_7 - \alpha_8$
	> CH ₂ scissors	$S_9 = (\sqrt{6} + 2)\epsilon - (\sqrt{6} - 2)\theta - \gamma_4 - \gamma_5 - \delta_4 - \delta_5$
	=CH ₂ scissors	$S_{10} = 2\omega - \zeta_1 - \zeta_2$
	CH ₃ symmetric deformation	$S_{11} = \alpha_6 + \alpha_7 + \alpha_8 - \beta_6 - \beta_7 - \beta_8$
	> CH ₂ wag	$S_{12} = \gamma_4 + \gamma_5 - \delta_4 - \delta_5$
	=CH i.p. bend	$S_{13} = \chi - \psi$
	C–C–C antisymmetric stretch	$S_{14} = S - T$
	CH ₃ rock	$S_{15} = 2\beta_6 - \beta_7 - \beta_8$
	=CH ₂ i.p. wag	$S_{16} = \zeta_1 - \zeta_2$
	C–C–C symmetric stretch	$S_{17} = S + T$
	C=C–C i.p. bend	$S_{18} = 2\phi - \chi - \psi$
	C–C–C bend	$S_{19} = (\sqrt{6} + 2)\theta - (\sqrt{6} - 2)\epsilon - \gamma_4 - \gamma_5 - \delta_4 - \delta_5$
A''	CH ₃ antisymmetric stretch	$S_{20} = r_7 - r_8$
	> CH ₂ antisymmetric stretch	$S_{21} = r_4 - r_5$
	CH ₃ antisymmetric deformation	$S_{22} = \alpha_7 - \alpha_8$
	> CH ₂ antisymmetric twist	$S_{23} = \gamma_4 - \gamma_5 - \delta_4 + \delta_5$
	> CH ₂ antisymmetric rock	$S_{24} = \gamma_4 - \gamma_5 + \delta_4 - \delta_5$
	=CH ₂ twist	$S_{25} = \rho$
	=CH ₂ o.p. bend	$S_{26} = \sigma_2$
	CH ₃ antisymmetric rock	$S_{27} = \beta_7 - \beta_8$
	=C–H o.p. bend	$S_{28} = \sigma_1$
	CH ₃ torsion	$S_{29} = \tau_1$
	Asymmetric torsion	$S_{30} = \tau_2$

6-31G(d) basis set corresponding to the unscaled results and the Raman activities are from the HF calculations. It is remarkable that the calculated infrared intensities for all the low frequencies ν_{19} , ν_{29} and ν_{30} have very low values in agreement with the need for the high pressures to record the far infrared spectra so these modes could be observed. The calculated wavenumbers for the d₃ isotopomer in both conformers are given in Table 7 without intensities and potential energy distribution, as a guide to searching for weak bands in its far infrared spectrum.

There are some significant differences in our vibrational assignments with those recently given by Gallinella and Cadioli [8]. For example these authors [8] report an infrared band at 1306.2 cm⁻¹ in the spectrum of the gas which they assign as ν_{13} with the corresponding band in the Raman spectrum of the

liquid at 1299 cm⁻¹ with medium intensity. However, we did not observe the 1299 cm⁻¹ band in the krypton solution and the 1306 cm⁻¹ maximum is the P-branch of the 1319 cm⁻¹ band (ν_{12} of the *gauche* conformer) overlapped with the R-branch of the 1295 cm⁻¹ band (ν_{13} of the *cis* form) and therefore not a fundamental. Gallinella and Cadioli assigned the 1295 cm⁻¹ band as a fundamental of the *gauche* conformer but the closest predicted fundamental below ν_{12} is at 1271 cm⁻¹, which we assigned at 1268 cm⁻¹.

The next region where we differ with the assignment from Gallinella and Cadioli [8] is the doublet we observed at 1080 and 1071 cm⁻¹ in the krypton solution, which we assign as ν_{24} (*cis*) and ν_{15} (*gauche*), respectively. Gallinella and Cadioli [8] report an infrared band in the spectrum of the gas at 1065 cm⁻¹ as ν_{24} (*gauche*), which we did not observe.

Table 5

Vibrational frequencies of *cis* 1-butene

Description	Vib. No.	MP2 6-31G(d) unscaled	MP2 6-31G(d) scaled	obs. ^a	Kr soln.	IR Int. ^b	Raman Act. ^b	P.E.D.
A'								
=CH ₂ antisymmetric stretch	ν_1	3312	3106	3089	3082	14.0	44.2	100S ₁
=CH ₂ symmetric stretch	ν_2	3226	3026	3020	–	5.0	114.6	92S ₂
CH ₃ antisymmetric stretch	ν_3	3200	3001	3009	3013	23.3	134.8	98S ₃
=CH stretch	ν_4	3198	3000	2999	3003	20.7	35.3	90S ₄
CH ₃ symmetric stretch	ν_5	3111	2918	2917	2921	16.6	204.4	100S ₅
> CH ₂ symmetric stretch	ν_6	3085	2894	2887	2879	22.7	23.8	100S ₆
C=C stretch	ν_7	1737	1644	1643	1645	6.9	14.4	66S ₇ ,15S ₁₀
CH ₃ antisymmetric deformation	ν_8	1575	1477	1474	1466	4.3	12.6	88S ₈
> CH ₂ scissors	ν_9	1547	1452	1443	1438	4.6	12.4	96S ₉
=CH ₂ scissors	ν_{10}	1500	1408	1419	1416	3.6	4.9	67S ₁₀ ,12S ₁₁ ,10S ₁₃
CH ₃ symmetric deformation	ν_{11}	1469	1380	1380	1376	3.7	13.2	73S ₁₁
> CH ₂ wag	ν_{12}	1427	1342	1347	1346	2.7	1.4	63S ₁₂ ,13S ₁₁ ,11S ₁₄
=CH i.p. bend	ν_{13}	1361	1280	1295	1292	0.2	30.4	62S ₁₃ ,16S ₇ ,12S ₁₆
C–C–C antisymmetric stretch	ν_{14}	1183	1123	1131	1128	4.7	3.7	23S ₁₄ ,24S ₁₅ ,23S ₁₆ ,10S ₁₉
CH ₃ rock	ν_{15}	1065	1004	1017	1018	0.7	12.3	37S ₁₅ ,27S ₁₄ ,23S ₁₂
=CH ₂ i.p. wag	ν_{16}	1034	975	975	974	0.4	8.7	45S ₁₆ ,20S ₁₄ ,17S ₁₇ ,11S ₁₃
C–C–C symmetric stretch	ν_{17}	874	827	836	836	1.8	6.8	70S ₁₇ ,12S ₁₅ ,12S ₁₆
C=C–C i.p. bend	ν_{18}	553	537	545	–	0.3	3.2	46S ₁₈ ,30S ₁₉ ,10S ₁₆
C–C–C bend	ν_{19}	293	288	292	–	0.3	3.1	56S ₁₉ ,40S ₁₈
A''								
CH ₃ antisymmetric stretch	ν_{20}	3201	3003	2978	2982	25.9	62.7	99S ₂₀
> CH ₂ antisymmetric stretch	ν_{21}	3122	2929	2935	2939	17.3	88.3	99S ₂₁
CH ₃ antisymmetric deformation	ν_{22}	1564	1467	1464	1459	6.3	17.4	94S ₂₂
> CH ₂ antisymmetric twist	ν_{23}	1334	1251	1266	1263	0.2	9.4	72S ₂₃ ,21S ₂₇
> CH ₂ antisymmetric rock	ν_{24}	1150	1080	1081	1080	2.4	6.6	36S ₂₄ ,33S ₂₇ ,19S ₂₃
=CH ₂ twist	ν_{25}	1050	1028	994	997	14.0	1.1	65S ₂₅ ,32S ₂₈
=CH ₂ o.p. bend	ν_{26}	927	870	911	910	38.8	1.2	99S ₂₆
CH ₃ antisymmetric rock	ν_{27}	832	785	790	790	0.3	0.5	38S ₂₇ ,38S ₂₄
=C–H o.p. bend	ν_{28}	570	546	552	552	10.5	8.5	47S ₂₈ ,27S ₂₅ ,19S ₂₄
CH ₃ torsion	ν_{29}	289	288	276	–	0.0	2.4	96S ₂₉
asymmetric torsion	ν_{30}	152	152	154	–	0.1	4.1	99S ₃₀

^a From mid-infrared gas spectrum.^b Infrared intensity in km mol^{−1} and Raman activities in in Å⁴ u^{−1}.

We assign the 1001 cm^{−1} band from the spectrum of the gas as ν_{14} of the *gauche* conformer and the 994 cm^{−1} in the same phase as ν_{25} of the *cis* rotamer. These assignments were reversed in the earlier assignment [8]. Similarly, the 975 cm^{−1} band is assigned to the *cis* conformer (ν_{25}), whereas it was assigned as a *gauche* fundamental in the recent study [8]. For most of the other fundamental assignment there is a reasonable agreement with those proposed earlier [8] in the 400–1500 cm^{−1} region.

Considering the skeletal bending vibration ν_{19} , the *gauche* ab initio frequency is higher than the *cis* but both fall under the broad hump around 310 cm^{−1}. It

appears, however, that the *gauche* intensity swamps the *cis* mode since there is no strong Q spike as expected for a molecule, which is not nearly a symmetric top. Indeed, the calculated intensity of ν_{19} for the *gauche* conformer is 1.6 times higher than ν_{19} in the *cis* form, since there is a near double degeneracy of torsional levels in the *gauche* ground state giving an intensity ratio of about 3.2. The small peak at 311 cm^{−1} is assigned to the *gauche* conformer as an approximate in-plane vibration and may have an A-type contour component. The value of ν_{19} in the *cis* conformer is 292 cm^{−1} or less on the basis of the ab initio predicted frequency and because of the possible

Table 6

Vibrational wavenumbers for the fundamentals of *gauche* 1-butene-d₀

Vib. No. ^a	MP2 6-31G(d) unscaled	MP2 6-31G(d) scaled	Obs. ^b	Kr soln	IR Int. ^c	Raman Act. ^c	P.E.D.
ν_1	3303	3098	3089	3072	15.6	78.3	98S ₁
ν_2	3212	3014	3009	—	3.4	108.0	86S ₂ , 11S ₄
ν_3	3193	2995	2968	2971	4.3	55.3	36S ₃ , 36S ₄ , 24S ₂₀
ν_4	3195	2998	2968	2971	41.7	109.8	49S ₄ , 35S ₃
ν_5	3106	2913	2917	2921	24.1	112.9	99S ₅
ν_6	3092	2901	2896	2900	23.1	81.8	97S ₆
ν_7	1737	1643	1648	1645	4.0	21.0	68S ₇ , 13S ₁₀
ν_8	1570	1473	1474	1466	5.2	17.2	75S ₈ , 16S ₉
ν_9	1549	1454	1449	1444	2.8	16.2	79S ₉ , 18S ₈
ν_{10}	1502	1410	1425	—	1.7	13.8	73S ₁₀
ν_{11}	1469	1378	1378	1376	2.3	11.2	96S ₁₁
ν_{12}	1391	1307	1319	1317	1.6	2.3	68S ₁₂
ν_{13}	1351	1271	1268	1271	1.1	27.6	64S ₁₃ , 12S ₇ , 11S ₁₆
ν_{14}	1074	1011	1001	997	4.2	2.9	48S ₁₄ , 22S ₂₅
ν_{15}	1132	1071	1073	1071	2.6	4.1	37S ₁₅ , 12S ₁₇ , 11S ₁₉
ν_{16}	1016	955	—	—	3.4	3.9	42S ₁₆ , 14S ₁₅ , 11S ₁₄ , 11S ₂₇
ν_{17}	892	842	854	852	1.4	6.8	51S ₁₇ , 22S ₁₅ , 16S ₁₆
ν_{18}	441	430	439	440	0.6	4.6	65S ₁₈
ν_{19}	327	321	311	—	0.6	4.7	67S ₁₉
ν_{20}	3201	3003	3009	3013	31.1	84.9	67S ₂₀ , 28S ₃
ν_{21}	3144	2950	2948	2944	10.8	37.3	92S ₂₁
ν_{22}	1564	1467	1463	1459	6.1	6.4	92S ₂₂
ν_{23}	1332	1250	1263	1263	0.1	12.9	69S ₂₃ , 18S ₂₇
ν_{24}	818	770	790	790	2.9	1.7	47S ₂₄ , 35S ₂₇
ν_{25}	1040	1023	987	992	11.0	1.0	45S ₂₅ , 24S ₂₈ , 18S ₁₄
ν_{26}	933	875	914	910	40.1	8.7	99S ₂₆
ν_{27}	1239	1172	1186	1174	0.2	19.7	15S ₂₇ , 21S ₂₄ , 18S ₁₆ , 12S ₁₈
ν_{28}	663	638	636	636	9.6	7.2	45S ₂₈ , 24S ₂₅
ν_{29}	246	245	241	—	0.0	0.6	85S ₂₉
ν_{30}	108	107	113	—	0.1	7.2	87S ₃₀

^a Same vibrational numbers as used for the *cis* conformer for ease of comparison between the two conformers.^b From infrared spectrum of the gas.^c Infrared intensity in km mol⁻¹ and Raman activities in in Å⁴ u⁻¹.

Fermi resonance but no Q peak is observed. These ν_{19} assignments for the *cis* and *gauche* conformers are the opposite of that previously given [7], but the ν_{18} assignments [7] are supported by the ab initio calculation (Tables 5 and 6). In 1-butene-d₃, the more definite peak at 293 cm⁻¹ is assigned to ν_{19} of the *gauche* conformer on the same basis as for the d₀ isotopomer, and also correspondingly the value of ν_{19} is 270 cm⁻¹ or less for the *cis* conformer. Although the values of ν_{19} frequencies of the *cis* and *gauche* forms of both the d₀ and d₃ species have been given in Tables 5–7 as observed to good

precision, the choice of values has been guided to some extent by the ab initio frequencies.

Conformational stability. The determination of the conformational stability is rather difficult since many of the fundamentals are predicted to be near coincident. The most noteworthy pair is the *cis* band at 551 cm⁻¹ and the *gauche* band at 635 cm⁻¹ (Fig. 3). However, the latter band is in the spectral region where the absorption of the silicon windows on the cold cell results in a very poor signal-to-noise ratio. However, there are two other conformer pairs at 784 (*gauche*), 818 (*cis*), 836 (*cis*) and 852 (*gauche*) cm⁻¹

Table 7

Vibrational wavenumbers for the fundamentals of CH₂=CHCH₂CD₃

		<i>cis</i>					<i>gauche</i>				
		MP2 6-31G(d) unscaled	MP2 6-31G(d) scaled	Infrared gas	Raman gas	Raman Liquid	MP2 6-31G(d) unscaled	MP2 6-31G(d) scaled	Infrared gas	Raman gas	Raman Liquid
A'	ν_1	3312	3106	3106	3089	3083	3303	3098	3100	3089	3083
	ν_2	3225	3026		3018	3010	3212	3014			
	ν_3	2372	2225	2227	2237	2228	2367	2220	2223		
	ν_4	3198	3000	2997	3008	3000	3194	2997	2988	2985	2984
	ν_5	2236	2098	2135	2135	2128	2232	2094	2088	2089	2083
	ν_6	3085	2894	2863	2867	2855	3093	2901	2871	2881	2871
	ν_7	1737	1644	1646	1647	1642	1737	1643	1646		
	ν_8	1133	1064	1061	1054	1060	1130	1060	1061		
	ν_9	1548	1452	1443	1445	1439	1553	1457	1443	1439	1439
	ν_{10}	1498	1407	1423	1425	1419	1501	1410		1425	1419
	ν_{11}	1199	1132	1130	1097	1112	1184	1116	1116		
	ν_{12}	1426	1343	1346	1346	1343	1380	1297	1302		
	ν_{13}	1360	1279	1293	1305	1302	1350	1270	1285	1295	1292
	ν_{14}	998	943		937	955	996	940			
	ν_{15}	949	899		906	923	1032	984			
	ν_{16}	1117	1054	1061	1054	1060	994	909			
	ν_{17}	781	737	741	743	742	771	727			
	ν_{18}	518	501				434	424	430	432	434
	ν_{19}	271	266	270	276	270	303	297	293	281	293
A''	ν_{20}	2323	2226	2227	2237	2228	2373	2226	2227		
	ν_{21}	3124	2930	2922	2914	2916	3146	2951	2935	2924	2925
	ν_{22}	1127	1058	1061	1054	1060	1126	1057			
	ν_{23}	1296	1216	1238	1241	1238	1302	1225	1238		
	ν_{24}	703	664	668		666	688	647	665		
	ν_{25}	1048	1015				1048	1019	1020		
	ν_{26}	927	870	911	892	910	932	875	911	892	910
	ν_{27}	1082	1028	996	983	1001	1201	1135			
	ν_{28}	563	538	545		549	645	619	617	622	620
	ν_{29}	216	216	201			183	182	171		
	ν_{30}	144	144	144			103	102	107	96	

which are reasonably well separated and can be used for temperature dependent studies. The 784 cm⁻¹ band has been assigned to the *gauche* conformer on the basis that ν_{24} has a predicted conformer intensity of near ten times that of the ν_{27} fundamental of the *cis* conformer predicted at nearly the same frequency but is assigned at 818 cm⁻¹. There are some other bands in the 1200–1400 cm⁻¹ for the *gauche* conformer, which are relatively free from absorptions from the *cis* fundamentals. However, the choice of the bands for the enthalpy determinations depends on the correct assignment, which is difficult since one cannot obtain a single conformer in the solid state [8]. Repeated

annealing of the sample does not change significantly the conformational concentrations so it is not possible to identify the bands of an individual conformer from such data. Nevertheless, it is believed that the assignments given for the conformer pairs to the individual bands are the correct ones so that the ΔH values can be determined.

Variable temperature studies of the infrared spectrum of 1-butene dissolved in both liquid xenon and krypton were conducted to determine the enthalpy difference between the two stable conformers, *cis* and *gauche*. The temperature dependence of the infrared bands assigned to one of the conformer

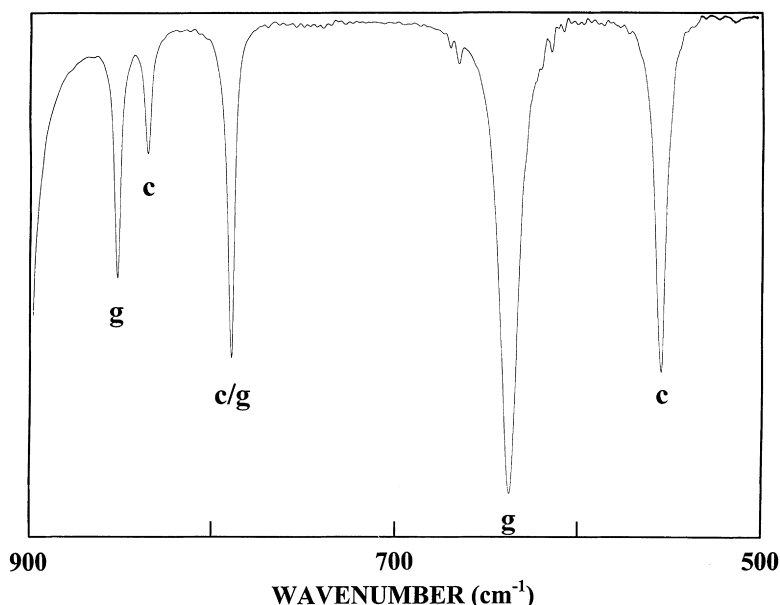


Fig. 3. Infrared spectrum of 1-butene in krypton solution at -125°C in the region of $500\text{--}900\text{ cm}^{-1}$.

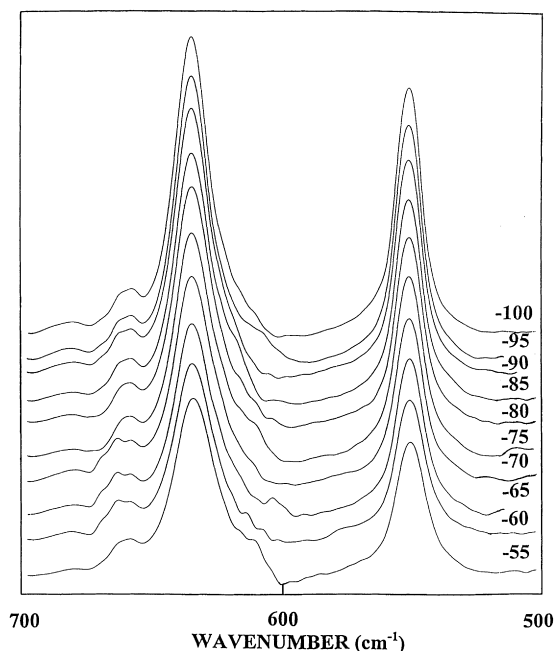


Fig. 4. Temperature dependent infrared spectrum ($500\text{--}750\text{ cm}^{-1}$) of 1-butene in liquid xenon.

pairs is shown in Fig. 4. The ΔH values for 1-butene dissolved in liquid xenon are given in Table 8. The two conformer pairs ranged from a low value of $34 \pm 12\text{ cm}^{-1}$ to a high value of $94 \pm 9\text{ cm}^{-1}$. The average value for these three conformer pairs is $64 \pm 10\text{ cm}^{-1}$ ($183 \pm 29\text{ cal/mol}$) with the *cis* conformer being the more stable form. The ΔH values for 1-butene dissolved in liquid krypton are given in Table 9. The enthalpy values for the four conformer pairs ranged from a low value of $35 \pm 4\text{ cm}^{-1}$ to a high value of $115 \pm 29\text{ cm}^{-1}$. The average value for these four determinations is $73 \pm 6\text{ cm}^{-1}$ ($209 \pm 17\text{ cal/mol}$) with the *cis* conformer being the more stable form. These values are in good agreement with the value obtained from the previous Raman temperature study [7] in which the *cis* conformer was determined to be more stable by 77 cm^{-1} in the liquid phase. In addition, the ΔH values determined in this study also agree very well with the recent infrared study [8] of the gas where it was concluded that the *cis* conformer is more stable by 77 cm^{-1} .

Methyl torsions. In the region predicted for the methyl torsional bands by the value of the microwave torsional barrier for *cis* 1-butene- d_0 (i.e. the energy difference $\text{Ce} - \text{Cs}$ in Table 1, 1396 cm^{-1}) and with an F value from either the microwave or ab initio data,

Table 8

Temperature and intensity ratios from the conformational study of 1-butene-d₀ in xenon

<i>T</i> (°C)	1000/ <i>T</i> (K)	<i>I</i> _{551/635}	<i>I</i> _{551/852}
−55	4.59	0.809	2.070
−60	4.69	0.831	1.996
−65	4.81	0.878	2.111
−70	4.93	0.852	2.082
−75	5.05	0.880	2.175
−80	5.18	0.880	2.058
−85	5.32	0.918	2.122
−90	5.46	0.919	2.138
−95	5.62	0.948	2.155
−100	5.78	0.963	2.182
ΔH^a		$94 \pm 9 \text{ cm}^{-1}$	$34 \pm 12 \text{ cm}^{-1}$

^a Average value of ΔH is $64 \pm 10 \text{ cm}^{-1}$ with the *cis* conformer, the more stable form.

the fundamental is predicted near 250 or 260 cm^{-1} , respectively. No sharp peaks are observed in this wavenumber region in spite of the *cis* 1-butene being far from a symmetric top ($\kappa = -0.77$) and its contours expected to show strong central peaks. Some rotational fine structure (Fig. 1) is observed centered near 240 cm^{-1} but it is difficult to distinguish individual lines from some of the pressure-broadened rotational lines of residual water. However, in the spectrum of the d₃ isotopomer near the frequency of 193 cm^{-1} indicated by the ab initio methyl barrier, a series of peaks are evident in spite of the weakness of the absorption. The transitions start a little higher than predicted at 201 cm^{-1} . The

four peaks are fitted well with a two parameter potential energy function yielding $V_3 = 1678 \text{ cm}^{-1}$ with a small V_6 term as listed in Table 10. This barrier height is almost 300 cm^{-1} higher than the value deduced from the splitting of microwave lines but although the bands are weak, the goodness of the fit is convincing for the assignment. There are a few other weak bands in the 200 cm^{-1} region of the d₃ spectrum (Fig. 5).

Employing the barrier height derived from the infrared spectrum of the d₃ species, the positions of the methyl torsional transitions of the normal species can be predicted more accurately if one assumes that the potential functions will be similar. In the case of propanal, the value of V_3 derived for CD₃CD₂CHO is significantly higher than the values for the normal and other deuterated species perhaps due to more top–top coupling in the heavier methyl group. However, from this assumption, the small shoulder on a rotational structure head or edge seen at 276.0 cm^{-1} matches well with this prediction and it is assigned as the $1 \leftarrow 0$ methyl torsional transition of the *cis* 1-butene-d₀. At lower frequencies, some rotational structure is seen leading to another edge at 263 cm^{-1} . Such extremely weak absorption is entirely consistent with the intensities predicted from the ab initio dipole derivatives shown in Table 5. Fitting these two very weak absorptions yields a value of V_3 of 1695 cm^{-1} very near that for the d₃ isotopomer and again it is obvious that this V_3 is much larger than the microwave or ab initio values. The previous assignment [7] of the weak Raman features starting at 411 cm^{-1} is not sustained;

Table 9

Temperature and intensity ratios from the conformational study of 1-butene-d₀ in krypton

<i>T</i> (°C)	1000/ <i>T</i> (K)	<i>I</i> _{551/784}	<i>I</i> _{551/635}	<i>I</i> _{551/852}	<i>I</i> _{551/1315}
−105	5.95	0.179	0.610	1.659	3.317
−110	6.13	0.184	0.642	1.747	3.537
−115	6.33	0.169	0.634	1.697	3.595
−120	6.54	0.177	0.651	1.726	3.727
−125	6.76	0.188	0.673	1.762	3.854
−130	6.99	0.192	0.675	1.752	4.000
−135	7.25	0.192	0.704	1.791	4.200
−140	7.52	0.200	0.716	1.812	4.386
−145	7.81	0.209	0.749	1.851	4.567
−150	8.13	0.222	0.768	1.885	4.820
ΔH^a		$70 \pm 11 \text{ cm}^{-1}$	$70 \pm 36 \text{ cm}^{-1}$	$35 \pm 4 \text{ cm}^{-1}$	$115 \pm 3 \text{ cm}^{-1}$

^a Average value of ΔH is $73 \pm 6 \text{ cm}^{-1}$ with the *cis* conformer, the more stable form.

Table 10

Potential energy functions and torsional transitions (all constants and transitions in cm^{-1} . Only the A–A transitions are shown and fitted but the A–A/E–E splittings are not greater than 1 cm^{-1} for the transitions listed) for methyl torsions of 1-butene- d_0 and - d_3 in the *cis* and *gauche* conformations

	d_3				d_0			
	Ab initio	Obs.	Fit	MW ^a	Ab initio	(V 's from) d_3	Obs.	Fit
<i>cis</i>								
F	2.9594			5.6310	5.6319			
V_3	1500.9		1677.6	1396	1500.9	1677.6		1695.1
V_6			−16.7			−16.7		−14.6
$1 \leftarrow 0$	193.04	201.07	201.04	252.62	262.48	273.92	276.0	276.0
$2 \leftarrow 1$	185.79	194.46	194.60	238.18	248.12	261.10	263.0	263.0
$3 \leftarrow 2$	178.04	187.48	187.65	222.12	232.22	246.76		248.5
$4 \leftarrow 3$	169.67	180.50	180.10					
<i>gauche</i>								
F	3.2074			5.9005	5.8891			
V_3	1110.9		1113.0	1105	1110.9			1179.9
$1 \leftarrow 0$	171.53	171.7	171.70	228.1	228.55		236	236.0
$2 \leftarrow 1$	163.51	–	163.67	213.6	213.04		219	220.6

^a Ref. [6].

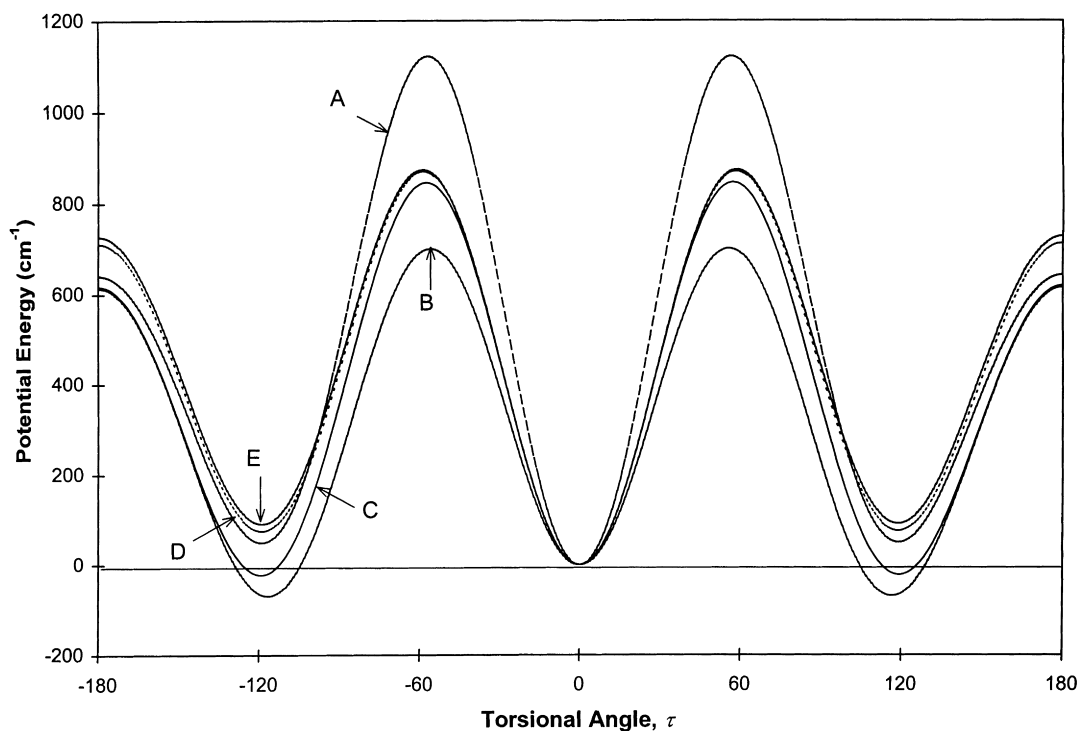


Fig. 5. Potential energy functions for asymmetric torsion of 1-butene: (A) a function fitted to the barriers and conformation energy differences of Ref. [7]; (B) ab initio function as given in Table 9; (C) from constants of fit 1 of the observed torsional frequencies for the d_0 species in Table 11; (D) from constants of fit 2 of the observed torsional frequencies for the d_0 species in Table 11; and (E) from constants of fit 3 of the observed torsional frequencies for the d_0 species in Table 11.

Table 11

Potential energy functions and torsional transitions (transitions are in cm^{-1} except the microwave splittings 0^- , $1^+ - 1^-$, $2^- - 2^+$ which are in MHz. The *gauche* torsional angle is in degrees. Transitions are calculated using a series of *F*-kinetic constants calculated from the MP2/6-31G(d) geometric structures of both *cis* and *gauche* conformers. Parts of the cosine series for the d_0 and d_3 species— d_0 : $F_0 = 2.4877$, $F_1 = 0.1832$, $F_2 = 0.06010$, $F_3 = 0.00946$, $F_4 = 0.00237$, $F_5 = 0.00041 \text{ cm}^{-1}$, d_1 : $F_0 = 2.2762$, $F_1 = 0.1575$, $F_2 = 0.05711$, $F_3 = 0.00787$, $F_4 = 0.00209$, $F_5 = 0.00032 \text{ cm}^{-1}$, d_3 for asymmetric torsions of 1-butene- d_0 and - d_3

	d ₀			d ₃		
	Ab initio ^a	Obs.	Fit 1 ^b	Fit 2 ^b	Fit 3 ^b	
V ₁	-93.8		-164.4 ± 15	-54.0 ± 22	-35.8 ± 24	-93.8
V ₂	-78.7		45.6 ± 16	72.8 ± 22	76.8 ± 24	-78.7
V ₃	707.5		781.6 ± 13	765.4 ± 17	763.1 ± 18	707.5
V ₄	87.6		89.3 ± 11	82.9 ± 14	81.7 ± 15	87.6
cis/gauche ^c	697		846	869	873	697
gauche/gauche ^c	682		639	635	635	682
ΔE _{GS-Cs}	-68		-22	76	92	-68
1 ← 0	142.21	153.81	153.76	153.69	153.68	134.92
2 ← 1	132.00	(150.06)	144.11	144.31	144.34	125.93
3 ← 2	120.53	132.78	133.52	134.08	134.17	115.92
4 ← 3	106.85	124.31	121.49	122.57	122.74	104.49
1 [±] ← 0 [±]	106.5	113.3	113.56	111.76	105.14	107.49
2 [±] ← 1 [±]	100.9		108.19	106.39	100.19	102.73
0 ⁻ ← 0 ⁺	0.000	-	0.002	0.002	0.002	0.000
1 ⁺ ← 1 ⁻	0.035	0.354	0.21	0.20	0.19	0.015
2 ⁻ ← 2 ⁺	1.862	9.76	10.62	9.61	9.29	0.830
τ _{min}	116.6	119.9	119.2	118.9	118.9	116.6
ΔH ₁ ^d	-85.2	+57 ± 19	-42.8	54	70	-83
		+73				+73

^a Ab initio potential energies (in cm^{-1}) from MP2/DZ(2d,p) calculations.

^b Fit to all data in observed column. Error is the standard error of the fit.

^c *Cis/gauche* and *gauche/gauche* energy barriers.

^d ΔH corresponds to (0[±] ← 0) and is positive if the *cis* conformer is the more stable form.

these features must correspond to other combination or difference transitions.

Starting again with the spectrum of 1-butene- d_3 , there are no prominent sharp features in the region predicted for the methyl torsional transitions of the *gauche* conformer from the microwave or ab initio values of V_3 (i.e. the energy difference $G_e - G_s$ in Table 1, 1105 cm^{-1}). However, the *gauche* conformer is very near to a symmetric top and the approximate C-type bands will not have a prominent central spike especially if the excited state rotational constants are a little different from those of the ground state. In the region concerned there is indeed a very broad hump of absorption covering at least 40 cm^{-1} with maximum absorption around 165 cm^{-1} and with some not very strong or regular rotational fine structure. A slight minimum may indicate the origin but a small peak at 172 cm^{-1} has been chosen to fit a methyl barrier in agreement with the microwave value as seen in Table 10.

In the spectrum of the normal species, the whole of the broad peak from 200 to 260 cm^{-1} must be due to methyl torsional transitions of the *gauche* conformer and the structure observed is rotational K structure rather than a series of torsional transitions. The series of sub-bands from 236 to 241 cm^{-1} probably lie near the origin of the $1 \leftarrow 0$ transition, and the low frequency side may represent the edge of a degrading central peak of a C-type band. It certainly yields a value of V_3 in agreement with all the ab initio and the microwave values of V_3 , and in agreement with the d_3 isotopomer. The stronger peak at 241 cm^{-1} leads to a higher value of V_3 in poorer agreement. An average methyl barrier for the *gauche* conformer as obtained from two or three bands in the spectra is $1150 \pm 50\text{ cm}^{-1}$ with an uncertainty to reflect the breadth of the bands.

Those determinations of methyl torsional frequencies ν_{29} for both the *cis* and *gauche* forms are included as observed in Tables 5–7. Although the derived methyl torsional barrier for the *cis* form is higher than the ab initio or microwave estimates, the agreement with frequencies obtained from the ab initio second derivatives is very good with the ab initio values slightly higher in both isotopomers.

Asymmetric torsion. In the previous analysis [7] of the far infrared spectrum of 1-butene there was an attempt to interpret the two distinct sharp bands at

153.8 and 150.1 cm^{-1} as consecutive asymmetric torsional transitions in the *cis* form. Since they are rather close, that interpretation leads to a potential energy function that has the high *cis* to *gauche* barrier of 1114 cm^{-1} which is much higher than any ab initio value reported in Table 1. The relevant microwave study [6] did not provide this parameter as the line splittings in the microwave spectrum were employed in determining the *gauche* to *gauche* barrier, which is similar to the ab initio values from basis sets built on DZ. The coefficients of a potential energy function derived from ab initio energies calculated at MP2/DZ(2d,p) are given in Table 11. It was found to be necessary, in this case, to evaluate four potential energy constants in the series

$$V(\tau) = \sum_i \frac{1}{2} V_i (1 - \cos i\tau)$$

and energies have been calculated at torsional angles other than minima and transition states where at $\tau = 30$ and 90° the energy differences from *cis* (C_s) are 389 and 224 cm^{-1} , respectively. The value of V_6 term was found to be small and hence V_6 is neglected in predictions and fits. Corrections for the zero-point energies of all the vibrations other than the asymmetric torsion might be applied to the ab initio energies before fitting to a potential function [18]. Such correction would increase the magnitude of the *gauche*–*cis* energy difference ΔE by 13 cm^{-1} if the experimental frequencies in Tables 5 and 6 were used but by as much as 28 cm^{-1} if the MP2 frequencies were used.

Torsional transitions and splittings have been calculated from this potential energy function using the F series calculated from the MP2/6-31G(d) geometrical structures and they are given in Table 11. The predicted *cis* torsional fundamental is only 10 cm^{-1} lower than the first observed band, but the interval between the first two transitions is 10 cm^{-1} and not 3.7 cm^{-1} . Also, the *gauche* fundamental predicted at 106.5 cm^{-1} is near to the fundamental from the ab initio force constant calculation (Table 6) but much lower than the *cis* fundamental wave-number.

The appearance of two close asymmetric torsion transitions is exactly similar to the situation in normal propanal where it has been proposed [11] that the

excited state of the second band, i.e. the second excited asymmetric torsional level, is in Fermi resonance with the skeletal bending excited state ν_{15} , and the second torsional transition is at a higher frequency than without perturbation. In 1-butene, $2\nu_{29} = 153.8 + 150.1 \text{ cm}^{-1}$ is higher than $\nu_{19} \approx 292 \text{ cm}^{-1}$. In some deuterated propanal species the asymmetric torsional series does not begin with two bands close together but instead the second excited state of propanal- d_1 , for example, is *lowered* by the Fermi resonance with ν_{15} , and the second torsional transition is at a lower frequency than without perturbation. By recording the far infrared spectrum of 1-butene- d_3 , it was hoped that 1-butene would mirror the propanal situation. Instead the first two asymmetric torsional transitions at 143.8 and 140.4 cm^{-1} are separated by almost the same interval as in the normal species and the Fermi resonance is like the normal species: $2\nu_{29} = 143.8 + 140.4 \text{ cm}^{-1}$ is higher than $\nu_{19} \approx 270 \text{ cm}^{-1}$. Therefore in attempting to derive an asymmetric torsional potential energy function, the $2 \leftarrow 1$ transition is omitted, as in propanal, and a lower frequency band is assigned as the $3 \leftarrow 2$ transition, i.e. 132.8 cm^{-1} in the d_0 species and 127.8 cm^{-1} in the d_3 species.

The frequency of the fundamental torsional transition of the *gauche* form is also essential for fitting a potential function. The *gauche* asymmetric torsional bands are expected to show the very broad rotational contour of a near-prolate symmetric top ($\kappa = -0.99$) as for the methyl torsion. Such a broad absorption is seen in the spectrum of the d_0 species between 70 and 130 cm^{-1} with a maximum near 108 cm^{-1} and small peak at 113.7 cm^{-1} , which was chosen as a Q peak for fitting purposes. This is higher than the choice made in the Raman spectrum [7] but this does not rule out that the weak series observed may be the higher *gauche* asymmetric torsional transitions. In the far infrared spectrum of the d_3 species, the maximum of the corresponding band is a little lower and 107 cm^{-1} is chosen as corresponding to the choice in the d_3 species.

Further information is required if at least three parameters are to be determined. The dihedral angle of the molecule in the *gauche* form is 119.9° from the microwave r_o structure [6]. The splitting of the *gauche* energy levels in the first and second excited torsional states is also available from the same study [6]. A value of the difference between the *gauche* and the

cis zero-point energy levels called ΔH in Table 11 has to be assumed. If the ab initio value of ΔE for MP2/DZ(2d,p) was corrected both for the zero-point energy differences of the asymmetric torsions and for all the other vibrations of the *cis* and *gauche* conformers, the ΔH value would be 18 cm^{-1} , which is higher than any observed. Instead the value of ΔE as given in Table 1 has been used; this makes the *gauche* form lower than the *cis* in agreement with the microwave prediction [6]. Combining these transitions, splittings and angle in a least-squares fit yields the potential energy function in Table 11. It was found impossible to fit such a large difference between the fundamentals of *cis* and *gauche* conformers as found in the frequency calculations without a V_4 term. Because of zero-point energy differences, the value of ΔH ($0 \leftarrow 0^\pm$) is greater in *magnitude* than the difference between the minima of the potential energy function (ΔE). The splittings of the *gauche* torsional levels and the fourth *cis* torsional transition are not fitted well, but in terms of *cis* to *gauche* and *gauche* to *gauche* barrier heights, the potential energy function is fairly similar to the ab initio function.

For the d_3 species, splittings of the *gauche* torsional levels are not available and the fit for d_3 in Table 11 is not constrained in the same way as for d_0 . The barrier heights obtained for the d_3 species are quite near to those for the d_0 species although the standard errors of the V_1 – V_4 constants are large. The standard errors on V_1 and V_2 are particularly large but it is perhaps significant that the sum of V_1 and V_2 were almost constant at around -160 cm^{-1} for all the various fits performed. With a bias in favor of the d_0 potential, the barrier heights to asymmetric torsion are $835 \pm 48 \text{ cm}^{-1}$ for *cis* to *gauche*, $615 \pm 51 \text{ cm}^{-1}$ for *gauche* to *gauche* and $883 \pm 33 \text{ cm}^{-1}$ for *gauche* to *cis* forms.

5. Structural parameters

In the earlier structural study [6] of 1-butene there were no heavy atom substitution so the authors were only able to obtain the r_s coordinates of the hydrogen atoms. For the *cis* conformer the four carbon atoms are located in the symmetry plane so eight coordinates remain undetermined from the deuterium substituted data. These coordinates were calculated from the center-of-mass conditions, $\sum_i m_i a_i = 0$ and $\sum_i m_i b_i =$

Table 12

Fit of the rotational constants from the r_o adjusted parameters listed in Tables 2 and 3 for 1-butene

Molecule	Rotational constant	<i>cis</i>			<i>gauche</i>		
		Obs.	Calc.	Δ	Obs.	Calc.	Δ
$\text{CH}_2=\text{CHCH}_2\text{CH}_3$	<i>A</i>	15302.54	15302.52	0.02	22557.33	22551.34	5.99
	<i>B</i>	5574.92	5577.78	−2.86	4156.28	4157.28	−1.00
	<i>C</i>	4303.14	4303.94	−0.80	4056.21	4057.45	−1.24
$\text{CDH}=\text{CHCH}_2\text{CH}_3$ 1-d	<i>A</i>	14279.29	14282.45	−3.16	21083.7	21086.03	−2.33
	<i>B</i>	5518.02	5515.32	2.70	4006.04	4004.77	1.27
	<i>C</i>	4185.50	4183.35	2.15	3924.16	3921.80	2.36
$\text{CDH}=\text{CHCH}_2\text{CH}_3$ 2-d	<i>A</i>	15154.73	15159.25	−4.52	22159.8	22139.02	20.78
	<i>B</i>	5197.01	5197.27	−0.26	3924.04	3924.51	−0.47
	<i>C</i>	4063.89	4063.57	0.32	3823.00	3823.56	−0.56
$\text{CH}_2=\text{CDCH}_2\text{CH}_3$ 3-d	<i>A</i>	14381.80	14379.06	2.74	20477	20472.91	4.09
	<i>B</i>	5456.94	5459.91	−2.97	4108.80	4110.74	−1.94
	<i>C</i>	4159.06	4159.51	−0.45	4002.65	4003.55	−0.90
$\text{CH}_2=\text{CHCDHCH}_3$ 4-d (5-d)	<i>A</i>	14261.64	14261.81	−0.17	20592.9	20616.18	−23.28
	<i>B</i>	5474.89	5477.54	−2.65	4143.13	4142.78	0.35
	<i>C</i>	4207.41	4208.24	−0.83	3993.69	3993.76	−0.07
$\text{CH}_2=\text{CHCDHCH}_3$ 5-d <i>gauche</i>	<i>A</i>				20342.4	20358.58	−16.18
	<i>B</i>				4113.03	4111.56	1.47
	<i>C</i>				3981.11	3980.10	1.01
$\text{CH}_2=\text{CHCH}_2\text{CDH}_2$ 6-d	<i>A</i>	15233.15	15236.33	−3.18			
	<i>B</i>	5209.19	5208.96	0.23			
	<i>C</i>	4077.42	4076.25	1.17			
$\text{CH}_2=\text{CHCH}_2\text{CDH}_2$ 7-d (8-d)	<i>A</i>	14367.82	14367.24	0.58			
	<i>B</i>	5441.16	5439.73	1.43			
	<i>C</i>	4197.86	4196.25	1.61			
$\text{CDH}=\text{CDCH}_2\text{CH}_3$ 1,3-d ₂	<i>A</i>	14197.37	14197.94	−0.57			
	<i>B</i>	5105.83	5106.43	−0.60			
	<i>C</i>	3937.88	3937.34	0.54			
	<i>B + C</i>				7838.17	7835.53	2.64
$\text{CDH}=\text{CDCH}_2\text{CH}_3$ 2,3-d ₂	<i>A</i>				20173.00	20157.97	15.03
	<i>B</i>				3880.38	3881.56	−1.18
	<i>C</i>				3780.03	3780.30	−0.27
$\text{CH}_2=\text{CHCDHCDH}_2$ 4,7-d ₂	<i>B + C</i>				7922.96	7922.37	0.59

0, which are necessary along with the requirements that all of the hydrogen atoms are fixed at the positions determined by the d-substitution. The structural parameters obtained by this method were referred to as r_s -like parameters for the *cis* form (Table 2).

The structural parameters for the *gauche* form are much more difficult to determine because of the lack of symmetry. These earlier investigators [6] found

that the c_s coordinate of the H_1 atom was imaginary when the Kraitchman equation was applied to the B_o 's of normal and the corresponding deuterated species. In fact almost all of the atoms of the *gauche* conformer are located near the *a*-axis which makes it nearly impossible to obtain the r_s parameters for this form. Therefore, Kondo et al. [6] obtained the structure of the *gauche* conformer by fixing the

vinyl C–H bond lengths at 1.090 Å and the C–H bond distances for the methylene and methyl groups at 1.095 Å and varied the other nine parameters, C₁–C₂, C₂–C₃, C₃–C₄, \angle C₁C₂C₃, \angle C₃C₂H₃, \angle C₃C₄H_{6,7,8} and \angle H₄C₃H₅, to fit the moments of inertia. The structure obtained by this method was referred to as the *r_o*-like structural parameters (Table 3) and a similar process was used to obtain the *r_o*-like structural parameters for the *cis* conformer (Table 2).

We have found that we can obtain good structural parameters by fixing the differences in the parameters to the values obtained from the ab initio calculations and use the microwave experimental data to fit the rotational constants (computer program A&M, ab initio and microwave) for both conformers [19]. In order to reduce the number of independent variables, the structural parameters are separated into sets according to their types. Bond lengths in the same set keep their relative ratio, and bond angles and torsional angles in the same set keep their differences in degrees. This assumption is based on the fact that the errors from the ab initio calculations are systematic.

The parameters obtained by this method are listed in Tables 2 and 3. It is estimated that the heavy atom distances should be accurate to ± 0.005 Å and the carbon–hydrogen distances to ± 0.003 Å. The angles are expected to be $\pm 0.5^\circ$ with the possible exception of the dihedral of the *gauche* conformer where the ab initio calculations are the least sensitive. The fit of the 47 rotational constants is given in Table 12 and the agreement with the experimental rotational constants is usually better than 2 MHz except for the *A* rotational constants where the difference is better than 10 MHz except for the *gauche* conformer. It should be noted that the *A* rotational constants for the *gauche* conformer were not as accurately determined as those for the *cis* conformer and in some cases not at all because of the need to assign A-type Q-branches or B-type R-branches. For the *gauche* conformer the dipole moments were determined [6] to be $\mu_b = 0.08 \pm 0.011$ Debye and $\mu_c = 0.059 \pm 0.016$ Debye which makes it difficult to assign any transitions except the A-type transitions.

The *r_o*-adjusted parameters obtained in this study are listed in Tables 2 and 3 and the differences between these parameters and those previously reported [6] are within the experimental uncertainties

previously published. For example the C₃–C₄ bond distance is found to be significantly shorter with a value of 1.530 Å but this is the lower limit of the value (1.536 ± 0.006 Å) of this parameter as an *r_o*-like distance and coincides with the *r_s*-like distance given earlier [6] for the *cis* conformer. Similarly, the C₂–C₃ distance is significantly shorter than that given earlier as an *r_o*-like distance but the uncertainty previously published of 0.010 Å still places it within the value of the *r_o*-adjusted parameter. It should be noted that we believe the *r_o*-adjusted parameters should all be within 0.005 Å for distances, which is a considerably lower uncertainty than those given in the earlier microwave study [6]. Additionally, we have given the angles so a complete structural determination has been provided. The fit of the rotational constants for the *cis* conformer is excellent and those for the *gauche* conformer are quite good except for the A-moments.

6. Conclusion

There are not many features in the far infrared spectra of 1-butene-*d*₀ and -*d*₃ but the current analysis has employed all the information that is available to make assignments of the bending and torsional transitions of the two conformers of both butenes. With regard to the existence of the two conformers, a potential energy function has been derived for asymmetric torsion from the available experimental data, which is consistent with the ab initio calculations, and with the constants and intervals obtained from the microwave spectrum.

References

- [1] J.R. Durig, G.A. Guirgis, S. Bell, J. Phys. Chem. 93 (1989) 3487.
- [2] N. Sheppard, J. Chem. Phys. 17 (1949) 74.
- [3] L.A. Harah, D.W. Mayo, J. Chem. Phys. 33 (1960) 298.
- [4] A.A. Bothnerby, C. Naar-Colin, H. Gunther, J. Am. Chem. Soc. 84 (1962) 2748.
- [5] G.J. Karabutsos, R.A. Teller, Tetrahedron 24 (1968) 3923.
- [6] S. Kondo, E. Hirota, Y. Morino, J. Mol. Spectrosc. 28 (1968) 471.
- [7] J.R. Durig, D.A.C. Compton, J. Phys. Chem. 84 (1980) 773.
- [8] E. Gallinella, B. Cadioli, Vib. Spectrosc. 13 (1997) 163.
- [9] V.K. Kanshik, P. Venkateswarlu, Chem. Phys. Lett. 51 (1977) 516.

- [10] A. Bouchy, G. Roussy, M.S. Ledoux, F.G. Gault, J. Chim. Phys. 76 (1979) 357.
- [11] A. Bouchy, G. Roussy, J. Chim. Phys. 78 (1981) 669.
- [12] J.R. Durig, G.A. Guirgis, S. Bell, W.E. Brewer, J. Phys. Chem. 101 (1997) 9240.
- [13] J.R. Durig, S. Bell, G.A. Guirgis, Spectrochim. Acta A 52 (1996) 1843.
- [14] K.B. Wiberg, S.L. Schreiber, J. Org. Chem. 53 (1988) 783.
- [15] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.A. Robb, J.R. Cheeseman, T.A. Keith, G.A. Petersson, J.A. Montgomery, K. Raghavachari, M.A. Al-Laham, V.G. Zakrzewski, J.V. Ortiz, J.B. Foresman, J. Cioslowski, B.B. Stefanov, A. Nanayakkara, M. Challacombe, C.Y. Peng, P.Y. Ayala, W. Chen, M.W. Wong, J.L. Andres, E.S. Replogle, R. Gomperts, R.L. Martin, D.J. Fox, J.S. Binkley, D.J. Defrees, J. Baker, J.P. Stewart, M. Head-Gordon, C. Gonzalez, J.A. Pople, GAUSSIAN 94 (Revision B. 3), Gaussian Inc., Pittsburgh, PA, 1995.
- [16] T.H. Dunning, J. Chem. Phys. 53 (1970) 2823.
- [17] T.H. Dunning, J. Chem. Phys. 55 (1971) 716.
- [18] S. Bell, J. Mol. Struct. 320 (1994) 125.
- [19] B.J. van der Veken, W.A. Herrebout, D.T. Durig, W. Zhao, J.R. Durig, J. Phys. Chem. A 103 (1999) 1976.