

Preferred Rotameric Conformations of Isobutyraldehyde, Their Dipole Moments and Vibrationally Excited States by Microwave Spectroscopy

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The earlier prediction of the preferred and the less stable rotameric conformations of isobutyraldehyde, $(\text{CH}_3)_2\text{CHCHO}$, has been confirmed experimentally by microwave spectroscopy. The compound exists mainly in a *gauche* conformation, in which one of the methyl groups is eclipsed by the oxygen atom, and the less stable rotamer is the *trans* conformation, in which the oxygen atom eclipses the isopropyl hydrogen.

Ground state rotational constants (in MHz) and centrifugal distortion constants (in kHz), together with dipole moments (in D), are:

	<i>Gauche</i>	<i>Trans</i>
<i>A</i>	7494.62 ± 0.02	7707.84 ± 0.03
<i>B</i>	4107.51 ± 0.02	3736.63 ± 0.02
<i>C</i>	2980.70 ± 0.02	2815.08 ± 0.02
Δ_J	1.9 ± 0.5	0.7 ± 0.4
Δ_{JK}	-0.3 ± 0.3	48.4 ± 0.7
Δ_K	11.2 ± 0.7	19.0 ± 5.0
δ_J	0.28 ± 0.02	0.18 ± 0.02
δ_K	3.6 ± 0.2	25.0 ± 0.5
$ \mu_a $	2.43 ± 0.02	2.82 ± 0.02
$ \mu_b $	0.80 ± 0.03	0.0 by symmetry
$ \mu_c $	0.83 ± 0.02	0.46 ± 0.03
$ \mu_{\text{total}} $	2.69 ± 0.03	2.86 ± 0.03

Rotation spectra due to three torsionally excited states of each rotamer have been identified, along with satellites arising from CH_3 internal rotation and CC_2 wagging.

I. Introduction

It is now some time ago since we predicted [1] the intramolecular barrier functions, and hence the preferred and less stable rotamers of the compounds $(\text{CH}_3)_2\text{CHCOX}$ with $\text{X} = \text{H}, \text{F}, \text{OH}$. This prediction was based on the observation that the threefold potential term, V_3 , which opposes internal rotation about the bond linking the COX group to the rest of the molecule, remains approximately constant between acetyl fluoride [2] and propionyl fluoride [1], as well as along the series acetaldehyde [3], propionaldehyde [4], pivalaldehyde [5]. Against this background we interpreted the sum, V^* , of the one-, two- and fourfold terms, which becomes apparent

only when asymmetric internal rotors are studied, as the difference in interaction with the COX group between a hydrogen and a methyl group. It followed that for replacement of a second hydrogen by a methyl group this difference V^* has to be added, with the appropriate phase shift, to the known potentials of the propionyl compounds to give (predicted) barrier functions for the compounds $(\text{CH}_3)_2\text{CHCOX}$. The results of this procedure suggested that all three compounds should exist preferentially in *gauche* conformations, in which the oxygen atom eclipses one of the methyl groups, while the sterically favored *trans* conformations, in which the oxygen atom eclipses the hydrogen of the isopropyl group, should be less stable than the *gauche* forms by ~ 1 kcal/mole.

Since this prediction was somewhat contrary to chemical intuition we felt compelled to proceed

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with its check by experiment. The ensuing work showed quickly that all three compounds indeed preferred the *gauche* conformations, and qualitative potential functions for isobutyraldehyde (isopropyl carboxaldehyde) and isobutyryl fluoride were reported in the early 1970s [6].

The accurate determination of an intramolecular potential function requires of course the best possible knowledge of the rotameric structures, which enter the barrier calculation via the dihedral angle between the two rotamers and via the kinetic energy matrix elements, G_{ii}^{-1} , and it requires precise knowledge of the torsional frequencies about the bond linking the two parts of the molecule for both rotamers. Developments in double resonance modulated (DRM) microwave spectroscopy [7] allowed the required structural information to be obtained by 1976 [8], and advances in high-resolution vibrational spectroscopy nowadays permit the torsional frequencies to be determined with much higher accuracy than could be hoped for by microwave techniques alone.

For isobutyraldehyde (isopropyl carboxaldehyde) this important vibrational information has been established recently by J. R. Durig and collaborators [9]. This makes it timely to report now in a formal way the early microwave work to identify the preferred conformers of isobutyraldehyde, including the determination of their dipole moments and the study of vibrationally excited states. The determination of the structures of the two rotamers will be described in the following paper, and all microwave information pertaining to the precise shape of the potential barrier functions will be combined with the i.r. data of Durig and collaborators in a subsequent, joint publication.

II. Experimental

Spectroscopic work was carried out on a commercial sample which was used without further purification. The majority of experiments was conducted on a DRM spectrometer [7] with an "empty" K-band absorption cell of length 20 m. The pump source (OKI klystrons of V10 and V10A series) was frequency modulated, and the signal radiation was frequency-swept over ranges of ~ 10 MHz at a rate of 50 Hz – 0.1 Hz. An initial survey of the spectrum was made on a Stark effect modulated (SEM) spectrometer [10] of conventional

design. The dipole determinations (section IV) were also carried out on this instrument. On both spectrometers signals were observed on the oscilloscope. Sample pressures ranged from 20–40 mTorr, and for most experiments the absorption cell was cooled to dry-ice temperature (200 K).

III. Assignment of Ground State Spectra and Identification of Rotameric Forms

a) Background Information

The predicted intramolecular barrier function for isobutyraldehyde is shown in Figure 1a. But if prediction and prejudices were cast aside, isobutyraldehyde could be expected to occur in either pair of the four rotameric conformations shown in Fig. 1b. Accordingly, rotational constants were computed with assumed structure parameters for dihedral angles between $\theta = 0$, where the oxygen atom eclipses the isopropyl hydrogen (*trans* form), and $\theta = 180^\circ$, where the two hydrogens eclipse each other (*cis* form). The results, which are plotted in Fig. 1c, show that the rotational constants do not change dramatically with the dihedral angle. The values of observed rotational constants alone are therefore not a very decisive criterion for the distinction between rotamers such as the *trans* configuration and the *gauche I* form (aldehydic hydrogen eclipsing a methyl group), or between the *gauche I* and *gauche II* conformation (oxygen eclipsing a methyl group). For this reason, the components of the dipole moment along the principal axes were computed for each of the four possible rotamers on the assumption of a total dipole moment of 2.6 D with its direction deviating from the $C=O$ bond by about 17° toward the $C-H$ bond [3, 4, 5]. The values obtained from this calculation are seen (bottom of Fig. 1c) to provide a more decisive distinction between the different rotamers than the rotational constants. Thus, the *cis* and *trans* conformers, in which μ_b is zero by symmetry, can be distinguished from each other by the relative size of the *a*- and *c*-components of the dipole moment, which would result in an intensity ratio between *a*- and *c*-type transitions of $\sim 30:1$ for the *trans* configuration, but of only $\sim 2:1$ for the *cis* form. Both *gauche* conformations would show *b*-type transitions at least 10 times weaker than the *a*-type lines which are the strongest transitions in all four conforma-

tions. But the *gauche II* form would also show *c*-type lines comparable in intensity with μ_b -lines, whereas no such transitions should be observable for the sterically most favored *gauche I* form.

b) Assignments

With the described background information about the spectra of the four possible rotamers, experimental work was started with a brief survey of the K-band spectrum (DRM pump range) in the SEM spectrometer. On the basis of intensities and resolved Stark effects, candidates for the transitions $2_{02}-3_{03}$, $2_{11}-3_{12}$ and $3_{13}-4_{14}$ were readily picked out for subsequent examination under DRM. The ensuing experiments, which are summarized in the double resonance map [7] of Fig. 2a and interpreted in Fig. 2b, yielded not only the expected *a*-type transitions (heavy dots in Fig. 2a, solid vertical arrows in Fig. 2b), which would occur in the same frequency areas for all four rotameric forms, but also three *b*-type transitions (small dots in Fig. 2a, dashed arrows in Fig. 2b) which could not occur for the *cis* or *trans* conformation. Most importantly, however, the DRM experiments also yielded two *c*-type transitions (small open circles in Fig. 2a, dash-dot arrows in Fig. 2b) of an intensity comparable with that of *b*-type lines.

These few initial DRM experiments thus yielded not only 11 interconnected transitions, which left no possible doubt on the assignment of the spectrum, but they also provided unequivocal proof in the *c*-type transitions that the assigned predominant rotamer is indeed the *gauche* conformation expected from the predicted potential barrier (Figure 1a).

During the subsequent detailed study of the ground state spectrum of the predominant rotamer, for which 85 transitions were measured with *J*-values up to $J = 29$, *a*-type R-branch transitions of the less stable *trans* conformer were assigned up to $J = 6$. Suspected $J = 2-3$ transitions were first used as pump lines to identify the connected $J = 3-4$ transitions, and these were subsequently used as pump transitions to find the $J = 4-5$ transitions. After the transition $5_{05}-6_{06}$ had been identified by the same method, it was used as (known) signal transition in a search for the Q-branch (pump) transitions $5_{05}-5_{24}$ and $6_{06}-6_{25}$. These two transitions helped to define the rotational constant *A* well

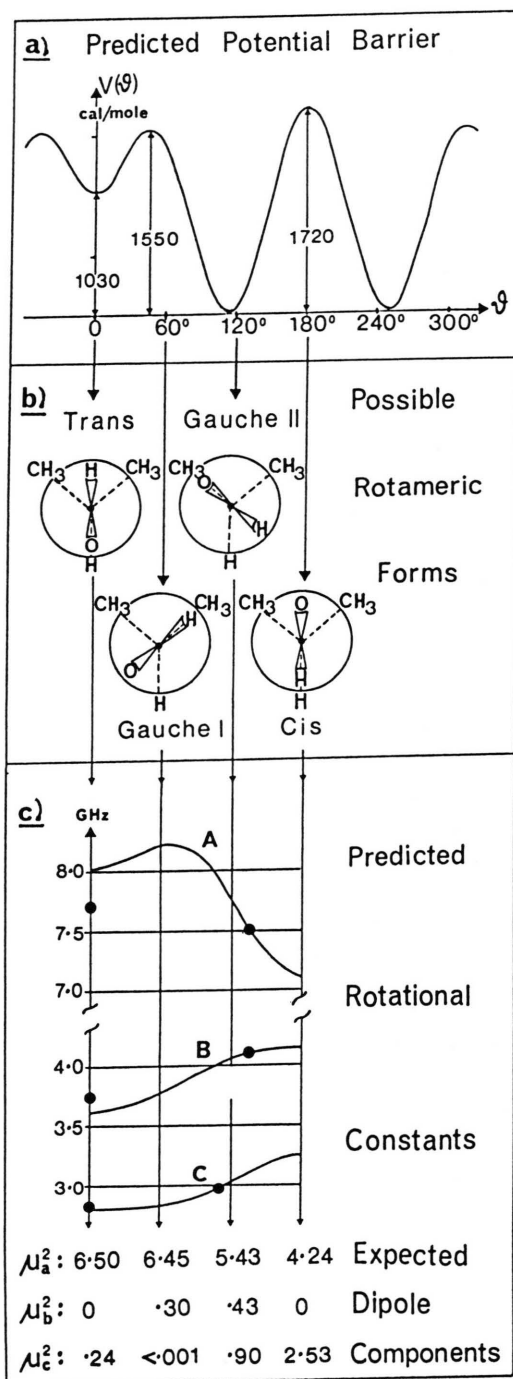


Fig. 1. Background information used for the assignment of the spectra and for the identification of the preferred *gauche* and the less stable *trans* rotamer of isobutyraldehyde.

Table I. Rotational and centrifugal distortion constants (with 3 σ -limits) and measured transitions of the *gauche*- and *trans*-conformation of isobutyraldehyde (isopropyl carboxaldehyde).

Rotational and distortion constants					
GAUCHE			TRANS		
$A = 7494.62 \pm 0.02$ MHz			$A = 7707.84 \pm 0.03$ MHz		
$B = 4107.51 \pm 0.02$ MHz			$B = 3736.63 \pm 0.02$ MHz		
$C = 2980.70 \pm 0.02$ MHz			$C = 2815.08 \pm 0.02$ MHz		
$\Delta_J = 1.90 \pm 0.45$ kHz			$\Delta_J = 0.67 \pm 0.40$ kHz		
$\Delta_{JK} = -0.25 \pm 0.23$ kHz			$\Delta_{JK} = 48.37 \pm 0.67$ kHz		
$\Delta_K = 11.20 \pm 0.71$ kHz			$\Delta_K = -19.11 \pm 4.35$ kHz		
$\delta_J = 0.28 \pm 0.02$ kHz			$\delta_J = 0.18 \pm 0.03$ kHz		
$\delta_K = 3.63 \pm 0.19$ kHz			$\delta_K = 25.00 \pm 0.46$ kHz		
Measured transitions (in MHz)			Measured transitions (in MHz)		
1 0 1 - 2 0 2	13938.86	7 2 6 - 7 3 5	25470.36	2 0 2 - 3 0 3	19106.26
1 1 1 - 2 1 2	13049.65	7 3 5 - 7 4 4	27972.44	2 1 2 - 3 1 3	18189.70
1 1 0 - 2 2 1	15303.16	7 3 4 - 7 4 3	23615.38	2 1 1 - 3 1 2	20939.88
2 0 2 - 3 0 3	20376.82	8 0 8 - 8 1 7	31757.84	2 2 1 - 3 2 2	19653.89
2 1 2 - 3 1 3	19438.75	8 1 7 - 8 2 6	22270.80	2 2 0 - 3 2 1	20202.52
2 1 1 - 3 1 2	22786.89	8 2 7 - 8 3 6	28379.01	2 0 2 - 3 2 1	38214.90
2 2 1 - 3 2 2	21264.62	8 3 6 - 8 4 5	28873.77	3 0 3 - 4 0 4	24948.46
2 2 0 - 3 2 1	22151.89	8 3 5 - 8 4 4	21612.35	3 1 3 - 4 1 4	24115.72
3 0 3 - 4 0 4	26425.50	9 1 8 - 9 2 7	27764.94	3 1 2 - 4 1 3	27718.88
3 1 3 - 4 1 4	25705.04	9 2 8 - 9 3 7	31831.90	3 2 2 - 4 2 3	26093.70
3 1 2 - 4 1 3	30025.15	9 3 7 - 9 4 6	30409.92	3 2 1 - 4 2 2	27350.70
3 2 2 - 4 2 3	28165.68	9 3 6 - 9 4 5	19971.60	4 0 4 - 5 0 5	30572.58
3 2 1 - 4 2 2	30088.82	9 4 5 - 9 5 4	31551.75	4 1 4 - 5 1 5	29958.36
4 0 4 - 5 0 5	32293.79	10 2 8 - 10 3 7	22431.10	4 1 3 - 5 1 4	34286.54
4 1 4 - 5 1 5	31859.04	10 3 8 - 10 4 7	32596.24	4 2 3 - 5 2 4	32440.65
4 1 3 - 5 1 4	36882.30	10 3 7 - 10 4 6	19364.45	4 2 2 - 5 2 3	34617.44
4 2 3 - 5 2 4	34914.60	10 4 6 - 10 5 5	29288.93	5 0 5 - 6 0 6	36114.91
4 0 4 - 4 2 3	18667.11	11 2 9 - 11 3 8	27732.81	5 1 5 - 6 1 6	35728.48
5 0 5 - 5 2 4	21288.10	11 3 8 - 11 4 7	20280.20	5 2 4 - 6 2 5	38677.37
7 0 7 - 7 2 6	28473.24	11 4 7 - 11 5 6	26786.31	5 0 5 - 5 2 4	21431.00
7 1 6 - 7 3 5	27188.85	12 3 9 - 12 4 8	22954.82	6 0 6 - 6 2 5	23993.50
8 0 8 - 8 2 7	32642.22	12 4 8 - 12 5 7	24733.00	7 1 7 - 7 1 6	23331.40
8 1 7 - 8 3 6	29263.25	13 4 10 - 13 5 9	39383.90	7 1 6 - 7 3 5	29491.21
16 5 12 - 16 5 11	27614.40	13 3 10 - 13 4 9	27324.03	9 0 9 - 9 2 8	34528.94
19 6 14 - 19 6 13	31300.62	13 4 9 - 13 5 8	23857.93	9 2 8 - 9 2 7	21582.20
22 7 16 - 22 7 15	34878.60	14 3 11 - 14 4 10	32966.03	12 3 10 - 12 3 9	23830.20
23 8 16 - 23 8 15	20248.00	14 5 9 - 14 6 8	31783.45	13 3 11 - 13 3 10	30085.90
25 9 17 - 25 9 16	14709.64	14 4 10 - 14 5 9	24686.44	14 4 11 - 14 4 10	18797.90
26 9 18 - 26 9 17	22386.20	15 4 11 - 15 5 10	27453.95	15 4 12 - 15 4 11	25190.74
29 10 20 - 29 10	24482.48	16 4 12 - 16 5 11	32059.37	17 5 13 - 17 5 12	19021.28
2 0 2 - 3 1 3	21936.52	17 5 12 - 17 6 11	28984.60	18 5 14 - 18 5 13	25792.82
2 1 1 - 3 2 2	31425.61	18 5 13 - 18 6 12	31840.76	20 6 15 - 20 6 14	18711.50
3 0 3 - 4 1 4	27264.69	19 6 13 - 19 7 12	32518.78	21 6 16 - 21 6 15	25751.62
3 1 3 - 4 0 4	24865.85	20 6 14 - 20 7 13	33196.32	24 7 18 - 24 7 17	25178.18
4 1 4 - 5 0 5	31454.51	23 7 16 - 23 8 15	37335.98	3 1 2 - 4 2 2	38669.60
5 1 5 - 5 2 4	20883.59	2 0 2 - 3 1 2	28665.20	5 2 4 - 5 3 2	23647.90
5 2 4 - 5 3 3	21530.91	2 1 1 - 3 2 1	32550.70	19 5 14 - 19 6 14	19072.90
6 0 6 - 6 1 5	21584.76	3 1 2 - 4 2 2	39852.80	22 6 16 - 22 7 16	24636.52
6 1 6 - 6 2 5	24446.10	6 3 3 - 6 4 3	25198.30		
6 2 5 - 6 3 4	23182.20	11 4 7 - 11 5 7	24633.74		
6 3 4 - 6 4 3	27452.62	17 6 11 - 17 7 11	33104.42		
6 3 3 - 6 4 2	25352.44	18 6 12 - 18 7 12	27148.20		
		28 9 19 - 28 10 19	28710.10		
Standard deviation: 76 kHz			Standard deviation: 97 kHz		

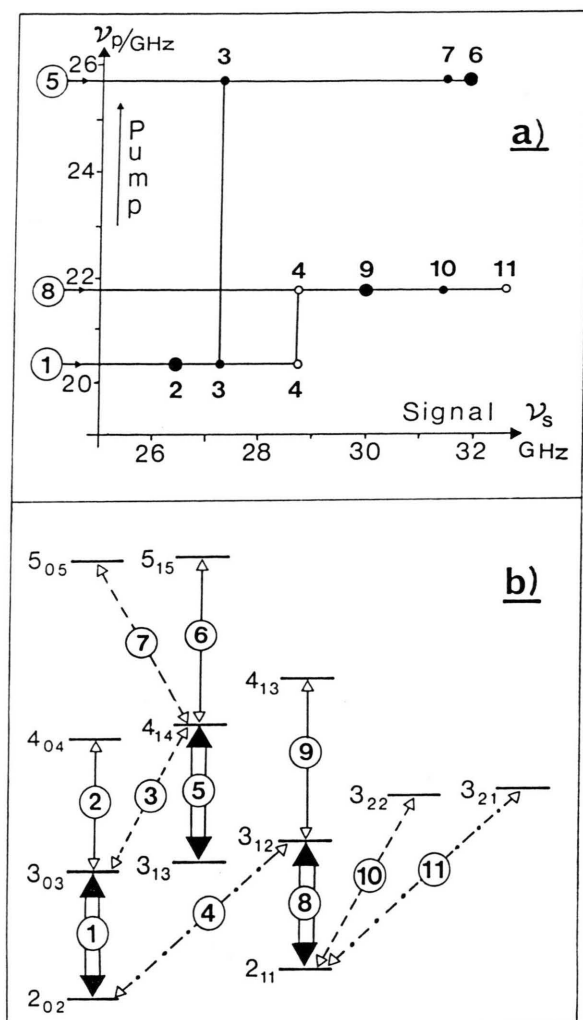


Fig. 2. a) Double resonance map illustrating the assignment of *gauche* isobutyraldehyde through the observation of *a*-type (large dots), *b*-type (small dots) and *c*-type (open circles) transitions. Different signals arising from the same pump transition are connected horizontally and identical signals produced with different pump frequencies are connected vertically. — b) Energy levels and transitions identified from the experiment summarized in a).

enough to allow identification of further Q-branch lines up to $J = 24$. The assignment of the *trans* conformer was completed with the observation under DRM of two weak *c*-type transitions with intensities ~ 50 times less than the *a*-type signals. This intensity ratio confirmed that the second rotamer was the expected *trans* conformation, since no other rotamer would have a comparable ratio between μ_a and μ_c (compare bottom of Figure 1c).

The deduced rotational constants are inserted as solid dots in Figure 1c. Accurate values of the rotational and distortion constants are listed together with observed transitions in Table 1.

IV. Dipole Moments

Quantitative values for the components of the dipole moments of *gauche* and *trans* isobutyraldehyde were derived from Stark effects in the usual way. This work was carried out primarily with a view to the subsequent determination of the energy difference between the two rotamers from a comparison of the intensities of their rotational absorptions. The Stark cell was calibrated against the $M = 0$ and $M = 1$ lobe of the $J = 1-2$ transition of OCS, for which a dipole moment of 0.71521 D has been determined by Muentert [11]. Stark coefficients were calculated by the method of Golden and Wilson [12]. The results of the dipole determinations are collected in Table 2.

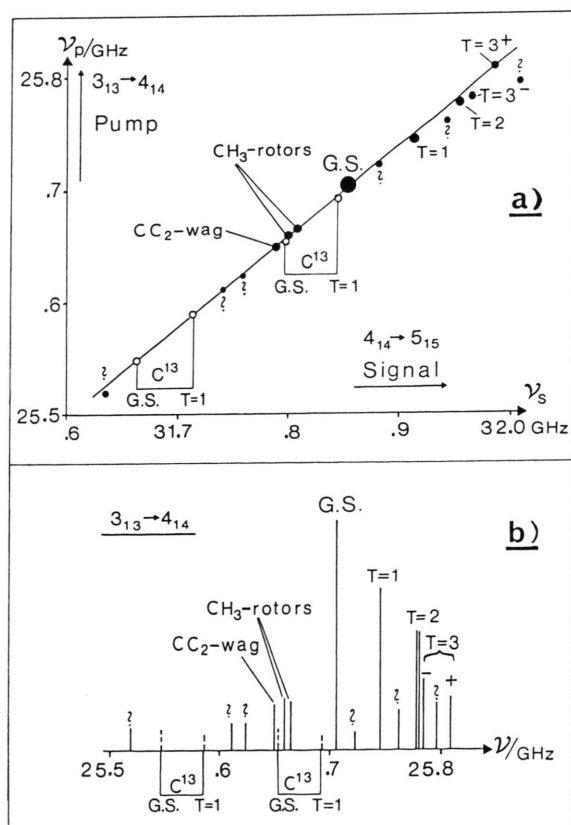
In conjunction with the structure data (part II), the dipole moment is found to lie in the plane of the aldehyde group and it deviates from the $C = 0$ direction towards the C—H bond by $12.3 \pm 2^\circ$ in the *gauche*-, and by $17.3 \pm 2^\circ$ in the less stable *trans* configuration. The magnitude of the moment of the *gauche* form (2.69 ± 0.03 D) agrees within experimental error with the dipole moments of acetaldehyde [3] (2.69 ± 0.03 D) and pivalaldehyde [5] (2.66 ± 0.04 D). Its variation (0.17 ± 0.06 D) between the *gauche* and the less stable *trans* conformation is the same as between *cis* and *gauche* propionyl fluoride [1] (0.19 ± 0.10 D), between *cis* and *gauche* fluoropropene [14] (0.17 ± 0.03 D), and between *gauche* and *trans* propyl fluoride [13] (0.15 ± 0.10 D), with the less stable rotamer always having the slightly larger dipole moment.

V. Vibrational Satellite Spectra

The DRM technique reveals readily (see Fig. 3a) that every *a*-type R-branch transition of the *gauche* conformation is accompanied by ~ 20 satellite lines. While some of these are due to C^{13} -forms, the majority arises from molecules in vibrationally excited states. The presence of these satellites adds considerably to the complexity of the overall spec-

Table 2. Stark effects in isobutyraldehyde.

Transition	$ M $	$\Delta\nu/E^2$		Dipole moment
		MHz $\times 10^6$ per (V/cm) ²		Debye units
		Calc.	Obs.	
<i>Gauche</i> -conformation				
$2_{12}-3_{13}$	1	12.223	12.05	$ \mu_a = 2.43 \pm 0.02$
$2_{02}-3_{03}$	2	18.767	19.20	
$2_{21}-3_{22}$	0	9.536	9.54	$ \mu_b = 0.80 \pm 0.03$
$2_{11}-3_{12}$	0	-1.070	-1.11	
	1	-10.567	-10.37	$ \mu_c = 0.83 \pm 0.02$
$3_{13}-4_{14}$	0	-1.318	-1.31	
	1	2.195	2.18	$ \mu_{\text{tot.}} = 2.69 \pm 0.03$
	2	12.734	12.63	
	3	30.298	30.44	
<i>Trans</i> -conformation				
$3_{13}-4_{14}$	0	-1.873	-1.88	$ \mu_a = 2.82 \pm 0.02$
	1	1.187	1.19	
	2	10.364	10.32	$ \mu_b = 0$ by symmetry
$3_{12}-4_{13}$	0	-1.683	-1.70	$ \mu_c = 0.46 \pm 0.03$
	1	-2.797	-2.80	
	2	-6.139	-6.14	$ \mu_{\text{tot.}} = 2.86 \pm 0.03$



trum, and the full analysis of every satellite spectrum would be very tedious.

On the high frequency side of the ground state transitions (see Fig. 3b) the first excited state of the torsion about the rotameric axis is readily identified by its large intensity. Effects due to tunnelling through the *gauche/gauche* barrier (see Fig. 1a) are not observable in this state, but the second excited state of this mode shows narrow doublets in its *a*- and *c*-type transitions. Wider doublets occur in the *b*-type transitions which connect the even and the odd component of this level. In the third excited state corresponding rotational transitions within the even and odd component are fully separated from each other, and the *b*-type inversion doublets reach separations of up to 100 MHz.

On the low-frequency side three satellites with about 15–20% of the ground state intensity are prominent. Examination of the Q-branch transitions associated with these satellites reveals doublets for

Fig. 3. a) Double resonance map showing the position of vibrational satellites and C^{13} isotopes of the transition $3_{13}-4_{14}-5_{15}$ (connection 5/6 of Fig. 2a) of *gauche* isobutyraldehyde. b) Vibrational satellites of the pump transition $3_{13}-4_{14}$ as deduced from a) in traditional presentation.

Table III. Rotational and distortion constants (with 3 σ -limits) of excited vibration states of *gauche* and *trans* isobutyraldehyde (isopropyl carboxaldehyde)

Vibrational mode:		Asymmetric torsion about C ^{isobut.} - C ^{ald.} <i>Gauche</i> -conformation			CH ₃ internal rotation		CC ₂ - wag
M.W. i.r. ^{d)}	designation	$T = 1$ $\nu_{33} = 1$	$T = 2^a)$ $\nu_{33} = 2$	$T = 3^a)$ $\nu_{33} = 3$	$IR3^{b,c)} = 1$ $\nu_{32} = 1$	$IR4^c) = 1$ $\nu_{19} = 1$	$CC2 = 1$ $\nu_{18} = 1$
Transitions measured		26 R & 55 Q	21 R & 3 Q	19 R & 3 Q	11 R & 40 Q	11 R & 29 Q	11 R & 22 Q
Range of J -values		1-6 & 4-29	1-6 & 5-14	1-6 & 3-5	2-5 & 8-29	2-5 & 8-29	2-4 & 10-29
Standard dev. in MHz		0.08	0.07	0.17	0.11	0.13	0.12
A B C	in MHz	7478.33±0.02	7467.18±0.06	7461.50±0.18	7485.11±0.02	7489.97±0.03	7500.01±0.03
		4110.33±0.02	4111.25±0.02	4109.73±0.06	4102.74±0.03	4101.99±0.02	4104.05±0.02
		2986.60±0.02	2991.30±0.02	2994.46±0.08	2975.64±0.02	2974.62±0.02	2972.84±0.02
Δ_J Δ_{JK} Δ_K δ_J δ_K	in kHz	1.75±0.33	1.89 ^{e)}	1.89	1.89	1.89	1.89
		-0.6 ±0.2	-0.25	-0.25	-0.25	-0.25	-0.25
		11.9 ±0.9	7.3 ±5.4	8.0 ±2.1	11.7 ±0.4	10.8 ±0.5	11.2 ±0.7
		0.30±0.02	-0.03±0.02	0.6 ±0.6	0.28±0.01	0.29±0.01	0.28±0.01
		3.8 ±0.2	6.6 ±2.0	-5.8 ±12	3.7 ±0.1	3.5 ±0.2	3.7 ±0.2
<i>Trans</i> -conformation							
M.W. i.r. ^{d)}	designation	$T = 1$ $\nu'_{33} = 1$	$T = 2$ $\nu'_{33} = 2$	$T = 3$ $\nu'_{33} = 3$	$IR3/4 = 1^f)$		$CC2 = 1^f)$ $\nu'_{18} = 1$
Transitions measured		16 R & 6 Q	16 R & 4 Q	14 R & 4 Q	8 R		8 R
Range of J -values		2-6 & 5-9	2-6 & 5-7	2-6 & 5-7	2-5		2-5
Standard dev. in MHz		0.19	0.19	0.25	0.11		0.13
A B C	in MHz	7713.8 ±0.3	7717.2 ±0.3	7718.0 ±0.4	7694.0 ±1.6		7698.1 ±1.8
		3767.06±0.04	3798.43±0.07	3835.07±0.09	3737.53±0.08		3734.42±0.09
		2818.23±0.03	2820.74±0.07	2824.03±0.10	2813.26±0.06		2812.87±0.06
Δ_J Δ_{JK} Δ_K δ_J δ_K	in kHz	0.67 ^{e)}	0.67	0.67	0.67		0.67
		59.8 ±4.5	50.5 ±5.1	80.7 ±9.1	48.4		48.4
		-19.1	-19.1	-19.1	-19.1		-19.1
		-0.9 ±0.2	-0.3 ±0.6	-1.4 ±0.9	0.18		0.18
		13.0 ±2.5	27.3 ±7.8	39.5 ±11.1	25.0		25.0

a) Constants derived from center frequencies of selected a- and c-type doublets.

b) $IR3$ refers to the methyl group eclipsed by the oxygen atom.

c) Constants derived from center frequencies of A/E doublets

d) Assignment by J.R. Durig, G.A. Guirgis and T.S. Little (private communication).

e) Distortion constants without error limits were held fixed in the fit of the spectrum

f) Vibrational assignment tentative

the two stronger spectra, while the third spectrum consists of singlets throughout. According to our analysis, the spectrum nearest to the ground state arises from molecules in which the CH₃ internal rotor which eclipses the oxygen atom is excited by one quantum ($IR3 = \nu_{32} = 1$), and the second dou-

blet spectrum must therefore arise from excitation of the other CH₃ internal rotor ($IR4 = \nu_{19} = 1$). On account of its relative intensity the singlet spectrum can now be correlated with the CC₂ wagging motion ($\nu_{18} = 1 = 273\text{ cm}^{-1}$), as proposed by Durig and collaborators [9].

Since the sensitivity of the DRM spectrometer is sufficient to detect the spectra of C^{13} species and their first torsionally excited states in natural abundance, it follows that vibrational satellites due to all normal modes below $\sim 600\text{ cm}^{-1}$ are detectable in the pure rotation spectrum. Such vibrations are associated with the twisting, bending and deformation of the heavy-atom skeleton, and this most likely accounts for the remaining vibrational satellites observed. A correlation of these weak satellites with particular vibrations has not been attempted, however.

A similar satellite pattern to that of Fig. 3 is also exhibited by the R-branch lines of the *trans* conformer. Three torsionally excited states are observed on the high-frequency side and two satellites, which are likely to correspond to internal rotation and CC_2 wagging, are easily detected on the low-frequency side of the ground state transitions, amongst many less intense satellites.

Details of the analysis of the second and third torsionally excited state and of the CH_3 internal rotors of the *gauche* conformation will be combined with the complementary information from i.r. spectroscopy in the final part of this work. Rotational constants of the satellite spectra which have been studied by microwave techniques are collected in Table 3. This table also gives information about the number and type of transitions which have been measured in each case, but individual frequency tables are not reproduced here. These may be obtained from the author.

VI. Discussion

The conformational analysis reported here confirms the correctness of the prediction of preferred rotameric conformations of the compounds

$(CH_3)_2CHCOX$ for the case of isobutyraldehyde ($X=H$). Analogous results have also been obtained [6] for isobutyryl fluoride ($X=F$). Isobutyric acid ($X=OH$) also exists predominantly in the *gauche* conformation with one methyl group eclipsing the carbonyl oxygen [6]. These results lend support to the validity of the proposed method [1] for constructing potential barriers from those of simpler compounds. Since our method did not involve assumptions about the nature of the forces which give rise to potential barriers and conformational energy differences, the idea originally advanced [1], and verified here, should remain of some use for anticipating the relative stability of rotameric forms irrespective of future interpretations of the underlying forces.

The assignment procedure of section III might merit brief attention: As the size of molecules and their conformational possibilities increase the rotational constants generally tend to become less decisive indicators of the molecular configuration, and additional information such as the dipole components has to be utilized to distinguish between the various rotameric forms. In the absence of DRM techniques this would have been a laborious task in the present case since transitions due to the small *b*- and *c*-component would have been difficult to identify in this rich spectrum. All these difficulties were by-passed by 'stringing together' through DRM a series of transitions (Fig. 2b) which defined not only all three rotational constants, but which also defined the rotameric conformation through the relative size of *b*- and *c*-type transitions. We have used the same approach for the rapid conformational analysis of isobutyryl fluoride, and a later example of this method for the quick assignment of a difficult spectrum has been described for 2,6-difluoropyridine [15].

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