Far-Infrared Spectrum, ab Initio Calculations, Conformational Energy Differences, Barriers to Internal Rotation, and r_0 Structure of Propanal[†]

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The far-infrared spectrum has been recorded from 50 to 360 cm^{-1} at a resolution of 0.10 cm^{-1} for normal propanal CH_3CH_2CHO and for the three isotopic species CH_3CH_2CDO, CH_3CD_2CHO, and CD_3CD_2CHO. Along with the fundamental asymmetric torsional transition, several hot band transitions of the cis conformer have been observed and assigned for each isotopic species. The geometrical structures of the cis and gauche conformers have been determined by ab initio calculations in order to compare them with previously reported microwave structures and to calculate inertial constants for the two internal rotations. A wide range of basis sets and ab initio theoretical methods up to MP4 have been used in order to determine the cis to gauche conformational energy difference. Using both the observed and calculated data, along with the previously reported gauche dihedral angle and microwave splittings for the gauche ground state for the CH_3CH_2CHO and CH_3CH_2CDO molecules, the asymmetric torsional potential function has been redetermined, from which the following constants have been obtained: $V_1 = 125 \pm 15$, $V_2 = 365 \pm 17$, $V_3 = 456 \pm 20$, and $V_6 = -14 \pm 10$ cm^{-1}. From this potential function, values of 787 ± 20, 237 ± 12, and 442 ± 20 cm^{-1} were obtained for the cis to gauche, gauche to gauche, and gauche to cis barriers, respectively, while the enthalpy difference was constrained to 320 cm^{-1}. The fundamental and a few other excited-state methyl torsional transitions have been observed for both the cis and gauche conformers for all four isotopic species, and 3-fold barriers to internal rotation of 1084 ± 40 cm^{-1} (3.10 ± 0.11 kcal/mol) for the cis conformer and 790 ± 56 cm^{-1} (2.26 ± 0.16 kcal/mol) for the gauche conformer have been determined. The value for the cis conformer differs significantly from the value reported from microwave splitting data.

Introduction

More than 30 years ago, it was shown by Butcher and Wilson using microwave spectroscopy[1] that propanal exists in the gas phase in two stable conformers. The conformer with all four heavy atoms coplanar, called cis (also known as synplanar), was shown to be significantly lower in energy than the other conformer with a dihedral angle of ≈131°, which along with the original authors we are calling gauche (also known as anticlinal). Before then there were indications from proton NMR spectroscopy[2] that propanal existed in two forms in the liquid phase. Since these early reports, the spectrum of propanal has been the subject of numerous studies by various types of spectroscopic and computational techniques.[3−16]

Most of these studies have been addressed, at least in part, to the determination of the energy separation of the cis and gauche conformers. In the original microwave study,[1] the enthalpy difference was determined from relative intensities of microwave lines to be 315 ± 35 cm^{-1}. In an infrared study,[3] an enthalpy difference of 360 ± 45 cm^{-1} was obtained from the temperature dependence of the intensities of conformer bands at 660 and 517 cm^{-1} in the liquid phase. The infrared and Raman spectra[4] of propanal-d_0, -d_1, and -d_2 in the gaseous, liquid, and solid phases were assigned on the basis of propanal possessing two stable conformers, where some bands were assigned as resulting from the gauche conformer as they disappeared at low temperature. For the same vibrational frequencies as in the infrared study[3] of the temperature dependence of intensities, a corresponding study of Raman bands,[5] again in the liquid phase, led to an enthalpy difference of about 420 cm^{-1} (1.20 kcal/mol).

In a second gas-phase microwave study[6] the spectrum of the gauche conformer of CH_3CH_2CHO was studied in detail, and from measurements of splittings of microwave lines it was shown that the lowest asymmetric torsional levels of 0^- and 0^+ of the gauche conformer were split by 471.8 MHz and that the gauche torsional angle was 122.5°. A potential function for the asymmetric torsion was given which was determined from these measurements and the enthalpy difference of Butcher and Wilson.

In a previous study[7] by one of the current authors, the far-infrared spectrum of normal propanal, CH_3CH_2CHO, was recorded and assignment made of torsional transitions of the methyl internal top and of the asymmetric rotor (ethyl group or CHO group depending on which part of the molecule is regarded as stationary). From a fitted asymmetric torsional energy function with four V_n constants, the enthalpy difference between cis and gauche was deduced to be 240 ± 45 cm^{-1} on the basis of a particular assignment of bands. However, the assignment for normal propanal was difficult because of unexpected band separations and intensities. It was hoped that a further far-infrared study involving some deuterated isotopic propanal species might give sufficient further asymmetric torsional transition data to lead to a more definite potential energy function governing the conformational interchange.

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Since that initial report of the far-infrared spectrum,[7] spectroscopic studies of microwave line splittings due to torsional−rotation interaction have determined values for both kinetic and potential energy parameters for methyl torsion in both cis and gauche forms.[8,9] It was found that the barrier to methyl torsion in the gauche form (886 ± 10 cm^{-1}) is greater than in the cis form (768 ± 8 cm^{-1}). Another microwave report[10] gives a methyl barrier for cis propanal not greatly different at 784 cm^{-1}. Since these barriers are rather different from those previously reported,[7] a further study of the far-infrared spectrum is required.

From the microwave spectra of isotopically substituted species,[11] a complete r_s structure of the cis conformer has been determined by Kraitchman's method. For the gauche conformer, only the heavy atom structural parameters have been obtained but they are sufficient to yield a more accurate skeletal torsional CCCO angle of 128.8°. The gauche spectrum was difficult to assign, but the torsional splitting of the lowest asymmetric torsional levels of 0^- and 0^+ has been determined for propanal and two isotopomers.[12] From the relative intensity comparison of the gauche lines in the microwave spectrum with a cis line,[12] the enthalpy difference has been calculated to be 420 ± 27 cm^{-1}. Employing both the gauche splitting and this ΔH value along with all of the previous assignments of the asymmetric torsional transitions from the far-infrared spectrum,[7] Randell et al.[12] have produced a torsional potential energy function for conformational interchange. The fitted function is inadequate in two essential features i.e., the enthalpy difference ΔH between the zero-point levels of the two conformers does not correspond to the value obtained by the intensity comparisons of microwave lines, and the angle of the minimum for the gauche conformer is 8° larger than that obtained from the microwave determination of the structural parameters.

The present study is primarily concerned with the far-infrared spectra of CH_3CH_2CHO (propanal-d_0) and three of its isotopomers CH_3CH_2CDO (d_1), CH_3CD_2CHO (d_2), and CD_3CD_2CHO (d_5). A preliminary report has been published[13] but a significant change in the assignment of the asymmetric torsional transitions is proposed based on ab initio calculations.

A number of ab initio electronic structure calculations have been reported but only those related to conformation energy differences and torsional potential energy functions are relevant, so attention is being drawn to the more recent reports by Wiberg et al.[14−16] Barriers to internal rotation of methyl groups adjacent to double bonds are readily obtained with no great variation with different basis sets and "levels of theory", and in general, the values are in good agreement with experimental values. However, for asymmetric internal rotation of groups adjacent to double bonds there is considerable variation in energy differences. In the case of propanal, ab initio calculations have given high-energy differences, ΔE, of similar magnitude to the ΔH quoted above. Indeed with the 6-31G(d) basis set, the higher the level of theory used for the calculation, the higher the value of ΔE obtained: 402 cm^{-1} from Hartree−Fock calculations, 485 cm^{-1} from second-order Møller−Plesset (MP2) calculations, and 498 cm^{-1} from MP3 calculations. These values appear to support the higher value of the enthalpy difference found be Randell et al.[12] In a recent report of the electronic spectrum of propanal,[17] electronic structure calculations made at a similar level to those of Wiberg et al.[14−16] support these values.

As well as the new far-infrared spectra, new results from ab initio calculations are now reported with a wide range of basis sets constructed from both Pople types and Dunning−Huzinaga types of functions. This range of ab initio calculation has been pursued in order to achieve some convergence toward a value of ΔE in agreement among the different procedures.

It is usual to treat molecules such as propanal with two internal rotors as if the two torsional vibrational modes are independent of each other so that a potential energy function is determined from spectra or by ab initio calculation for each mode separately. Only in the case of two identical internal rotors, for example, two methyl groups in acetone,[18−20] has it been shown to be necessary to use a two-dimensional treatment because of the relatively large top−top coupling constants. In the present study, the approximately symmetric methyl torsion and the asymmetric torsion (ethyl torsion or CHO torsion) have been treated as one-dimensional torsional motions except that the methyl torsional kinetic constant for the gauche conformer is allowed to be different from that for the cis rotamer. However, it turns out in this model that the potential energy functions for the different isotopomers are not identical as expected in the independent approximation.

Experimental and Theoretical Methods

The sample of CH_3CH_2CHO was purchased from Aldrich Chemical Co., Inc., Milwaukee, WS. The samples of CH_3CH_2CDO, CH_3CD_2CHO, and CD_3CD_2CHO were obtained from Merck Chemical Co., St. Louis, MO. Purification was carried out by means of a low-temperature, low-pressure fractionation column.

The far-infrared spectra of the gases were recorded using a 1 m cell fitted with polyethylene windows. These data were collected on 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 μm Mylar beam splitter and transformed with a boxcar truncation function.

The Raman spectra of propanal-d_0 were recorded with a Cary model 82 spectrophotometer equipped with a Spectra-Physics model 171 argon ion laser on the 5145 Å line. The spectrum of the gas was recorded using a standard Cary multipass accessory and a laser power of 2 W. The temperature study in this phase was performed by applying a heat gun to the sample cell. The spectrum of the liquid was recorded with the sample contained in a sealed capillary, and the spectrum of the solid was obtained using a Miller−Harney cell.[21]

Most of the electronic structure calculations were made with the Gaussian 92 program[22] but some of the larger calculations were made with the more recent version Gaussian 94. Many calculations were made at the restricted Hartree−Fock (given as HF) level or used the Møller−Plesset method to second-order (MP2), but a few calculations used the method to higher order (MP3, MP4). Since large basis set effects are seen, a range of calculations were made with the conventional split-valence 6-31G basis set augmented by various amounts of polarization functions and diffuse functions. Nearly as many calculations were made with the double-ζ (DZ) basis set of Dunning[23] also augmented by polarization functions. Finally, the most extended fundamental sp basis set used was the triple-ζ (TZ) basis of Dunning,[24] which can be written as (10s6p;5s)/[5s3p;3s], and it was extended with two sets of d polarization functions on C and O and one set of p functions on H.

For all basis sets and calculation methods and for all conformers, the geometric structure was fully optimized, but geometric structure parameters are reported only for cis and gauche conformers obtained with only a few methods. Only for the cis and trans conformers was the molecule constrained

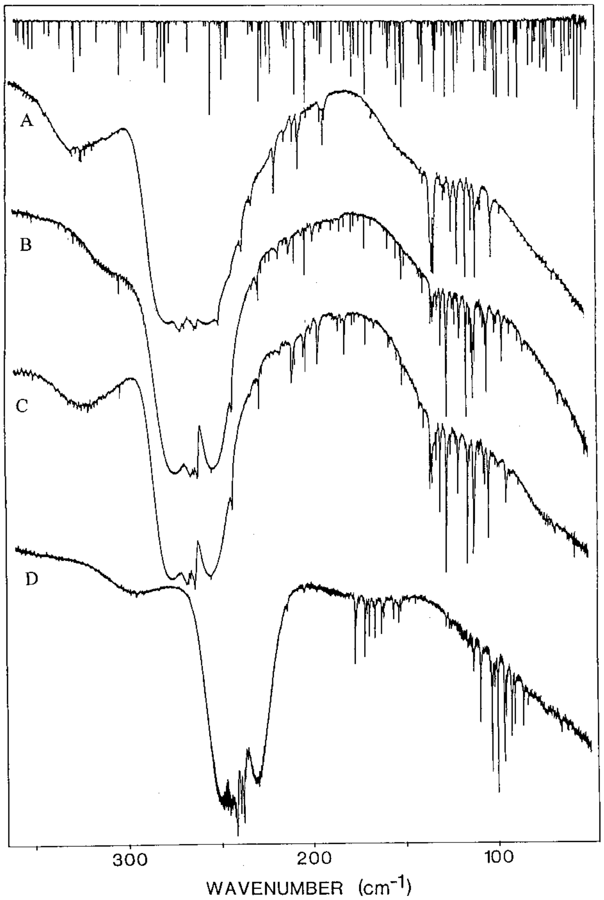

Figure 1. (A) Far-infrared spectrum of propanal-d_0; (B) far-infrared spectrum of propanal-d_1; (C) far-infrared spectrum of propanal-d_2; (D) far-infrared spectrum of propanal-d_5. Top spectrum is that of water vapor.

to C_s symmetry in order to separate in-plane and out-of-plane modes in the frequency calculations.

Results

The far-infrared spectra of propanal-d_0, -d_1, -d_2, and -d_5 recorded between 380 and 50 cm^{-1} are shown in Figure 1. The frequency measurements of all significant bands are given in Table 1. In descending frequency, the far-infrared regions of the spectra each divide conveniently into three sections corresponding to skeletal bending bands, methyl torsional transitions, and asymmetric torsional transitions. In the far-infrared spectrum of the parent molecule (Figure 1A), the strongest band with a Q peak at 264 cm^{-1} is assigned to the CCC bending frequency ν_{15} of the cis conformer as indicated in Table 1 and in agreement with ab initio calculations of vibrational frequencies with the MP2/DZ(d) method. The corresponding band of the gauche conformer is assigned to the much weaker, broad band observed at 324 cm^{-1}. A series of Q peaks between 220 and 194 cm^{-1} are assigned to the methyl torsions, and the series of bands between 135 and 100 cm^{-1} are assigned to the asymmetric (ethyl) torsional mode. It is expected that torsional transitions of both the cis and gauche conformers should be present, and some assignments are given in Table 1 in anticipation of the discussion below.

The far-infrared spectrum of gaseous propanal-d_1 is shown in Figure 1B. The CCC bending vibration of the cis conformer is assigned as the strong band with Q peak at 265 cm^{-1} whereas the shoulder with some partly resolved rotational structure at 315 cm^{-1} is assigned to CCC bend of the gauche conformer. The rotational K structure interval ($A - [B + C]/2$) of approximately 1.3 cm^{-1} is consistent with the structural parameters of the gauche conformer[11] but not with those of the cis rotamer. The methyl torsions are observed between 212 and 184 cm^{-1} and the asymmetric torsions between 130 and 85 cm^{-1}. The far-infrared spectrum of the d_2 compound (Figure 1C) is very similar to that of the d_1 molecule except that the vibrational band assigned to the broad band centered at 320 cm^{-1} to the CCC bend of the gauche conformer is more pronounced. In fact, the spectrum of the d_2 molecule in the asymmetric torsional region is nearly the same as that for the d_1 compound, and it is difficult to distinguish between the two except for the very small differences in the observed frequencies.

In the infrared spectrum of gaseous propanal-d_5 (Figure 1D), the three sections of the spectrum are well-separated because of the mass changes of the methyl and methylene groups. The Q branch on the very strong band at 238 cm^{-1} is assigned to the CCC skeletal bending frequency ν_{15} of the cis conformer. In each of the isotopomer spectra, there are three or more Q branches on each of these strong bands, and it is assumed that some of them are hot bands involving other low-frequency modes. In propanal-d_5, the methyl torsional transitions are between 177 and 153 cm^{-1} and the asymmetric torsional transition and accompanying "hot bands" between 128 and 86 cm^{-1}. The approximate intensities given in Table 1 are only locally relative, i.e., a band in the methyl torsion region marked as strong (s) may be only strong relative to other bands in this region of the far-infrared spectrum.

From the analysis of the Raman spectra of propanal-d_0 in the gas, liquid, and annealed solid states, the identification of a conformer pair is made at 849 and 871 cm^{-1}. These vibrational bands which are assigned to the CCC symmetric stretching mode ν_{13} are observed in the gas and liquid. However, the Raman line at 871 cm^{-1} is not present in the spectrum of the solid. From ab initio calculations and previous studies, the cis conformer has been determined to be the thermodynamically preferred conformer and the only conformer present in the annealed solid state. Hence, the Raman line at 871 cm^{-1} is assigned to the CCC symmetric stretch ν_{13} of the gauche conformer.

The enthalpy difference between the cis and gauche conformers in the gas phase can be found by measuring the temperature dependence of the Raman lines at 849 and 871 cm^{-1}. From the equation $\ln K = -\Delta H/RT + \Delta S/R$, the enthalpy difference between the two conformers can be calculated under the assumption that ΔH and ΔS are invariant with temperature. In this case, $K = I_{871}/I_{849}$ where I_{849} is the intensity of the Raman line at 849 cm^{-1} for the cis conformer and I_{871} is the intensity of the Raman line at 871 cm^{-1} for the gauche conformer. The plot of the data listed in Table 2 is shown in Figure 2. The best fit of the data gives an enthalpy difference of 249 ± 27 cm^{-1}. This value should be compared to previously reported values, where the enthalpy difference in the gas phase has been reported in the range from a low value[7] of 240 cm^{-1} to a high value[12] of 420 cm^{-1}. This experimental value may be low particularly when one compares the value to that obtained for 2-methylpropanal,[25] a similar molecule. The enthalpy difference between the gauche (one methyl group eclipsing the oxygen) and trans (the secondary hydrogen eclipsing the oxygen) conformers of 2-methylpropanal[25] has been measured as 248 ± 35 cm^{-1} in the gas phase by the same method. However, as in propanal,[3,5] the enthalpy difference appears to be higher at 440 ± 17 cm^{-1} in the liquid phase[26] and ab initio calculations support a larger value. Therefore, the ΔH value for propanal in the liquid state should be considered as the lower limit for

TABLE 1: Observed Transitions[a] in the Far-Infrared Spectra of Propanal-d_0, -d_1, -d_2, and -d_5 in cm^{-1}

assignment[b]		CH_3CH_2CHO		CH_3CH_2CDO		CH_3CD_2CHO		CD_3CD_2CHO	
g	ν_{15}	324	w, br	315	w, br	320	w, br	300	w, br
		271.43	vs, Q	265.36	vs, Q	266.19	vs, Q	241.80	vs, Q
		269.39	s, Q	263.50	s, Q	264.99	s, Q	239.62	s, Q
c	ν_{15}	264.13	vvs, Q	261.68	vvs, Q	262.55	vvs, Q	237.88	vvs, Q
		262.49	s, h						
c	2 ← 0 asym			242.58	w, h	242.55	w, h	213.40	w, h
		250.69	m, h	231.35	vw	232.62	vw		
		244.18	m						
c	3 ← 1 asym			228.32	w, h	228.10	vw, h	204.30	vw, h
		237.91	w, h						
c	4 ← 2 asym	232.15	w, h	217.13	w, h	216.40	vw, h	197.40	vvw
c	1 ← 0 Me	219.90	s	211.53	m	210.20	s	177.12	s
								176.27	m
								174.96	w
								171.78	s
		210.21	w	204.65	w	203.82	w	170.34	w
				201.41	vw	200.02	vw	169.28	m
c	2 ← 1 Me	207.44	s	198.51	m	196.23	s	166.33	m
								162.71	m
		195.28	w					161.45	mw
c	3 ← 2 Me	192.56	w	186.92	w	185.19	w	156.05	m
						183.45	vw		
g	1 ← 0 Me	193.69	m	183.73	w	181.64	ms	153.40	ms
g	2 ← 1 Me					165.70	vw		
c	$\nu_{15} - \nu_{24}$			134.79	w	135.53	w	128.00	vw
				133.69	w	134.37	w	126.15	vw
				133.13	vw	133.58	w	125.15	vw
				131.26	w				
				129.44	m			113.06	w
c	1 ← 0 asym	135.13	vs	126.43	vs	126.79	vs	109.61	m
				123.11	w	124.49	w		
				119.42	m	120.37	m		
c	2 ← 1 asym	133.83	s	115.88	vs	115.40	s	103.53	s
		128.19	w	113.91	w	113.91	w	101.79	w
		124.10	m	113.05	m				
c	3 ← 2 asym	121.13	ms	112.25	s	112.15	s	100.40	vs
		116.46	s			111.85	s		
		113.96	w	107.88	w	111.40	ms	96.86	s
		113.09	m	106.77	w	109.12	vw		
				105.47	mw	106.82	w		
c	4 ← 3 asym	110.73	ms	104.80	s	104.15	s	95.74	m
		108.06	w	99.55	vw	98.14	vw	92.99	m
		107.76	w					91.18	m
		102.33	w						
c	5 ← 4 asym	101.58	m	96.43	m	94.56	mw	86.60	mw
		96.59	vw					84.07	vw
c	6 ← 5 asym			85.15	vw				

[a] Approximate intensities are given in range vvs, vs, s, ms, m, mw, w, vw, vvw; br = broad, h = head with low-frequency edge. [b] Most of the strong features in the spectrum are given assignments in other tables.

TABLE 2: Variation of the Intensity Ratio of Raman Lines of Propanal at 849 and 871 cm^{-1} over a Range of Temperature

T (°C)	$10^3/T$(K)	$K = I_{871}/I_{849}$	ln K
55	3.05	0.0621	−2.78
49	3.10	0.0610	−2.80
44	3.15	0.0606	−2.80
38	3.21	0.0588	−2.83
27	3.33	0.0562	−2.88

the vapor, and the value obtained from this Raman investigation of the vapor probably has a larger uncertainty than the statistical value.

The energy results of a large range of ab initio electronic structure calculations are summarized in Table 3. The lowest conformer is always cis ($\tau = 0°$, where τ is the torsional angle of the ethyl group relative to the CHO group, dihedral $OC_1C_2C_3$) with the methyl staggered ($\phi_1 = 180°$) and so is labeled Cs; the energies of Cs are given in atomic units (E_h). The energies of other conformations are given as an energy difference with respect to the lowest conformer in order to obtain important points on the potential energy surface for the ethyl torsion and for the methyl torsion of the cis species. Only the energy of the gauche ($\tau \approx 120°$) eclipsed methyl ($\phi_1 \approx 0°$) conformer (Ge) is given relative to gauche staggered methyl (Gs) form.

The energy difference ΔE between the gauche and cis conformers, both with the methyl group staggered, is the focus of interest herein. With the fundamental basis set 6-31G, the energy difference is 357 cm^{-1}, and on adding polarization functions it rises a little to about 400 cm^{-1}. With inclusion of correlation energy to any MP level, the energy difference rises even more to 480 cm^{-1}. This might appear to give confirmation to the high value of ΔH of 420 cm^{-1} deduced from microwave intensities. These values of ΔE are near to those of Wiberg and Martin[14] except that their geometries were not fully optimized, which also is true for those of Metha et al.[17] However, with the fundamental basis set DZ, despite the HF energy differences being remarkably low, the value of ΔE is notably consistent at 290−320 cm^{-1} for all MP calculations.

TABLE 3: Ab Initio Energies[a] (in E_h) and Energy Differences between Conformers[b] (in cm^{-1}) for Propanal

	E	Δ*E*				
	Cs	Gs	Bs	Ts	Ce	Ge
HF/6-31G	1.863 152 3	356.67	692.68	513.83	822.28	938.66
HF/6-31Gd	1.952 268 3	397.95	729.92	624.71	930.17	1007.45
HF/6-31Gdp	1.961 897 4	408.63				
HF/6-311G	1.907 004 9	287.21				
HF/6-31+Gd	1.867 716 8	227.45				
MP2full/6-31Gd	2.530 916 5	486.36	736.05	728.92		
MP2/6-31Gd[c]	2.511 460 9	480.79				
MP3/6-31Gd[c]	2.536 573 4	482.36				
MP2/6-31Gdp	2.561 928 0	479.75	733.60	727.47		
MP2/6-311Gd	2.594 470 2	459.60				
MP2/6-31+Gd	2.525 752 1	303.84	572.95	553.19	875.96	951.42
MP2/6-31+Gdp	2.572 944 2	314.09				
MP2/6-311+Gdp[d]	2.645 325 5	302.45				
HF/DZ	1.892 853 4	127.75	600.00	388.96	795.17	1003.78
HF/DZdp	1.997 639 7	245.42				
MP2full/DZd	2.595 071 5	288.36	660.13	586.05	847.81	986.82
MP2/DZd[e]	2.537 180 8	284.42	653.62	580.26		
MP2/DZ+d[e]	2.547 651 8	267.09	550.24	596.93		
MP2/DZdp[e]	2.587 661 8	299.07	676.44	594.70	837.23	977.50
MP3/DZdp[e]	2.615 318 5	320.48				
MP4/DZdp[e]	2.645 976 2	303.04				
MP2/TZdp[f]	2.693 301 2	299.31				

[a] Energy of cis conformer given as $-(E + 190)E_h$. All MP calculations are frozen core unless otherwise indicated as full. All geometries 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. Δ*E* is given relative to Cs except for Ge which is relative to Gs. [c] At geometries of corresponding HF. [d] At geometries of MP2/6-31Gdp. [e] At geometries of MP2full/DZd. [f] Conformers fully optimized with a polarized triple-ζ basis TZ(2d,p).

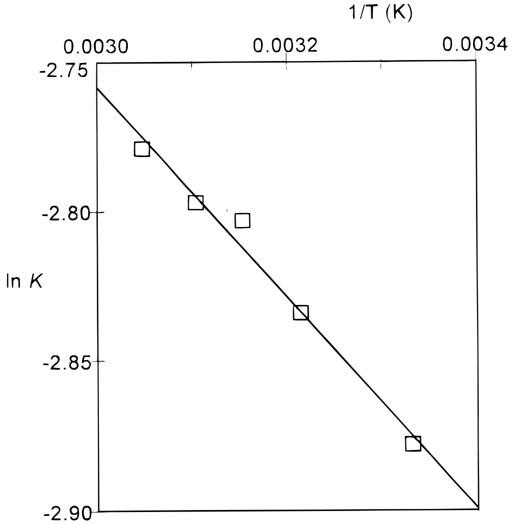

Figure 2. Temperature dependence of the ratio of the gauche conformer to the cis conformer of propanal in the gas phase.

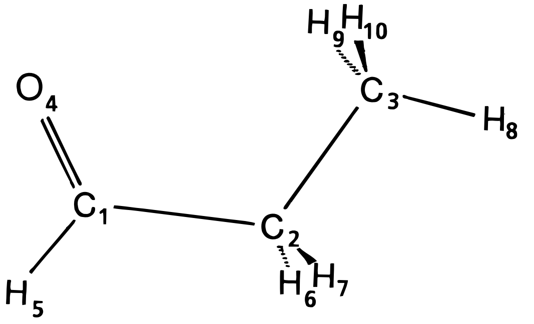

Figure 3. Molecular diagram of the atom numbering of propanal.

It appears that the 6-31G fundamental basis set is not adequate to represent the torsional potential energy function for propanal, possibly because it does not describe lone pairs well. The use of the triple-split valence basis 6-311G changes Δ*E* by only 20 cm^{-1}, but the addition of diffuse functions to 6-31G(d) lowers the value of Δ*E* by 170 to 180 cm^{-1} in both HF and MP2 calculations and makes it similar to those from the DZ(d) or DZ(d,p) calculations at both the HF and MP2 levels. The addition of diffuse functions to DZ(d) lowers the MP2 value by only 17 cm^{-1}. Although the value from the HF/6-31G(d) calculation is closer to the 300 cm^{-1} value than that obtained from the MP2/6-31G(d) calculation, it is evident that the effect of the electron correlation on the torsional potential energy function or barriers is far from negligible as claimed by Berry et al.[27]

Potential energy functions for both the asymmetric torsion and methyl torsion, can be derived from the energy differences given in Table 3. The results for MP2/DZ(d,p) represent the highest level for which all the relevant energies and geometrical structures have been obtained and potential constants are derived and employed below to aid in the assignment of the far-infrared transitions.

The labeling of the structural parameters is given in Figure 3. For three of the basis sets used, the geometrical structures of the cis conformer obtained by MP2 calculations are given in Table 4. These values all compare well with the complete microwave r_s structure[11] apart from the consistently long C=O bond length. The MP2/6-31+G(d,p) structure gives the best agreement with the microwave rotational constants also shown in Table 4, and therefore, it has been chosen as the model from which internal rotational inertial constants are calculated and applied below, although the methyl internal rotation constant *F* obtained from the MP2/DZ(d,p) calculation gives better agreement.

For 2-methylpropanal,[26] it was found that good fits to the observed rotational constants of both conformers were obtained when calculating the heavy atom parameters utilizing only the rotational constants of the ^{13}C− and ^{18}O-substituted species along with ab initio hydrogen parameters. Because 15 rotational constants for five isotopomers of cis-propanal with heavy atom substitutions are available from the microwave spectra,[11] an r_0 geometry for the heavy atom skeleton can be obtained by a least-squares fitting method[28,29] instead of an r_s structure by Kraitchman's method. The H atom parameters are fixed at ab

TABLE 4: Geometrical Parameters[a] for *cis*-Propanal Obtained from ab Initio MP2 Calculations and Microwave Spectra

parameter	MP2 DZ(d,p)	MP2 6-31G(d,p)	MP2 6-31+G(d,p)	expt MW[b]	r_0[c]
C_1C_2	1.5124	1.5059	1.5048	1.509	1.504 ± 0.007
CO	1.2279	1.2235	1.2269	1.210	1.215 ± 0.004
OC_1C_2	124.51	124.19	124.48	124.4	124.3 ± 0.4
C_2C_3	1.5262	1.5194	1.5204	1.523	1.526 ± 0.003
$C_1C_2C_3$	113.72	113.14	113.79	113.8	114.0 ± 0.02
$OC_1C_2C_3$	0	0	0		0
C_1H_1	1.1087	1.106	1.105	1.115	1.097
$C_2C_1H_1$	115.19	115.33	115.55	115.1	115.9
$OC_2C_1H_1$	180.0	180.0	180.0	180.0	180.0
C_2H_2	1.0976	1.0945	1.0953	1.105	1.098
$C_1C_2H_2$	106.90	107.32	106.95	107.2	107.6
$OC_1C_2H_2$[d]	123.61	123.63	123.77	124.0	123.4
C_3H_4	1.0924	1.0881	1.089	1.096	1.093
$C_2C_3H_4$	110.37	110.76	110.45	111.9	110.5
$C_1C_2C_3H_4$	180.0	180.0	180.0	180.0	180.0
C_3H_5	1.0916	1.0876	1.0884	1.103	1.092
$C_2C_3H_5$	110.66	110.61	110.75	110.3	111.0
$H_4C_2C_3H_5$[e]	120.40	120.50	120.36	121.1	120.3
rotational constants					
A	16 495.6	16 513.3	16 586.7	16 669.7	16 670.8
B	5854.7	5964.0	5897.5	5893.5	5893.4
C	4563.4	4628.4	4594.6	4599.0	4600.0
I_τ	3.1599	3.1322	3.1373	3.160	
F	5.6460	5.6917	5.6863	5.660	

[a] Bond lengths in angstroms, angles in degrees, rotational constants in MHz, I_τ in amu Å^2, and F in cm^{-1}. [b] Reference 11. [c] Heavy atom parameters fitted and hydrogen parameters fixed at values indicated, and the differences between observed and calculated rotation constants are the following: $\Delta A = 1.1, 2.2, 0.7, 0.0, 0.1$; $\Delta B = 0.1, 0.4, 0.3, 0.4, 1.2$; $\Delta C = -1.0, -0.5, -0.8, -0.7, -0.3$ MHz for the isotopomers CH_3CH_2CHO, $CH_3CH_2{}^{13}CHO$, $CH_3{}^{13}CH_2CHO$, ${}^{13}CH_3CH_2CHO$, and $CH_3CH_2CH^{18}O$, respectively. [d] $OC_1C_2H_3$ is the negative of this angle. [e] $H_4C_2C_3H_6$ is the negative of this angle.

initio values. The rotational constants calculated from the fitted structure mostly fit to less than 1 MHz to the experimental values, and the structural parameters are included in Table 4 for comparison with the r_s structural values.

For the same basis sets as tabulated for cis-propanal, optimized geometric structures are given for the gauche conformer in Table 5. Only a partial microwave structure is available for the heavy atoms of gauche propanal. The comparison of calculated rotational constants with microwave values indicates that none of the basis sets give good agreement for the A constant, but those obtained from the DZ(d,p) calculation give slightly better agreement for the B and C constants. It is, however, clear that all calculated structures underestimate the ethyl torsion dihedral angle ($\tau = OC_1C_2C_3$) but that obtained from the 6-31+G(d,p) calculation gives an especially poor prediction.

The A rotational constant is rather sensitive to the torsional dihedral angle, and adjusting τ to the microwave value but retaining all the other calculated parameters unchanged produces agreement between the rotational constants from the MP2/6-31+G(d,p) calculation and those from the microwave data as well as for the cis conformer. This disagreement between ab initio torsional angle and the microwave value may be due, at least in part, to the fact that geometric structure optimization in the ab initio method leads to a prediction of an equilibrium r_e structure and not a zero-point r_0 or averaged r_s structure. Also, it will be seen that the torsional potential energy function has an asymmetric shape around the gauche minimum, as evident from the cis/gauche barrier being higher than the gauche/gauche barrier (i.e., at trans). The adjusted ab initio MP2/6-31+G(d,p) geometry has been used to calculate the inertial constants (F's) for the asymmetric potential function.

The geometric structure of propanal has been optimized for the transition-state barrier between cis and gauche and the corresponding energy has been labeled Bs in Table 3. The transition state between one gauche conformer and the other is trans, labeled Ts, and since it has C_s symmetry it is easily optimized. The energies for Cs, Bs, Gs, and Ts are fitted to the usual potential function

$$V(\tau) = \sum_n (^1/_2) V_n\,(1 - \cos n\tau)$$

to give the first three V_1, V_2, and V_3 terms in the potential function. However, for some of the smaller basis sets, energies have been obtained for three or more further torsional angles, and it has been shown that the higher V_4, V_5, and V_6 terms are a small fraction of the magnitude of the first three terms. Potential functions from ab initio calculations of other molecules with ethyl torsions show similar results.

The torsional transitions for the asymmetric torsion are calculated from the potential constants fitted to the MP2/DZ(d,p) energies using the program described by Groner et al.,[29] and these are given in Table 6. The kinetic F constants have been calculated from the MP2/6-31+G(d,p) geometries for both cis and gauche conformers with the structure varying with dihedral angle and given in the table footnote according to the series expression

$$F(\tau) = F_0 + \sum_n F_n \cos n\tau$$

The $1 \leftarrow 0$ transition of the cis conformer is predicted at 132 cm^{-1}, very near to the band at 135 cm^{-1} previously assigned to this transition. On the other hand, the prediction of the splitting of the lowest torsional level of the gauche species, $0^- \leftarrow 0^+$ is 37 MHz in comparison with the experimental value of 475 MHz. This splitting is mainly a measure of the gauche/gauche barrier height, and to obtain a larger splitting, the potential energy function can be adjusted to lower this barrier. This can be done by raising the gauche energy or by lowering the trans energy. To do the former changes the function so

TABLE 5: Geometrical Parameters[a] for *gauche*-Propanal Obtained from ab Initio MP2 Calculations and Microwave Spectra

parameter	MP2 DZ(d,p)	MP2 6-31G(d,p)	MP2 6-31+G(d,p)	MP2 6-31+G(d,p)[b]	expt MW[c]
C_1C_2	1.5107	1.5051	1.5029		1.509
C_1O	1.2278	1.2230	1.2271		
OC_1C_2	124.93	124.71	124.76		125.1
C_2C_3	1.5364	1.5296	1.5313		1.519
$C_1C_2C_3$	110.74	111.18	110.98		111.7
$OC_1C_2C_3$	123.73	123.15	121.91	128.2	128.2
C_1H_1	1.1096	1.1078	1.1064		
$C_2C_1H_1$	114.75	114.75	115.35		
$OC_2C_1H_1$	180.83	180.71	180.84		
C_2H_2	1.0968	1.0937	1.0944		
$C_1C_2H_2$	107.56	107.81	107.64		
$OC_1C_2H_2$	119.59	120.06	119.84		
C_2H_3	1.0921	1.0889	1.0895		
$C_1C_2H_3$	108.65	108.15	108.47		
$OC_1C_2H_3$	−123.02	−123.06	−123.03		
C_3H_4	1.0921	1.0880	1.0887		
$C_2C_3H_4$	110.494	110.72	110.55		
$C_1C_2C_3H_4$	177.48	176.87	177.07		
C_3H_5	1.0927	1.0888	1.0896		
$C_2C_3H_5$	110.76	110.80	110.73		
$H_4C_2C_3H_5$	119.89	119.98	119.83		
C_3H_6	1.0936	1.0898	1.0904		
$C_2C_3H_6$	111.06	111.05	111.13		
$H_4C_2C_3H_6$	−119.81	−119.86	−119.83		
rotational constants					
A	25 262.5	25 446.0	25 163.2	26 195.8	26 248.4
B	4309.3	4336.0	4344.1	4305.2	4318.0
C	4154.3	4186.7	4196.7	4136.6	4144.5
I_τ	3.1364	3.1304	3.1366	3.1366	3.160
F	5.9696	6.0209	5.9976	6.0450	6.014

[a] Bond lengths in angstroms, angles in degrees, rotational constants in MHz, I_τ in amu Å,^{2} and F in cm^{-1}. [b] Skeletal torsional angle τ set to MW value, all other parameters as MP2/6-31+G(d,p). [c] Reference 11.

TABLE 6: Potential Energy Functions and Torsional Transitions[a] for Asymmetric Torsions of Propanal-d_0 and -d_1

	d_0					d_1		
	ab initio[b]	ab initio adjusted[c]	obs	fit[d]	Δ	obs	fit[d]	Δ
V_1	151.5	92.9		121.9			111.8	
V_2	254.3	317.6		374.7			379.4	
V_3	443.2	409.8		459.5			467.4	
V_6				−16.4			−3.7	
c/g[e]	690.1	694.2		797.2			807.8	
g/g[e]	297.4	212.9		234.9			234.4	
ΔE	297.3	289.8		346.6			344.8	
$1 \leftarrow 0$	132.05	130.79	135.13	135.18	−0.05	126.43	126.4	0.03
$2 \leftarrow 1$	122.53	121.50	(133.83)	128.44		115.88	119.76	
$3 \leftarrow 2$	112.19	111.45	121.13	120.62	0.51	112.25	112.59	−0.34
$4 \leftarrow 3$	100.51	100.18	110.73	111.43	−0.70	104.80	104.72	0.08
$5 \leftarrow 4$	85.90	86.09	101.58	100.11	1.47	96.43	95.80	0.63
$6 \leftarrow 5$						85.15	84.75	0.40
$0^- \leftarrow 0^+$	37.30	475.97	475.27	474.30	0.97	142.44	137.25	5.19
τ_{min}	125.2	128.8	128.2	130.8	−2.6	128.2	129.6	−1.4
$1^\pm \leftarrow 0^\pm$	85.9	80.5		82.3			78.7	
ΔH	275.4	265.1		320.7			321.6	

[a] Transitions are in cm^{-1} except the microwave splitting $0^- \leftarrow 0^+$ which is in MHz. The gauche torsional angle is in degrees. Transitions are calculated using a series of F kinetic constants calculated from the MP2/6-31+G(d,p) geometric structures of both cis and gauche conformers. Parts of the cosine series for the d_0 and d_1 species -d_0: $F_0 = 2.9785$, $F_1 = 0.5384$, $F_2 = 0.2606$, $F_3 = 0.0509$, $F_4 = 0.0169$, $F_5 = 0.0038$ cm^{-1}. d_1: $F_0 = 2.4877$, $F_1 = 0.3995$, $F_2 = 0.1574$, $F_3 = 0.0306$, $F_4 = 0.0082$, $F_5 = 0.0018$ cm^{-1}. [b] Ab initio potential energies (in cm^{-1}) from MP2/DZ(d,p) calculations. [c] Adjusted by lowering the gauche/gauche energy barrier by 85 cm^{-1}. [d] Fit to cis transitions, microwave $0^- \leftarrow 0^+$ splitting, and gauche τ_{min}. [e] Cis/gauche and gauche/gauche energy barriers.

much that the cis torsional transitions are moved, whereas lowering the trans energy by 85 cm^{-1} leaves the four cis transitions fit, i.e., the cis potential well is changed very little, but the $0^- \leftarrow 0^+$ splitting is near to the microwave splitting value. By calculating the energy levels of the asymmetric internal rotor and fitting transitions and energy differences in a least-squares manner, a potential function much like the adjusted ab initio function is found when fitting the 135.1 cm^{-1} band as the cis $1 \leftarrow 0$ transition, 124.1 cm^{-1} as the $2 \leftarrow 1$ transition, and 116.5 cm^{-1} as $3 \leftarrow 2$ transition, and the microwave splitting and torsional angle of the gauche conformer. It should be noted here that the zero-point energy for the gauche form is always less than that for the cis so that ΔH is smaller than ΔE by 20−30 cm^{-1} for the functions in Table 6.

The $0^- \leftarrow 0^+$ splitting of 142 MHz has also been measured for propanal-d_1 although it was not previously used in fitting a

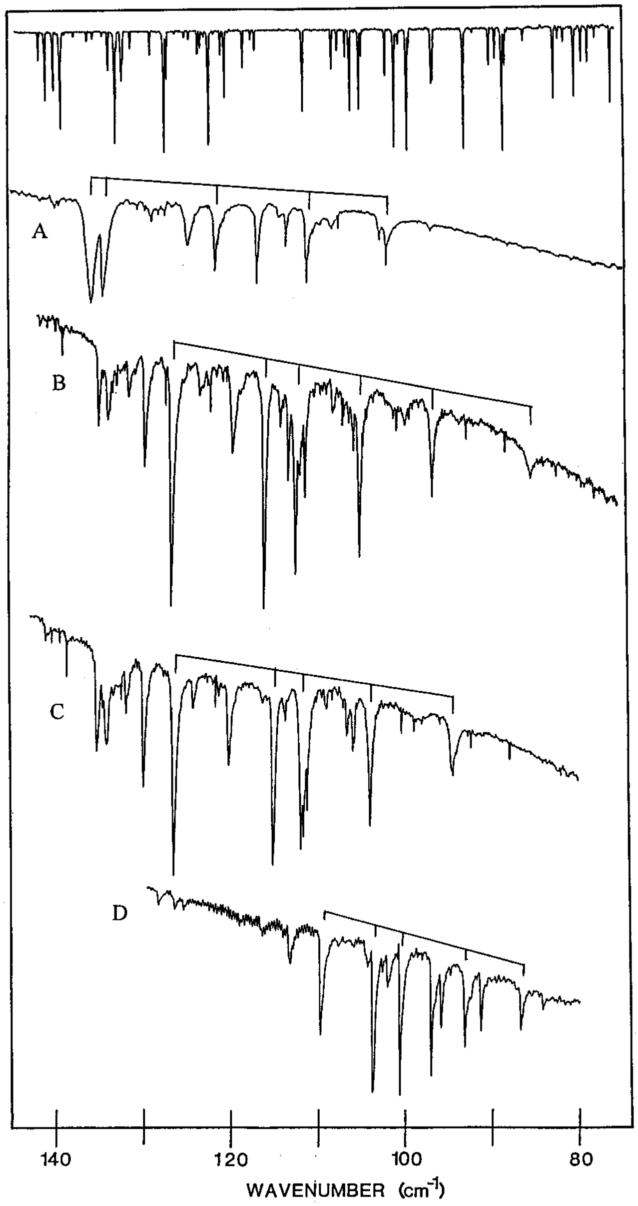

Figure 4. (A) Far-infrared spectrum of propanal-d_0 in the asymmetric torsional region; (B) far-infrared spectrum of propanal-d_1 in the asymmetric torsional region; (C) far-infrared spectrum of propanal-d_2 in the asymmetric torsional region; (D) far-infrared spectrum of propanal-d_5 in the asymmetric torsional region.

potential energy function.[12] The adjusted ab initio potential energy function yields a calculated value for this splitting of 179 MHz, and the predicted torsional transitions are not as near to the observed bands as those for propanal-d_0, but fitting the fairly obvious series gives a fit much like that for d_0. The fitted potential energy functions for these isotopomers predict the torsional fundamental for the gauche species to lie at 82 cm^{-1} for the d_0 molecule and at 78 cm^{-1} for the d_1 species, which are higher than the vibrational frequencies of 61 and 57 cm^{-1} found by ab initio harmonic force constant calculations and much lower than the 113 cm^{-1} value previously[7] assigned for this transition for the d_0 species.

Torsional Assignments and Discussion

The asymmetric torsional region of the far-infrared spectrum of d_0 is rather complicated as it starts (Figure 4A and Table 1) with two bands of almost equal intensity only 1.3 cm^{-1} apart. These are too close together to be fitted as well as consecutive sequence bands ($1 \leftarrow 0$, $2 \leftarrow 1$ transitions) by a potential energy function with the first three terms V_1, V_2, and V_3 predominant.[7,12] It would require a rather high cis/gauche barrier to fit better. Some weaker bands were previously used as a continuation of the sequence before the next strong band at 116.5 cm^{-1} was assigned. A weaker feature at 113.1 cm^{-1} was assigned[7] as the gauche asymmetric torsional fundamental $1^{\mp} \leftarrow 0^{\pm}$.

As well as employing the same far-infrared transitions, the function given by Randell et al.[12] included two microwave measurements, namely their cis − gauche enthalpy difference of 420 cm^{-1} and their splitting of 475 MHz for the lowest gauche torsional level. However, the determined function fits only the last datum well; it is especially unfortunate that the ΔH value from this potential function is 472 cm^{-1} and the gauche minimum of the function at 136.6° is about 8° higher than that obtained from gauche rotational constants. Since the fit to the far-infrared torsional transitions is not sensitive to the value of ΔH, the first fault can be corrected by slight adjustment of the coefficients of the function by least-squares fitting to the data, but the angle is still off by 8.5°. It would appear to be impossible to fit simultaneously both the value of the ground-state splitting and the torsional angle of the gauche conformer while retaining such a high value as 113 cm^{-1} for the gauche torsional fundamental.

In contrast to the spectrum of the d_0 species, the asymmetric torsional regions of the far-infrared spectra of d_1 and d_2 seen in Figure 4B,C appear less complicated, showing a series of four almost equally spaced bands, and despite different kinetic F constants, they have almost identical frequencies and intensities. Among them is a band of similar intensity at 112 cm^{-1}. It is tempting to assign the series as the cis torsional (ν_{24}) sequence of each of these deuterated species and to assign the extra peak at 112 cm^{-1} as the gauche ν_{24} fundamental. However, there are a number of weaker bands in both the d_1 and d_2 spectra which give essential additional information. In the previous report on the propanal far-infrared spectrum,[7] ν_{24} overtone (double-jump) bands appearing as small shoulders on the low-frequency side of the skeletal vibration were assigned. In the spectra of the d_1 and d_2 species on the low-frequency side of the ν_{15} band, there are more clearly visible features, called "heads" in Table 1, with rotational structure converging to a distinct edge. The pairwise combinations of the wavenumbers of adjacent bands in the asymmetric (single-jump) torsional region, including the band at 112 cm^{-1}, agree well (within 1 cm^{-1}) with the observed overtone bands. These overtone assignments are given in Table 1, and for d_1 and d_2, even the $5 \leftarrow 3$ torsional band may be present in the methyl torsional region. The overtone frequencies were not used in fitting a potential energy function as they are less accurate than the sharp singe-jump bands and they should be at the sum of the single-jump wavenumbers.

As indicated already, a search was made in the asymmetric torsional region for the gauche fundamental $1^{\mp} \leftarrow 0^{\pm}$. The appearance of a gauche band might be expected to be different from the cis asymmetric torsional band because of different rotational contours. Since the cis structure is far from that of a symmetric top ($\kappa = -0.78$), the C-type contour for out-of-plane vibrations should have a strong central peak[30] and the actual measurements in Table 1 are of such peaks. Whereas the gauche conformer is very near to a symmetric top ($\kappa = -0.99$) and C-type contours will not have a prominent central peak,[30] but since all bands should have hybrid contours, there may be sufficient A contour present to give a central peak. A second consideration is the intensity of cis and gauche bands where, in the harmonic approximation, the gauche ν_{24} funda-

TABLE 7: Potential Energy Functions and Torsional Transitions[a] for Asymmetric Torsions of Propanal-d_2 and -d_5

	d_2				d_5			
	V's from d_1 fit	obs	fit[b]	Δ	V's from d_1 fit	obs	fit[b]	Δ
V_1	86.5		136.8		86.5		131.5	
V_2	377.2		348.6		377.2		358.0	
V_3	473.1		436.5		473.1		458.9	
V_6	−4.3		−9.0		−4.3		−27.8	
c/g[d]	803.3		758.7		803.3		783.5	
g/g[d]	236.6		229.3		236.6		248.9	
ΔE	323.0		343.9		323.0		341.6	
$1 \leftarrow 0$	133.41	126.79	126.77	0.02	128.51	119.61	119.61	0.00
$2 \leftarrow 1$	125.97	(115.40)	120.03		121.57	(113.53)	115.80	
$3 \leftarrow 2$	117.91	112.15	112.51	−0.36	114.08	110.40	110.82	−0.42
$4 \leftarrow 3$	108.96	104.15	103.96	0.20	105.81	105.74	104.57	1.17
$5 \leftarrow 4$	98.64	94.56	93.77	0.78	96.37	96.60	96.70	−0.10
$0^- \leftarrow 0^+$	322.4	320	319.4	0.6	230.0	250.0	247.8	2.2
$\tau_{\min}$	129.8	128.2	129.5	−1.3	129.8	128.2	131.3	−3.1
$1^\pm \leftarrow 0^\pm$	78.6		79.3		81.7		77.0	
ΔH	300.0		320.8		300.2		321.0	

[a] Transitions are in cm^{-1} except the microwave splitting $0^- \leftarrow 0^+$ which is in MHz. The gauche torsional angle is in degrees. Transitions are calculated using a series of F kinetic constants calculated from the MP2/6-31+G(d,p) geometric structures of both cis and gauche conformers. Parts of the cosine series for the d_2 and d_5 species d_2: $F_0 = 2.7827$, $F_1 = 0.4015$, $F_2 = 0.2079$, $F_3 = 0.0323$, $F_4 = 0.0111$, $F_5 = 0.0021$. d_5: $F_0 = 2.6111$, $F_1 = 0.3369$, $F_2 = 0.2059$, $F_3 = 0.0298$, $F_4 = 0.0113$, $F_5 = 0.0020$ cm^{-1}. [b] Fit to cis transitions, microwave $0^- \leftarrow 0^+$ splitting, and gauche $\tau_{\min}$. [c] Frequencies for d_5 molecule increased by 10 cm^{-1} to account for Fermi resonance (see text). [d] Cis/gauche and gauche/gauche energy barriers.

mental is found from ab initio frequency and dipole derivative calculation to have about twice the intensity of the cis ν_{24} fundamental which may mean that the Boltzmann disadvantage is overcome. However, in this study, band peaks have not been assigned to the gauche torsional fundamentals for any of the isotopomers.

To calculate the torsional transitions of propanal-d_1, the kinetic F constants (Table 6 footnote) have been calculated from the ab initio MP2/6-31+G(d,p) geometries for both cis and gauche conformers using a flexible model, as for propanal-d_0 above, where the structure is allowed to vary with dihedral angle. When fitting torsional frequencies to the observed bands, the angle of the gauche conformer of 128.8° and the gauche microwave splitting of 142.44 MHz are also included as observables to be fitted. A good fit can be only obtained if the second band ($2 \leftarrow 1$ transition) is omitted. The second excited torsional energy level ($v = 2$) appears to be lowered by 4 cm^{-1} because it is in Fermi resonance with the ν_{15} first excited state. With a potential function with V_1, V_2, and V_3 predominant, the agreement with the observed torsional frequencies is very good, and the series of d_1 bands even includes the $6 \leftarrow 5$ transition. However, to fit a potential function it is necessary to input a value for $\Delta H(0^\pm{-}0)$, and it has been chosen from the predicted value obtained from the ab initio results. The raw gauche − cis energy difference from MP2/DZ(d,p) calculations is 300 cm^{-1} but a correction is needed for the difference in zero-point energies for all the vibrations of both conformers in addition to the asymmetric torsion,[31] and using ab initio vibrational frequencies a ΔE value of 352 cm^{-1} is obtained. The ΔH value requires a correction for the zero-point energies for the asymmetric torsion itself and employing ab initio harmonic frequencies a value of around 320 cm^{-1} is obtained. Although the ΔH value was included with a wide error range, it is fitted almost exactly (Table 6) since the data provided no restriction. The gauche splitting and the torsional angle of the gauche minimum are both determined by the gauche/gauche barrier height, and microwave values appear to be in some conflict with each other. The gauche torsional fundamental is predicted to be at 79 cm^{-1}.

Applying the potential energy function of propanal-d_1 to the interpretation of the asymmetric torsion in propanal-d_0, confirms that the second strong band in the d_0 spectrum at 133.8 cm^{-1} cannot be fitted as it is at too high a frequency, because the second excited torsional level is in even closer Fermi resonance with the ν_{15} excited state and is raised by over 5 cm^{-1}. There are a number of peaks at the top of the ν_{15} band, and in the current assignment the peak at 264.1 cm^{-1} is used as ν_{15} as it is near the middle of the band and a peak at higher wavenumbers at 269.4 cm^{-1} agrees with the combination 135.1 + 133.8 cm^{-1}. Further overtone bands are expected as in the propanal-d_1 spectrum, and the band at 232.2 cm^{-1} agrees as the $4 \leftarrow 2$ transition but the $3 \leftarrow 1$ transition is not observed being obscured perhaps by the broad P branch of the ν_{15} band. The potential function fitted to the torsional data, including the gauche splitting and $\tau_{\min}$ as in d_1, has a very similar set of V_n constants (Table 6) although the fit to the torsional frequencies is poorer. The predicted gauche fundamental is at 83 cm^{-1} in this case.

The asymmetric torsional bands of propanal-d_2 shown in Figure 4C are readily assigned by analogy with the d_1 spectrum. In Table 7 the transitions, energy differences, and torsional constants predicted from the d_1 potential function are given. Since no gauche $0^- \leftarrow 0^+$ splitting has been reported and since the fitted potential constants require some constraint to set the gauche/gauche energy barrier, a value of the splitting of 320 MHz, approximately as obtained from the d_1 potential, has been chosen as a constraint. The gauche to cis energy difference of 320 cm^{-1} also provides a constraint especially to V_1. A good fit to the torsional frequencies is obtained, but since the kinetic F constants (Table 7 footnote) are different from those for d_1, the values of the potential constants are a little different where the V_1 value is 30 cm^{-1} higher and the V_2 value is lower by about the same amount. The predicted gauche torsional angle is near to 130° as in d_1, and the predicted gauche torsional fundamental is 80 cm^{-1}. For both the d_1 and d_2 molecule a weak band not used in the above analysis appears in the methyl torsional region at 201 and 200 cm^{-1}, respectively, which corresponds with the $5 \leftarrow 3$ double-jump of the cis asymmetric torsional mode.

The asymmetric torsional region of the far-infrared spectrum of propanal-d_5 (CD_3CD_2CHO) shown in Figure 4D is fairly similar to those of d_1 and d_2 except that the torsional series of four almost equally spaced bands starts with a slightly weaker band toward the high wavenumber end of the region. The

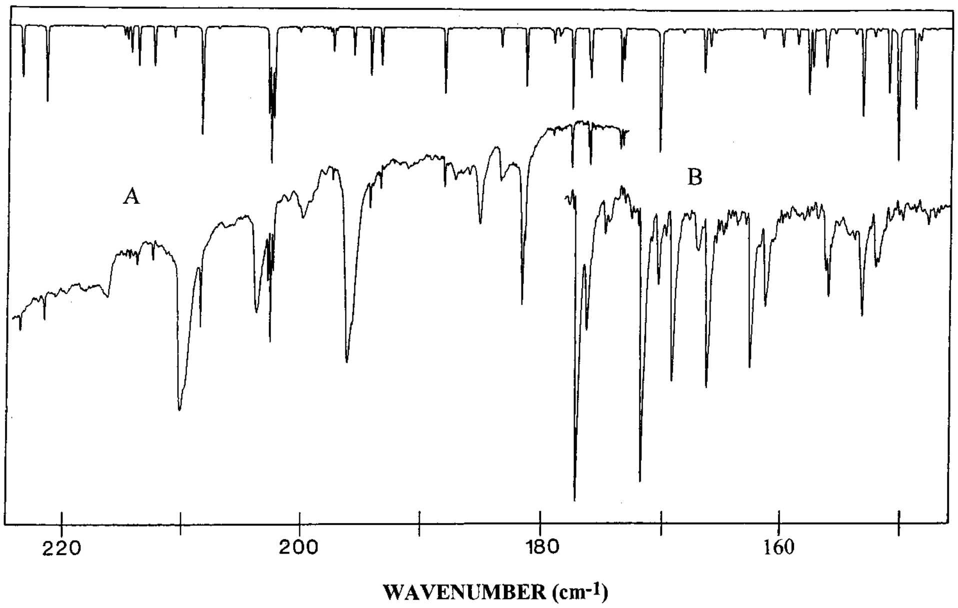

Figure 5. (A) Far-infrared spectrum of propanal-d_2 in the methyl torsional region; (B) far-infrared spectrum of propanal-d_5 in the methyl torsional region. Top spectrum is that of water vapor.

assignments are listed in Table 7 along with transition wavenumbers calculated from the fitted potential energy function. However, the asymmetric torsional transitions are at such a low frequency that the fitted potential constants are rather different from those of the lighter isotopomers. Correspondingly it will be seen below that the methyl torsional transitions of the propanal-d_5 spectrum are at a rather high frequency considering the mass effect on the value of the kinetic F constant. This apparent excessive separation of methyl and asymmetric torsional transitions is due to the heavier CD_3 internal top and the resulting top—top coupling. A function very similar to those for d_1 and d_2 is obtained if 10 cm^{-1} is added to the observed frequencies as listed in Table 7, and these adjusted frequencies are fitted fairly well. The fit is again constrained by a value of the gauche splitting of 250 MHz derived from the d_1 fitted potential and the adjusted ab initio potential function. The assignments of the transitions are again confirmed by the appearance of three weak overtone bands at 213.4, 204.3, and 197.4 cm^{-1}. The gauche minimum is predicted at approximately 131° as in the normal species, and the predicted torsional fundamental frequency is slightly less than in the lighter isotopomers despite the adjustment of cis torsional frequencies.

These assignments leave some pronounced bands unassigned in the asymmetric torsional region of each of the isotopomers. In the spectra of all three deuterated species, the weak band at the highest frequency corresponds very closely in each case to the difference of the cis skeletal bending frequency ν_{15} and the cis asymmetric torsional fundamental ν_{24}. At lower frequencies of the difference band is a series of bands which have not been assigned in detail, but since the difference band is due to a transition from the first excited torsional state to the first bending excited state, these other bands are probably due to transitions from the first torsional excited state to asymmetric torsional levels built on the bending excited state. In propanal-d_0 there are no difference bands to high frequencies of the cis torsional fundamental, but with ν_{15} assigned to the peak at 264 cm^{-1}, the $\nu_{15} - \nu_{24}$ difference band should lie at 128.0 cm^{-1} and a weak band is observed at this wavenumber among the main torsional series. There are also other weak bands and even a strong band at 116 cm^{-1} not assigned in the main torsional series that may correspond to other difference transitions as in the other species. Some weak bands may be hot bands involving the methyl torsion. Indeed, the fact that the asymmetric torsional potential function is not the same for all isotopomers also points to the need for a more sophisticated model with both potential and kinetic torsional top—top interaction constants. However, because of the Fermi resonance one would not expect the two-dimensional model to be overly successful.

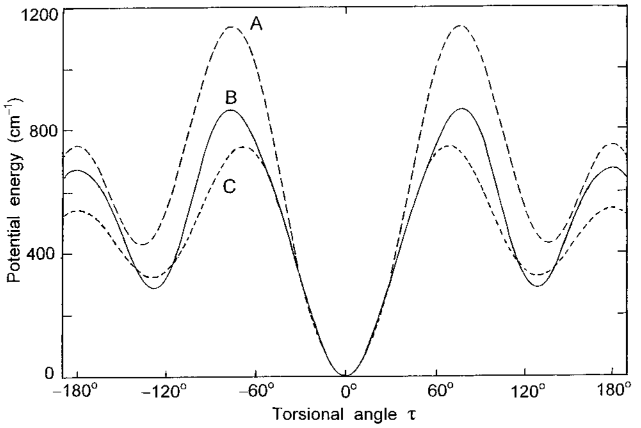

Figure 6. Potential energy functions for asymmetric torsion: (A) fit to data of Randell et al.;[11] (B) current fit to propanal-d_1 experimental data including gauche torsional angle; (C) ab initio function.

The methyl torsional barriers in both the cis and the gauche conformers have been redetermined recently from microwave line splittings[9] as 768 and 886 cm^{-1}, respectively. These are not in agreement with those previously derived[7] from an interpretation of the methyl torsional region of normal propanal shown in Figure 5. With the isotopic data available, the methyl torsional regions of the far-infrared spectrum of propanal also required reexamination. Once more the spectra of propanal-d_1 (Figure 1B) and -d_2 (displayed in Figure 5A) are very similar, with perhaps the main methyl torsional sequence of three members being most evident in the spectra of the d_2 species. The methyl torsional region of the d_5 spectrum shown in Figure 5B exhibits about twice as many bands as the other isotopomers.

From calculations of the vibrational force constants of propanal in the harmonic approximation at all ab initio levels of theory and with all basis sets, the methyl torsional frequency ν_{23} of the cis form is always at a higher wavenumber than the

TABLE 8: Potential Energy Functions and Torsional Transitions[a] for Methyl Torsions of Propanal and Isotopomers in the Cis and Gauche Conformations

	d_0			d_1		d_2		d_5	
	MW[b]	obs	fit	obs	fit	obs	fit	obs	fit
				Cis[c]					
F	5.660								
V_3	768		1114.6		1059.4		1044.1		1118.1
V_6			−17.7		−25.6		−22.2		48.6
$1 \leftarrow 0$		219.90	219.92	211.53	211.37	210.20	209.99	177.12	177.06
$2 \leftarrow 1$		207.44	207.27	198.51	199.83	196.23	198.09	166.33	166.76
$3 \leftarrow 2$		192.56	192.65	186.92	186.20	185.19	184.18	156.05	155.84
				Gauche[d]					
F	6.014								
V_3	886		798.0		731.5		733.8		897.6
V_6							−4.4		
$1 \leftarrow 0$		193.69	193.69	183.73	183.73	181.64	181.64	153.40	153.40
$2 \leftarrow 1$			176.78		166.68	165.70	165.70		145.25
$3 \leftarrow 2$									

[a] 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. [b] Reference 9. [c] Average value of V_3 is 1084 ± 33 cm^{-1}. [d] Average value of V_3 is 791 ± 68 cm^{-1}.

corresponding mode of the gauche rotamer. The values of the inertial constants were calculated from the ab initio MP2/6-31+G(d,p) calculated parameters of cis and gauche conformers. A constant value of F for each isotopomer and each conformer is assumed in the calculation of methyl torsion transition wavenumbers in Table 8. The F number for the gauche conformer is different from that for the cis rotamer, but since it is clear that they are not sufficiently different to change the order of fundamental frequencies, the highest wavenumber band and the prominent sequence are assigned to the cis form in contrast to what was done in the previous report[7] on the d_0 spectrum. There are several reasons for the change in the assignment. First, the ab initio calculations clearly indicate that the methyl torsion for the cis conformer should be at a higher wavenumber than the corresponding mode for the gauche conformer. Second, the methyl torsion for the cis conformer is expected to be much more intense than the methyl torsion for the gauche conformer, so the higher frequency Q branches must be assigned as the cis transitions. Third, the mixing of the asymmetric torsion with the methyl torsion is extensive for the cis conformer whereas such mixing is not predicted for the gauche rotamer. Finally, the pronounced Q branches are more reasonably assigned to the cis methyl torsion and associated "hot bands" because of the similarity of the observed bands for the asymmetric torsional transitions for the cis rotamer and their predicted relative intensities.

A potential energy function for methyl torsion is obtained by least-squares fitting and the $A-A$ transitions calculated from it are compared with observed values listed in Table 8. In every case, the magnitude of the torsional barrier means that the $A-A/E-E$ splitting is unresolvable. In the spectra of the d_0, d_1, and d_2 species, the band peaks of the cis sequence are fairly broad and tail off to lower wavenumbers. Among them are one or two other bands of the same appearance which may be hot bands of the cis rotamer but there is also a sharp spike which cannot belong to the cis form and is now assigned as the methyl torsion fundamental of the gauche conformer. The different band appearances may be consistent with the argument above about rotational band contours. The V_3 terms obtained by the fitting program are given in Table 8. In the case of d_2 a very weak band has been tentatively assigned as a second transition of the gauche form. The reasonable agreement between observed bands and the methyl torsional fundamental transitions predicted from ab initio calculations supports these assignments.

From the more complicated d_5 spectrum, a series of bands was taken for the methyl torsional mode for the cis sequence by analogy with the other isotopomers and the methyl torsional fundamental chosen likewise for the gauche rotamer. The band measurements, assignments, and potential constant fits are given in Table 8. The spectrum (Figure 5B) shows a sufficient number of other bands for at least one other sequence to be selected. There is a considerable amount of rotational fine structure with intervals approximately 0.29 cm^{-1} on the high-wavenumber side of the assigned methyl torsional transitions and also among the weak bands at the high-wavenumber end of the asymmetric torsional region as well as elsewhere. From the interval, this structure appears to be J structure of *cis*-propanal-d_5 but there is no evidence of K structure (interval approximately 1 cm^{-1}) for the gauche methyl torsional mode.

The potential energy functions obtained by fitting the observed torsional wavenumbers of the different isotopomers are expected to be identical within some error range. However, the fitted V_3 constants for the cis conformer vary from a low of 1044 cm^{-1} for the d_2 isotopomer to a high value of 1118 cm^{-1} for the d_5 species. In the case of the gauche conformer, the fitted V_3 constants vary from a low value of 732 cm^{-1} for the d_1 species to 898 cm^{-1} for the high value for the d_5 species. The high barriers in the d_5 species are due to the methyl torsion transitions being high by about 10 cm^{-1} and the asymmetric torsional transitions being low by nearly the same amount apparently from the energy level perturbations of these two vibrations. The different barriers among the different species cannot be due to measurement errors and are probably not due to assignment errors, but indicate the need for a two-dimensional model of internal rotation as well as taking into account the energy level perturbations.

The large average value of 1084 ± 33 cm^{-1} (Table 9) for the methyl barrier for the cis conformer compared to the value of 768 cm^{-1} obtained from the microwave splitting method can be rationalized on the basis that the torsional transitions are relatively high due to perturbation of the energy levels of the two torsional modes. For example the ab initio predicted value for the methyl torsional mode for the cis mode is 237 cm^{-1} with an observed value of 220 cm^{-1}. This difference of 17 cm^{-1} between the predicted and observed values for the cis conformer is almost one-half the value between the similar quantities (31 cm^{-1}) for the gauche conformer. Thus, we believe the methyl torsional mode for the cis conformer is significantly perturbed so the barrier calculated from the

TABLE 9: Observed and Calculated Low-Frequency Vibrational Fundamentals of Propanal-d_0, -d_1, -d_2, and -d_5

	d_0		d_1		d_2		d_5	
	obs	calc[a]	obs	calc[a]	obs	calc[a]	obs	calc[a]
				Cis				
A′								
ν_{14}	658	675.1	652	665.5	646	665.6		607.1
ν_{15}	264.1	257.8	261.7	256.6	262.6	256.9	237.9	236.3
A″								
ν_{22}	672	684.8	615	629.3	561	577.3		537.7
ν_{23}	219.9	237.5	211.5	230.1	210.2	229.2	177.1	186.7
ν_{24}	135.1	139.8	126.4	130.2	126.8	132.7	109.6	116.7
				Gauche				
ν_{14}	508	508.6	503	501.5	457	457.4		451.0
ν_{15}	324	329.0	315	303.9	320	323.8	300	300.6
ν_{22}		784.3		744.8		676.5		610.8
ν_{23}	193.7	224.7	183.7	223.3	181.6	223.6	153.4	165.0
ν_{24}	83[b]	78.4	79[b]	74.2	80[b]	76.9	78[b]	74.1

[a] From ab initio MP2/DZ(d,p) calculation unscaled. [b] From fits in Tables 6 and 7.

observed torsional transitions is significantly higher than the value obtained from the observed microwave splittings which should be directly related to the torsional barriers.

Conclusions

With our interpretation of the far-infrared spectra of four isotopomers of propanal, all of the low-frequency fundamentals have been assigned and measured. The measured frequencies for the fundamentals from the far-infrared data are collected in Table 9 along with some of the previous mid-infrared measurements.[4] The values of ν_{24} given for the gauche conformer in Table 9 are predictions made from fitting torsional data and not directly observed. Comparison is made with wavenumbers obtained by ab initio force constants from the MP2/DZ(d) calculation, which are given without scaling as appropriate for torsions and low-frequency skeletal bending vibrations.

For the asymmetric torsion, over the years a number of potential energy functions have been optimized to fit observed transitions or ab initio energies. The function obtained by fitting all the data of Randell et al.[12] is rather different from the ab initio function (Figure 6). It shows a cis/gauche energy barrier which is too high because too many cis torsional transitions with almost equal intervals have been assigned, i.e., the cis potential well is made too close to harmonic. There is no supporting evidence for the high value of 420 cm^{-1} for the gauche − cis enthalpy difference in the gas phase other than the low-quality ab initio calculations.[14−16] In the liquid phase, the conformational energy difference may be of this magnitude,[3,5] but the current Raman data suggest a lower value. The gauche/gauche barrier is also too high to simultaneously fit the gauche zero-level splitting and gauche torsional angle.

Although four different potentials have been given for the four isotopomers studied, they are not significantly different from one another whereas the cis/gauche barriers vary from 759 to 808 cm^{-1} with an average value of 784 cm^{-1} and the gauche/gauche barriers from 231 to 251 cm^{-1} with an average of 239 cm^{-1}. The gauche − cis energy difference varies only from 342 to 347 cm^{-1} because of the enthalpy difference of 320 cm^{-1} employed. It should be noted that for each of the isotopic species the potential energy function fitted has only three significant parameters (V_1, V_2, V_3) to fit the gauche splitting, the gauche torsional angle, and the cis asymmetric torsional transitions, whereas all of the previously proposed functions employ five parameters and have a rather large magnitude V_4 term. However, the variation of function with isotopomer and the apparent impossibility of fitting all the data simultaneously with independent torsional coordinates points to the need to treat top−top interaction in propanal. However, with the resonance which is clearly present in the asymmetric torsional transitions, the more complex top−top interaction model is not expected to be significantly more successful than the present treatment.

Methyl torsional barriers for *cis*- and *gauche*-propanal obtained from analysis of the far-infrared spectra have been calculated by one fitting model but can hardly be said to agree with the microwave value. For *gauche*-propanal the far-infrared barriers for all the isotopomers are lower than the microwave value except for the d_5 isotopomer with the average being 798 ± 68 cm^{-1} and two of the individual values in the 730 cm^{-1} range compared to the microwave value of 886 cm^{-1}. For *cis*-propanal, the average barrier of 1084 ± 33 cm^{-1} from the far-infrared data is much higher than the microwave barrier of 768 cm^{-1}. However, the fact that these derived barriers to methyl rotation vary so markedly simply indicates the significant differences between the methyl and asymmetric torsional interactions for the different isotopomers.

It is believed that significant top−top interaction also takes place in 1-butene, which is structurally similar to propanal and has a similar complex far-infrared spectrum.[32] The correct assignments of the observed transitions of propanal, 1-butene, and other similar molecules may depend on accounting for this interaction. However, in order to determine all of the relevant kinetic and potential coupling constants, more information may be required than offered by the far-infrared spectra.

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