

A theoretical determination of the methyl and aldehydic torsion far-infrared spectrum of propanal- d_0 with the vibrational zero point correction

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The methyl and aldehydic torsions far-infrared (FIR) spectrum of standard propanal is determined theoretically taking into account the vibrational zero point energy (ZPE) of the remaining small amplitude vibration modes in an anharmonic approach. For this purpose, the potential energy function obtained in a previous calculation at the 6-311(3df,p) restricted Hartree-Fock/second-order Møller-Plesset level [J. Chem. Phys. **109**, 2279 (1998)] is modified for the anharmonic ZPE corrections. With this corrected potential for the ZPE, the kinetic parameters, as well as the electric dipole moment variations, the FIR frequencies, and intensities for the methyl and aldehyde torsions of propanal were determined theoretically using a two-dimensional approach. The calculated torsional band structures of propanal determined without and with the ZPE corrections were compared between themselves and with the available experimental data. It is found that the theoretical calculations permit one to reproduce and assign 24 of the 25 observed bands. In the same way, the introduction of the ZPE corrections is seen to yield more satisfactory frequency values for the aldehyde torsion, double quanta, and methyl-aldehyde combination bands. © 2002 American Institute of Physics. [DOI: 10.1063/1.1436113]

I. INTRODUCTION

The far-infrared (FIR) spectra of gaseous propanal- d_0 ($\text{CH}_3\text{-CH}_2\text{-COH}$) and three of its symmetric isotopomers; $-d_1$ ($\text{CH}_3\text{-CH}_2\text{-COD}$), $-d_2$ ($\text{CH}_3\text{-CD}_2\text{-COH}$) and $-d_2$ ($\text{CH}_3\text{-CD}_2\text{-COH}$) and $-d_5$ ($\text{CD}_3\text{-CD}_2\text{-COH}$) were recorded by Durig *et al.* in the region of 300–60 cm^{-1} .^{1,2} Assignments from a one-dimensional calculation were proposed for 24 bands in Ref. 1, and better assignments from the analysis of the isotopomer spectra assisted by simple one-dimensional *ab initio* calculations were given in Ref. 2. In particular, the fundamental band for the aldehyde torsion in the *cis*-rotamer (ν_{24}) was assigned to an infrared absorption at 135 cm^{-1} and the methyl torsion at 219.9 cm^{-1} .

The FIR spectrum for the two-dimensional problem of simultaneous aldehydic and methyl torsions was also deduced by us using very sophisticated *ab initio* two-dimensional calculations in a previous paper.³ In these calculations, the C_3 symmetry⁴ of the methyl group as well as the variational principle were preserved simultaneously (symmetry dilemma).⁵ A series of progressions were found. In particular, methyl-aldehyde torsion combination bands were detected, which suggested new assignments. A very good agreement was found for the methyl torsion bands in the *cis*-rotamer 219.9 cm^{-1} . But, as will be seen this result has to be regarded as accidental.

Furthermore, the FIR spectra of some symmetric isotopomers of propanal were calculated and compared with the

available experimental measurements.⁴ Here again, the agreement with the experimental frequencies for the methyl torsion was excellent, except in the case of propanal- d_5 . This disagreement suggested to us to introduce in the calculations a mass effect such as the vibrational zero point energy correction (ZPE) with respect to the remaining small amplitude vibration modes. This correction was seen to greatly affect the inversion barrier in methylamine.⁶

The purpose of this paper is to repeat the gaseous propanal- d_0 calculations, introducing the vibrational ZPE corrections, and compare once more the calculated frequencies and intensities with the previous results and the experimental data. A general improvement is observed. The calculations for the deuterated species will be the object of a future paper.

II. THEORY

All the calculations presented here were developed following a series of previous papers.^{3,7–9}

Figure 1 shows the two torsions of the skeleton of the propanal molecule and the numbering of the atoms. The torsion of the aldehydic group around the C2C3 bond is defined by the dihedral angle $\tau = \text{O1C2C3C4}$, while the torsion of the methyl group around the C3C4 bond may be defined by the dihedral angle $\theta = \text{C2C3C4H6}$. These torsion angles will be considered as large amplitude vibration coordinates. The Hamiltonian operator restricted to only these two coordinates may be written as

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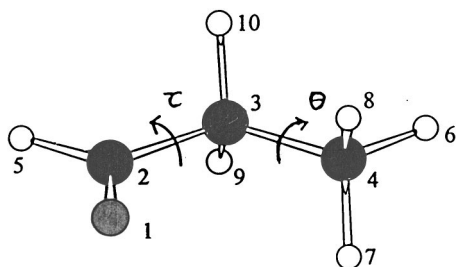


FIG. 1. Structure of propanal in its *cis* preferred conformation. Numbering of the atoms. Torsion angles, τ and θ .

$$H(\theta, \tau) = -\frac{\partial}{\partial \theta} B_{\theta}(\theta, \tau) \frac{\partial}{\partial \theta} - \frac{\partial}{\partial \theta} B_{\theta, \tau}(\theta, \tau) \frac{\partial}{\partial \tau} - \frac{\partial}{\partial \tau} B_{\tau, \theta}(\theta, \tau) \frac{\partial}{\partial \theta} - \frac{\partial}{\partial \tau} B_{\tau}(\theta, \tau) \frac{\partial}{\partial \tau} + V(\theta, \tau), \quad (1)$$

where B_{θ} and B_{τ} are the diagonal kinetic parameters, $B_{\theta, \tau} = B_{\tau, \theta}$ are the nondiagonal interacting terms, and $V(\theta, \tau)$ is the potential energy function.

From the optimized geometry the kinetic parameters are deduced for each conformation by inversion of the inertial matrix, according to the Harthcock and Laane's procedure:¹⁰

$$\begin{pmatrix} I & X \\ X^t & Y \end{pmatrix},$$

where I is the inertial tensor corresponding to the overall rotation, Y is the vibrational submatrix, and X_i the interaction terms between the external and internal motions. In particular we have

$$X_{ix} = \sum_a m_a \left(\vec{r}_a \times \frac{\partial \vec{r}_a}{\partial \alpha_i} \right)_x, \quad (2)$$

$$Y_{ij} = \sum_a m_a \left(\frac{\partial \vec{r}_a}{\partial \alpha_i} \right) \cdot \left(\frac{\partial \vec{r}_a}{\partial \alpha_j} \right),$$

where m_a is the mass of atom a , \vec{r}_a its displacement vector, and α_i the conformational angle.

The numerical results obtained for the potential and the kinetic parameters, at each conformation, were adjusted to a symmetry adapted functional form.

In order to classify the energy levels and the torsional functions it is convenient to associate them with the irreducible representations of the restricted nonrigid group (r-NRG) to which they belong.^{11,12} In its most symmetric conformation, propanal presents only a symmetry plane. In the frame of the r-NRG, it means that the Hamiltonian operator (1) is invariant with respect to the sense of the rotations, i.e., under the double switch operator, \hat{V} :

$$\hat{V}f(\theta, \tau) \equiv f(-\theta, -\tau). \quad (3)$$

On the other hand, propanal presents a methyl group, so that the Hamiltonian operator must be invariant under a threefold rotation of the methyl group:

$$\hat{C}_3 f(\theta, \tau) \equiv f\left(\theta + \frac{2\pi}{3}, \tau\right). \quad (4)$$

With these definitions, the r-NRG for the symmetric and asymmetric torsions is a group of order six, isomorphic to the C_{3v} symmetry point group:

$$C_3^I \wedge V^I = G_6 \sim C_{3v}. \quad (5)$$

The C_3^I and V^I subgroups are defined by the operations (4) and (3), respectively.

Applying the r-NRG (5), the symmetry adapted analytical form for the potential function and kinetic parameters is a function of periodicity three with respect to θ :

$$V(\theta, \tau) = \sum_{K,L} A_{KL} \cos 3K\theta \cos L\tau + \sum_{K,L} B_{KL} \sin 3K\theta \sin L\tau, \quad (6)$$

where no $\cos \times \sin$ cross terms appear.

In the optimization geometry procedure, however, the methyl group is seen to lose its C_3 symmetry because of the environmental effects. Indeed, propanal does not have the C_3 symmetry. As a result, the expansion (6) appears to lose its threefold periodicity:

$$V'(\theta, \tau) = \sum_{K,L} A_{KL} \cos K\theta \cos L\tau + \sum_{K,L} B_{KL} \sin K\theta \sin L\tau. \quad (7)$$

This result, however, is incompatible with the indistinguishability of the methyl group hydrogen atoms. To solve this difficulty only the energy values which make compatible expansions (6) and (7) have to be retained. They are: $\theta = 0^\circ, 90^\circ, 180^\circ$, and 270° .⁵

The vibrational ZPE corrections were determined in the following way: the total molecular ZPE was obtained in a force calculation with the Gaussian program together with the eigenvalues of the Hessian matrix.¹³ Half of the two lowest positive eigenvalues (corresponding to the methyl and aldehyde torsions) were then subtracted from the total ZPE after their correction for their harmonicity. The resulting values were added to the potential energy function.

In the spectrum calculations, the band frequencies and the intensities are roughly determined in absolute value. The band frequencies are evaluated as the differences between energy levels, and the intensities as the electric dipole moment variations,¹⁴

$$I_{if} = \frac{g}{3BR^2 e^2} [\epsilon_i - \epsilon_f] [C_i - C_f] \langle \varphi_i | \vec{\mu} | \varphi_f \rangle^2, \quad (8)$$

where ϵ , C , and φ are the energies, populations, and vibrational functions of the initial and final states, respectively. $\vec{\mu}$ is the dipole moment written as a function of the large amplitude coordinates. It is obtained in the calculations of the potential. The populations are given by the Boltzmann statistics. g and e are the nuclear statistical weight and the electric

TABLE I. Relative anharmonic ZPE corrections, in cm^{-1} , as a function of the torsion angles.

θ τ	0	30	60	90	120	150	180
0	28.2851	46.5824	87.0997	94.5618	74.6895	26.0099	7.2109
90	9.8271	40.4106	80.3989	85.9334	53.1291	12.5918	-3.327
180	0.0000	32.1885	67.8681	80.5734	60.0697	11.8067	-7.8587
270	7.7737	26.5559	63.6169	81.7992	67.6096	15.3010	-3.3916

elemental charge, respectively. Finally, B is the square root of the kinetic parameter determinant value, and R^2 the dot product of the radius vectors of the rotations around the methyl C_3 and aldehyde C_s axes respectively, both in the *cis* preferred conformation.

The transition probabilities thus depend on the dipole moment components of the molecule, which are also functions of the angles θ and τ . The dipole moment components which lie in the symmetry plane are symmetric with respect to the \hat{V} operation and may be expressed in terms of products of cosine functions and product of sine functions of the θ and τ angles, analogous to the expansion for the potential (6). In contrast, the perpendicular component, which is antisymmetric which respect to the \hat{V} operation, must be written in terms of products of cosine \times sine and sine \times cosine functions of the θ and τ angles.

Thus, the perpendicular component will have the following analytical form:

$$\mu_c(\theta, \tau) = \sum_{K,L} A_{KL}^{cs} \cos 3K\theta \sin L\tau + \sum_{K,L} A_{KL}^{sc} \sin 3K\theta \cos L\tau. \quad (9)$$

III. METHOD AND CALCULATIONS

The potential energy function was determined by calculating the formation energy (electronic + nuclear repulsion) for a series of fixed conformations as a function of the methyl and aldehydic torsion angles. The geometry is fully optimized for each conformation and the ZPE corrections with respect to the remaining small amplitude vibration modes added to make sure that the molecule is at the equilibrium. In this way, some interaction between the remaining vibration modes is taken into account.¹⁵ In this approach the potential energy function would depend slightly on the nuclear mass, so that different isotopomers would have slightly different potential energy functions.

The GAUSSIAN 94 system of programs¹³ was used to calculate the electronic energies, structures, and dipole moments of propanal, as well as the harmonic ZPE corrections. The calculations were carried out at the second-order Møller–Plesset (MP2) level, with frozen core, and with a triple Z basis set, the 6-311G(3df,p).

A MP2 full geometry optimization was first carried out to obtain the equilibrium structure of the most stable conformers: the *cis* conformer with $\theta=180^\circ$ and $\tau=0^\circ$ at -192.745186 a.u. and two *gauche* conformers with $\theta = \pm 177.27^\circ$ and $\tau = \mp 117.4^\circ$ at -192.743293 a.u.

The methyl torsion angle, θ , was then allowed to vary from -180° to 180° at 90° intervals, and the asymmetric torsion angle, τ , from 0° to 180° at 30° intervals, and full geometry optimizations were carried out for the fixed values of the dihedral angles. The origin was taken at the equilibrium geometry, characterized by $\theta=180^\circ$ and $\tau=0^\circ$.

Simultaneously, the vibrational ZPE of the whole molecule was determined, in a force calculation, from -180° to 180° at 90° intervals for the methyl torsion, and from 0° to 180° at 30° intervals for the aldehydic torsion angle. Half of the two lowest eigenvalues of the Hessian matrix, corresponding to both torsion modes, were then subtracted, when positive and after correction for anharmonicity, from the ZPE of the whole molecule.

It is significant to point out that no improvement is observed in the frequency values if only the harmonic ZPE corrections are taken into account. As is well known, the aldehyde and methyl torsions are strongly anharmonic modes, whereas the ZPE values given by the Gaussian package are determined in the harmonic approximation. The correction for anharmonicity was carried out by calculating the ZPE values exactly for the aldehyde and methyl torsion separately and at equilibrium ($\tau=0^\circ$ and $\theta=180^\circ$) in two independent one-dimensional calculations. The values, 80.4 and 102.2 cm^{-1} , were compared to those given by the Gaussian package: 70.24 and 118.88 cm^{-1} . As a result, the harmonic approach is seen to give too small values for the aldehyde torsion and too large for the methyl one, whereas the sum of both quantities coincide approximately with the two-dimensional value, 180.2 cm^{-1} (see Table III). The ratios between the exact and the Gaussian values were then applied as correction factor to the harmonic ZPE corrections for the remaining conformations.

The resulting anharmonic ZPE corrections are gathered in Table I. These corrections were added to the total formation energy values given in Ref. 3. The potential energy function was determined by fitting these values to the symmetry adapted functional form (6), the coefficients of which are given in Table II.

From the optimized structural geometries, the kinetic parameters were recalculated for each rotamer using the technique described in Ref. 16 and the same atomic mass values as those employed in the force calculations. The kinetic functions were determined by fitting them in the same way as the potential.

The Schrödinger equation for the methyl and aldehyde torsions was solved variationally introducing the potential energy function $V(\theta, \tau)$ and the kinetic parameters $B(\theta, \tau)$ in the Hamiltonian operator (1). The solutions were developed

TABLE II. Coefficients for the potential energy expansion (Ref. 6), in cm^{-1} , after anharmonic ZPE corrections: $V(\theta, \tau) = \sum_{K,L} A_{KL} \cos K\theta \cos L\tau + \sum_{K,L} B_{KL} \sin K\theta \sin L\tau$.

Coeff.	$K=0$	$K=3$	$K=6$
$A_{K,0}$	1024.185 46	491.963 27	10.686 64
$A_{K,1}$	-112.544 13	-1.560 28	-1.973 14
$A_{K,2}$	-232.322 53	-92.376 88	-3.539 34
$A_{K,3}$	-264.225 85	-28.474 36	-1.508 19
$A_{K,4}$	-23.656 22	16.231 92	-0.896 66
$A_{K,5}$	-0.928 61	12.320 90	-0.289 38
$A_{K,6}$	10.475 58	5.056 34	-0.482 59
$B_{K,1}$		4.170 42	
$B_{K,2}$		97.286 77	
$B_{K,3}$		13.206 78	
$B_{K,4}$		-7.287 07	
$B_{K,5}$		-14.868 72	

in terms of even and odd products of trigonometric functions.

To obtain the band intensities, the oscillator strength approximation, Eq. (8), was employed. The dipole moment components of each conformation were obtained in the *ab initio* calculations. The in-plane components (referred to the

molecule in its preferred conformation), μ_a and μ_b , were adjusted to a C_3 symmetric analytical form (6), whereas the perpendicular one, μ_c , was fitted to a C_3 antisymmetric form (9).³

It is interesting to note that, although all the geometrical parameters were left free to vary and no symmetry conditions were imposed, the lowest energy *cis* rotamer has six atoms strictly in the molecular plane (Fig. 1). In this conformation the calculated principal moments of inertia are: $I_A = 30.380$; $I_B = 84.487$; and $I_C = 108.69 \text{ u \AA}^2$. These values are in good agreement with the microwave experimental values for the *cis* conformation,¹⁷ and yield an asymmetry factor of $\kappa = -0.382$. Thus the propanal molecule shows some trend to behave as a prolate top.

Thus the dipole moment component along the *a* axis, μ_a , is expected to give rise to broad parallel **a**-type bands with *P*, *Q*, and *R* branches. The dipole moment component along the *b* axis, μ_b , will give rise to unfeatured broad **b**-type bands, and that along the *c*-axis, μ_c , is expected to give linelike **c**-type bands with a well-defined *Q* branch.

Since the **c**-type bands will give rise to the main features of the IR spectrum, the μ_c will be essentially considered here. The coefficients are given in Ref. 3. The dipole moment variations used in this paper were the same for all the isoto-

TABLE III. Energy levels for the methyl (ν) and asymmetric aldehyde (ν') torsions in propanal, without and with anharmonic ZPE corrections.

Levels	Symmetry	Energy in cm^{-1}		<i>Cis</i>		<i>Gauche</i>	
		Without	With	ν	ν'	ν	ν'
0	A_1	180.17	184.197		
1-1	E	180.17	184.197	0	0
2-2	E	308.41	318.971		
-3	A_2	308.42	318.976	0	1
3-4	E	400.05	405.847		
-5	A_2	400.06	405.860	1	0
4	A_1	430.47	447.409		
5-6	E	430.51	447.433	0	2
6	A_1	518.46	530.732		
7-7	E	518.70	530.917	1	1
8-8	E	546.30	569.558		
-9	A_2	546.32	569.610	0	3
9	A_1	548.56	602.828		
10-10	E	548.56	602.829		
-11	A_2	548.56	602.831	0	0
11-12	E	548.56	602.892		
12	A_1	605.81	614.361		
13-13	E	606.07	614.538	2	0
14-14	E	630.82	648.953		
-15	A_2	631.79	649.959	1	2		
15	A_1	627.57	677.719	0	1
16-16	E	627.57	677.720		
-17	A_2	627.58	677.794		
17-18	E	627.58	677.794		

TABLE IV. Torsional frequencies (in cm^{-1}) and intensities of the aldehyde group in nondeuterated propanal: $\text{CH}_3\text{-CH}_2\text{-CHO}$, (\mathbf{d}_0), with anharmonic ZPE corrections.

Transitions		Theoretical		Experimental ^a	
$\nu \rightarrow \nu'$	Symmetry	Frequency	Intensity $\times 10^4$	Frequency	Intensity ^b
<i>cis</i> -aldehyde torsion (<i>c</i> type)					
00 \rightarrow 01	$A_1 \rightarrow A_2$	134.78	0.891	135.13	vs
	$E \rightarrow E$	134.77	0.891		
01 \rightarrow 02	$E \rightarrow E$	128.46	0.693	133.83	vs
	$A_2 \rightarrow A_1$	128.43	0.693	(128.19)	(w)
02 \rightarrow 03	$A_1 \rightarrow A_2$	122.20	0.365	121.13	ms
	$E \rightarrow E$	122.13	0.364		
03 \rightarrow 04	$E \rightarrow E$	115.18	0.140	110.73	ms
	$A_2 \rightarrow A_1$	115.09	0.140		
04 \rightarrow 05	$E \rightarrow E$	106.07	0.029	101.58	m
	$A_1 \rightarrow A_2$	106.05	0.029		
<i>gauche</i> -aldehyde torsion (<i>c</i> type)					
00 \rightarrow 01	$A_1 \rightarrow A_2$	76.51	0.260		
	$E \rightarrow e$	76.51	0.260		
	$A_2 \rightarrow A_1$	76.45	0.260		
	$E \rightarrow E$	76.44	0.260		

^aReference 2.^bvs=very strong, s=strong, ms=medium strong, and m=medium.

omers of propanal. The μ_a component, however, will be taken into account for some double quanta transitions observed in the region of 280–250 cm^{-1} , the intensities of which are enhanced by resonance with the ν_{15} band at 271.5 cm^{-1} .

IV. RESULTS AND DISCUSSIONS

The energy levels obtained for propanal with the ZPE corrections are given in Table III. As expected, it is seen that the levels are clustered into doublets and quartets, the doublets corresponding to vibrations in the *cis* conformer, whereas the quartets to vibrations in the doubly degenerate *gauche* conformer. The first torsionally excited level corresponds to the aldehyde torsion in the *cis* form, the second to the methyl torsion, the fourth to a doubly excited methyl–

TABLE V. Double quanta torsional frequencies (in cm^{-1}) and intensities of the aldehyde group in nondeuterated propanal: $\text{CH}_3\text{-CH}_2\text{-CHO}$, (\mathbf{d}_0), with anharmonic ZPE corrections.

Transitions		Theoretical		Experimental ^a	
$\nu \rightarrow \nu'$	Symmetry	Frequency	Intensity $\times 10^4$	Frequency	Intensity ^b
Double quanta <i>cis</i> -aldehyde torsion (<i>a</i> type)					
00 \rightarrow 02	$E \rightarrow E$	263.24	0.031	262.49	s,h
	$A_1 \rightarrow A_1$	263.21	0.010		
01 \rightarrow 03	$A_2 \rightarrow A_2$	250.63	0.059	250.69	m,h
	$E \rightarrow E$	250.59	0.030		
10 \rightarrow 12	$A_2 \rightarrow A_2$	244.10	0.024	244.18	m
	$E \rightarrow E$	244.68	0.017		
02 \rightarrow 04	$E \rightarrow E$	237.30	0.026	237.91	w,h
	$A_1 \rightarrow A_1$	237.28	0.010		
11 \rightarrow 13	$E \rightarrow E$	231.76	0.018	232.91	w,h
	$A_1 \rightarrow A_1$	228.98	0.014		

^aReference 2.^bvs=very strong, s=strong, m=medium, w=weak, h=head.TABLE VI. Torsional frequencies (in cm^{-1}) and intensities of methyl group in nondeuterated propanal: $\text{CH}_3\text{-CH}_2\text{-CHO}$, (\mathbf{d}_0), with anharmonic ZPE corrections.

Transitions		Theoretical		Experimental ^a	
$\nu \rightarrow \nu'$	Symmetry	Frequency	Intensity $\times 10^4$	Frequency	Intensity ^b
<i>cis</i> -methyl torsion (<i>c</i> type)					
00 \rightarrow 10	$A_1 \rightarrow A_2$	221.66	0.249	219.90	s
	$E \rightarrow E$	221.65	0.249		
10 \rightarrow 20	$E \rightarrow E$	208.69	0.211	207.44	s
	$A_2 \rightarrow A_1$	208.50	0.213		
20 \rightarrow 30	$A_1 \rightarrow A_2$	196.18	0.113	193.69	m
	$E \rightarrow E$	194.47	0.110		
<i>gauche</i> -methyl torsion (<i>c</i> type)					
00 \rightarrow 10	$E \rightarrow E$	210.55	0.008	210.21	w
	$A_2 \rightarrow A_1$	210.55	0.007		
	$E \rightarrow E$	210.54	0.008		
	$A_1 \rightarrow A_2$	210.54	0.007		

^aReference 2.^bs=strong, ms=medium strong, m=medium, w=weak.

aldehyde torsion level, whereas the fundamental level for the aldehyde torsion in the *gauche* form appears at higher value. Also in Table III the energy levels found without the ZPE correction are given. It is seen that the ZPE corrected levels appear at higher values. Some inversions are observed at very excited levels.

The FIR spectra of propanal and some isotopomers were recorded by Durig *et al.* in the region of 300–100 cm^{-1} .^{1,2} The spectra are complex and consist of series of linelike features superimposed on a strong absorbing background.¹ In addition, series of very strong bands associated with the ν_{15} in-plane bending mode appear in the region of 280–250 cm^{-1} .

The main features of the FIR spectrum, calculated with the ZPE correction, at 0 °C for the *a*- or *c*-band types in nondeuterated propanal are given in Tables IV–VII, together

TABLE VII. Torsional frequencies (in cm^{-1}) and intensities for the methyl–aldehyde combination bands in nondeuterated propanal: $\text{CH}_3\text{-CH}_2\text{-CHO}$, (\mathbf{d}_0), with anharmonic ZPE corrections.

Transitions		Theoretical		Experimental ^a	
$\nu \rightarrow \nu'$	Symmetry	Frequency	Intensity $\times 10^4$	Frequency	Intensity ^b
<i>cis</i> -aldehyde–methyl combination bands (<i>c</i> type)					
02 \rightarrow 12	$A_1 \rightarrow A_2$	202.55	0.009
	$E \rightarrow E$	201.52	0.008
11 \rightarrow 21	$A_1 \rightarrow A_2$	196.72	0.030	195.28	w
	$E \rightarrow E$	193.98	0.034	192.56	w
10 \rightarrow 11	$E \rightarrow E$	125.07	0.172	124.87	m
	$A_2 \rightarrow A_1$	124.87	0.171		
11 \rightarrow 12	$A_1 \rightarrow A_2$	119.23	0.144	116.46	s
	$E \rightarrow E$	118.04	0.137		
12 \rightarrow 13	$E \rightarrow E$	113.72	0.083	113.96	w
	$A_2 \rightarrow A_1$	109.75	0.069	108.06	w
20 \rightarrow 21	$A_1 \rightarrow A_2$	113.09	0.025	113.09	w
	$E \rightarrow E$	110.36	0.022	107.76	w
13 \rightarrow 14	$A_1 \rightarrow A_2$	104.08	0.016	102.33	w
	$E \rightarrow E$	90.06	0.009	95.59	vw

^aReference 2.^bs=strong, ms=medium strong, m=medium, w=weak, vw=very weak.

with the last experimental data for comparison purposes.²

The frequencies and intensities of the five lowest **c**-type bands assigned to the aldehyde torsion in the *cis* conformer are gathered in Table IV. They appear in the spectrum region of 140–100 cm⁻¹. The chosen assignment is based on both the frequencies and intensities, and coincides to that of Durig,² but other assignments are possible. A clear progression is observed. Although the highest state calculated frequencies are too large, a very satisfactory correlation frequency intensity is observed. The first sequence transition value (128.46 cm⁻¹) does not match the somewhat surprising experimental one (133.83 cm⁻¹), but coincides with a weak unexplained band (128.18 cm⁻¹).

Table IV also shows the calculated frequencies and intensities of the fundamental **c**-type bands for the aldehyde torsion in the *gauche* conformer. These appear at lower frequencies, 76 cm⁻¹. Unfortunately no band is reported by Durig *et al.* in this region of the spectrum. These authors report a band at 96.59 cm⁻¹ which can be tentatively assigned to the 05→06 transition of the *cis* conformer.

Some **a**-band type transitions of the FIR spectrum of *cis* conformers of propanal are presented in Table V. All these transitions are theoretically relatively weak. They appear in the region of 260–220 cm⁻¹. Here again a progression is observed. The experimental values of the frequencies and intensities of broad bands reported by Durig *et al.* in this interval are also gathered in Table IV. Here a very good agreement is observed.

The frequencies and intensities of the three lowest **c**-type bands assigned to the methyl torsion in the *cis* conformer are gathered in Table VI. They appear at higher frequencies, 220–190 cm⁻¹. A clear progression is observed. Here the theoretical values appear to be 2 cm⁻¹ too high, in contrast with the ZPE noncorrected values the accuracy of which has to be considered as accidental. Also in Table VI the fundamental frequency for the methyl torsion in the *gauche* conformer is calculated at 210.55 cm⁻¹. This band can be associated to a weak band given by Durig at 210.21 cm⁻¹.

The frequencies and intensities of some excited **c**-type hot bands assigned to the aldehyde torsion in the *cis* conformer are gathered in Table VII. All these transitions are weak and appear also in the regions of 200–190 and 120–100 cm⁻¹. Clear progressions are again observed. Some weak experimental frequencies reported by Durig *et al.* in these regions are tentatively assigned to these combination bands.

In Table VIII, the root mean square deviations, between the calculated frequencies, without and with anharmonic ZPE corrections, and the experimental ones, for the aldehyde, double quanta, and methyl torsions, combination bands, and fundamentals are given. It is seen that the introduction of the anharmonic ZPE corrections gives rise to much smaller deviations, except in the case of the ZPE noncorrected methyl torsion, the values of which could be explained as error compensations. Anyway, the rms deviation is smaller than 1 cm⁻¹ in the case of the fundamentals.

TABLE VIII. Root mean square deviations (in cm⁻¹) between some calculated, without (Ref. 3) and with the anharmonic ZPE corrections, and the experimental frequencies of the FIR spectrum of nondeuterated propanal: CH₃–CH₂–CHO, (*d*₀).

Series	Without	With	<i>N</i>	<i>N'</i> ^a
<i>Cis</i> -aldehyde torsion	6.73	3.62	10	10
Double quanta torsion	10.04	1.53	8	8
Double quanta torsion	...	1.41	...	10
Methyl torsion	1.58	1.76	6	6
Combination bands	3.82	2.71	10	10
Combination bands	...	2.21	...	12
Fundamentals	7.09	0.96	8	8

^a*N* and *N'* are the numbers of frequencies retained in each series, without and with the anharmonic ZPE corrections, respectively.

V. CONCLUSIONS

The calculated FIR spectra of some symmetric isotopomers of propanal (propanal-*d*₅), obtained without the ZPE corrections, showed some serious disagreement with the experimental data, when compared with that of propanal-*d*₀.⁴ This disagreement suggested to us to introduce in the calculations some mass effect such as the vibrational (ZPE) with respect to the remaining small amplitude vibration modes. Single harmonic ZPE corrections were verified by us to yield still worse frequency values.

The introduction of the ZPE corrections, calculated as described in this paper, i.e., considering the anharmonicity of the torsion modes, seems to reproduce more accurately the experimental FIR spectrum. The theoretical results agree fairly well with experiment except for small errors of 1–3 cm⁻¹, usually in excess. This small deviation is probably due to some inaccuracy in the potential energy function. Anyway, 24 of the 25 experimental bands are successfully reproduced and assigned. The application of the method to propanal-*d*₅ is now in progress.

It may be concluded that the anharmonic ZPE corrections have to be considered to reach more accuracy even in the nondeuterated species in this kind of calculation.

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