

# A Theoretical Study of the Methyl and Aldehyde Torsion FIR Spectra in Symmetric Propanal Isotopomers

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This paper is an extension of the techniques developed by us [A. Vivier-Bunge, V. H. Uc, and Y. G. Smeyers, *J. Chem. Phys.* **109**, 2279 (1998)] for standard propanal. In that paper the potential energy surface for the simultaneous methyl and asymmetric aldehydic torsions was calculated at RHF/MP2 level using the 6-311(3df,p) basis set for propanal. The fit of the energy values to symmetry-adapted functional forms was carried out by using the 28 energy values which retain the  $C_3$  dynamical symmetry of the methyl group in the optimization procedure. With this potential, as well as with the kinetic parameters and the electric dipole moment variations, the FIR frequencies and intensities for the methyl and aldehyde torsions of seven symmetric isotopomers of propanal were determined theoretically using two-dimensional calculations. The calculated spectra of propanal and three of its isotopomers were compared with the available experimental data. It is found that the calculations for the *cis* conformer satisfactorily reproduce the aldehyde and methyl torsion spectra and furnish also methyl torsionally excited progressions for the aldehyde torsion modes. The methyl torsion frequencies agree especially well whenever the methyl group is nondeuterated. The small deviations encountered for the deuterated compound are probably due to some mass effect, such as the zero-point vibrational energy correction, which is not taken into account in the present calculations. Finally, the influence of the deuteration on the intensities is discussed. © 2000 Academic Press

**Key Words:** nonrigid molecules; large-amplitude vibration modes; *ab initio* FIR spectrum determination; propanal isotopomer FIR torsion spectra.

## 1. INTRODUCTION

The far-infrared (FIR) spectrum of gaseous propanal- $d_0$  ( $\text{CH}_3\text{--CH}_2\text{--COH}$ ) was recorded by Durig *et al.* in the region 300–100  $\text{cm}^{-1}$  (1). Assignments were proposed for 27 bands from a one-dimensional calculation. In particular, the fundamental band for the aldehyde torsion in the *cis*-rotamer ( $\nu_{24}$ ) was assigned to an infrared absorption at 135  $\text{cm}^{-1}$  and the corresponding torsion in the *gauche* form at 113.1  $\text{cm}^{-1}$ . Later the infrared spectrum was also reported by Van Nuffel *et al.* These authors gave assignments for fundamental bands of the *cis* and *gauche* conformers (2).

In a previous paper (3), the FIR spectrum for the double aldehydic and methyl torsions was deduced by us using very sophisticated *ab initio* two-dimensional calculations. In these calculations the  $C_3$  symmetry of the methyl group as well as the variational principle were preserved simultaneously (symmetry dilemma) (4). 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.

In the meantime, the FIR spectrum of propanal was again recorded by Durig *et al.*, who proposed new assignments

especially for the methyl torsion bands. In particular, the fundamental band for the methyl torsion in the *cis*-rotamer was assigned at 219.9  $\text{cm}^{-1}$ , in coincidence with our previous calculations (3).

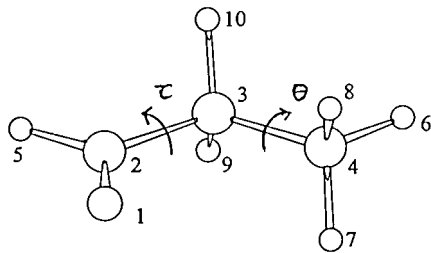
In the same paper, the FIR spectrum of three symmetric isotopomers of propanal- $d_1$  ( $\text{CH}_3\text{--CH}_2\text{--COD}$ ), - $d_2$  ( $\text{CH}_3\text{--CD}_2\text{--COH}$ ), and - $d_3$  ( $\text{CD}_3\text{--CD}_2\text{--COH}$ ) (5) were given together with their possible assignments. A request of P. Groner motivated the present work. The purpose of this paper is to repeat the propanal calculations, extend them to its symmetric isotopomers, and compare the calculated frequencies and intensities with the available experimental data.

## 2. THEORY

All the calculations presented here were developed following a series of previous papers (3, 6–8).

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

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**FIG. 1.** Structure of propanal in its *cis*-preferred conformation. Numbering of the atoms. Torsion angles,  $\tau$  and  $\theta$ .

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

where  $B_{\theta}$  and  $B_{\tau}$  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 (9),

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

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

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

$$Y_{ij} = \sum_a m_a \left( \frac{\partial \mathbf{r}_a}{\partial \alpha_i} \right) \cdot \left( \frac{\partial \mathbf{r}_a}{\partial \alpha_j} \right), \quad [2]$$

where  $m_a$  is the mass of atom  $a$ ,  $\mathbf{r}_a$  is its displacement vector, and  $\alpha_i$  is 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.

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 (10, 11). 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  $\theta$ ,

$$V(\theta, \tau) = \sum_{K,L} A_{KL}^{cc} \cos 3K\theta \cos L\tau + \sum_{K,L} A_{KL}^{ss} \sin 3K\theta \sin L\tau, \quad [6]$$

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] should lose its threefold periodicity:

$$V'(\theta, \tau) = \sum_{K,L} A_{KL}^{cc} \cos K\theta \cos L\tau + \sum_{K,L} A_{KL}^{ss} \sin K\theta \sin L\tau. \quad [7]$$

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  $270^\circ$  (4).

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 (12),

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

where  $\epsilon$ ,  $C$ , and  $\varphi$  are the energies, populations, and vibrational functions of the initial and final states, respectively.  $\mu$  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 elemental charge, respectively. Finally,  $B$  is the square root of the kinetic parameter determinant value, and  $R^2$  is 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  $\theta$  and  $\tau$ . 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  $\theta$  and  $\tau$  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  $\theta$  and  $\tau$  angles.

Thus, the perpendicular component will have the analytical form:

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

### 3. METHOD AND CALCULATIONS

The potential energy function is 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 to make sure that the molecule is at equilibrium with respect to the remaining small-amplitude vibration modes. In this way, some interaction between the vibration modes is taken into account.

A better way to take them into account would be to consider the zero-point vibrational energy (13). In this second approach the potential energy function would depend slightly on the nuclear mass, so that different isotopomers would have slightly different potential energy functions. In the present calculations we will not include the zero-point vibrational energy.

The GAUSSIAN94 system of programs (14) was used to calculate the electronic energies, structures, and dipole moments of different conformers of propanal. The calculations were carried out at the 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  $-192.745186$

TABLE 1  
Torsional Frequencies (in  $\text{cm}^{-1}$ ) and Intensities of the Aldehyde Group in Nondeuterated Propanal:  $\text{CH}_3\text{-CH}_2\text{-CHO}$  ( $d_0$ )

Transitions		Theoret.		Experim.[5]	
cis aldehyde torsion (c-type)					
$\nu \rightarrow \nu'$	symm.	freq.	int. $\times 10^4$	freq.	intens <sup>a</sup> .
00 $\rightarrow$ 01	$A_1 \rightarrow A_2$	128.24	0.835	135.13	vs
	$E \rightarrow E$	128.23	0.834		
01 $\rightarrow$ 02	$E \rightarrow E$	122.09	0.617	133.83	vs
	$A_2 \rightarrow A_1$	122.05	0.617		
02 $\rightarrow$ 03	$A_1 \rightarrow A_2$	115.84	0.310	116.46	s
	$E \rightarrow E$	115.74	0.310		
03 $\rightarrow$ 04	$E \rightarrow E$	108.61	0.109	110.73	ms
	$A_2 \rightarrow A_1$	108.53	0.109		
04 $\rightarrow$ 05	$E \rightarrow E$	98.81	0.016	101.58	m
	$A_1 \rightarrow A_2$	98.77	0.016		
gauche aldehyde torsion (c-type)					
00 $\rightarrow$ 01	$A_1 \rightarrow A_2$	79.02	0.321	96.59 (91.8) <sup>b</sup>	vw
	$E \rightarrow E$	79.02	0.321		
	$A_2 \rightarrow A_1$	79.01	0.321		
	$E \rightarrow E$	79.01	0.321		
Double quanta cis aldehyde torsion (a-type)					
00 $\rightarrow$ 02	$E \rightarrow E$	250.33	0.047	262.49	m,h
	$A_1 \rightarrow A_1$	250.29	0.046		
01 $\rightarrow$ 03	$A_2 \rightarrow A_2$	237.93	0.089	250.69	w,h
	$E \rightarrow E$	237.93	0.089		
10 $\rightarrow$ 12	$A_2 \rightarrow A_2$	231.74	0.000	237.91	w,h
	$E \rightarrow E$	230.77	0.004		
02 $\rightarrow$ 04	$E \rightarrow E$	224.46	0.017	232.15	w,h
	$A_1 \rightarrow A_1$	224.43	0.055		

<sup>a</sup> vs = very strong, s = strong, m = medium, w = weak, vw = very weak, h = head.

<sup>b</sup> van Nuffel, Ref. (2).

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,  $\theta$ , was then allowed to vary from  $-180^\circ$  to  $180^\circ$  at  $90^\circ$  intervals, and the asymmetric torsion angle,  $\tau$ , from  $0^\circ$  to  $180^\circ$  at  $30^\circ$  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  $\tau = 0^\circ$ .

In the present calculations, we use the same potential energy function, obtained with 28 points, for the different isotopomers in such a way that the mass effects will be only introduced through the kinetic parameters. From the optimized structural geometries, the kinetic parameters were calculated for each rotamer using the technique described in Ref. (15). The kinetic functions were determined by fitting them in the same way as the potential.

TABLE 2

**Torsional Frequencies (in  $\text{cm}^{-1}$ ) and Intensities of the Methyl Group in Nondeuterated Propanal:  $\text{CH}_3\text{-CH}_2\text{-CHO}$  ( $d_0$ )**

Transitions		Theoret.		Experim.[5]	
cis methyl torsion (c-type)					
$\nu \rightarrow \nu'$	symm.	freq.	int. $\times 10^4$	freq.	intens <sup>a</sup> .
00 $\rightarrow$ 10	$A_1 \rightarrow A_2$	219.88	0.221	219.90	s
	E $\rightarrow$ E	219.87	0.221		
10 $\rightarrow$ 20	E $\rightarrow$ E	206.02	0.169	207.44	s
	$A_2 \rightarrow A_1$	205.75	0.170		
20 $\rightarrow$ 30	$A_1 \rightarrow A_2$	192.68	0.089	193.28	m
	E $\rightarrow$ E	190.15	0.086		
cis aldehyde-methyl combination bands (c-type)					
02 $\rightarrow$ 12	$A_1 \rightarrow A_2$	201.31	0.014	210.21	w
	E $\rightarrow$ E	201.30	0.012		
11 $\rightarrow$ 21	$A_1 \rightarrow A_2$	193.89	0.018	195.28	w
	E $\rightarrow$ E	190.49	0.023		
10 $\rightarrow$ 11	E $\rightarrow$ E	118.66	0.159	124.10	m
	$A_2 \rightarrow A_1$	118.40	0.157		
11 $\rightarrow$ 12	$A_1 \rightarrow A_2$	113.34	0.125	121.13	ms
	E $\rightarrow$ E	112.12	0.120		
12 $\rightarrow$ 13	E $\rightarrow$ E	108.20	0.066	113.96	w
	$A_2 \rightarrow A_1$	104.42	0.058		
20 $\rightarrow$ 21	$A_1 \rightarrow A_2$	106.53	0.024	107.76	w
	E $\rightarrow$ E	103.12	0.021		
		102.33			w

<sup>a</sup> s = strong, mw = medium weak, w = weak, vw = very weak.

The Schrödinger equation for the methyl and aldehyde torsions was solved variationally by introducing the potential energy function  $V(\theta, \tau)$  and the kinetic parameters  $B(\theta, \tau)$  in the Hamiltonian operator [1]. The solutions were developed in terms of even and odd products of trigonometric functions.

The energy levels encountered for nondeuterated propanal are given in Ref. (3). In that paper, it can be 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 energy levels encountered for the symmetric deuterated isotopomers of propanal show the same trends.

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),  $\mu_a$  and  $\mu_b$ , were adjusted to a  $C_3$  symmetric analytical form [6], whereas the perpendicular one,  $\mu_c$ , 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  $I_C = 108.69$  amu  $\text{\AA}^2$ . These values are in good agreement with the microwave experimental values for the *cis* conformation (16) 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,  $\mu_a$ , 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,  $\mu_b$ , will give rise to unfeatured broad *b*-type bands, and that along the *c*-axis,  $\mu_c$ , is expected to give line-like *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  $\mu_c$  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 3

**Torsional Frequencies (in  $\text{cm}^{-1}$ ) and Intensities of the Aldehyde Group in Partially Deuterated Propanal:  $\text{CH}_3\text{-CH}_2\text{-CDO}$  ( $d_1$ )**

Transitions		Theoret.		Experim. [5]	
cis aldehyde torsion (c-type)					
$\nu \rightarrow \nu'$	symm.	freq.	int. $\times 10^4$	freq.	intens <sup>a</sup> .
00 $\rightarrow$ 01	A <sub>1</sub> $\rightarrow$ A <sub>2</sub>	120.11	0.796	126.43	vs
	E $\rightarrow$ E	120.10	0.796		
01 $\rightarrow$ 02	E $\rightarrow$ E	114.31	0.609	115.88	vs
	A <sub>2</sub> $\rightarrow$ A <sub>1</sub>	114.29	0.609		
02 $\rightarrow$ 03	A <sub>1</sub> $\rightarrow$ A <sub>2</sub>	108.39	0.322	112.25	s
	E $\rightarrow$ E	108.38	0.322		
03 $\rightarrow$ 04	E $\rightarrow$ E	101.87	0.128	104.80	s
	A <sub>2</sub> $\rightarrow$ A <sub>1</sub>	101.86	0.128		
04 $\rightarrow$ 05	A <sub>1</sub> $\rightarrow$ A <sub>2</sub>	94.10	0.031	96.43	m
	E $\rightarrow$ E	93.06	0.002		
gauche aldehyde torsion (c-type)					
00 $\rightarrow$ 01	A <sub>1</sub> $\rightarrow$ A <sub>2</sub>	73.30	0.273	85.15	vw
	E $\rightarrow$ E	73.30	0.273		
	A <sub>2</sub> $\rightarrow$ A <sub>1</sub>	73.29	0.273		
	E $\rightarrow$ E	73.29	0.273		
Double quanta cis aldehyde torsion (a-type)					
00 $\rightarrow$ 02	E $\rightarrow$ E	234.41	0.032	242.58	w,h
	A <sub>1</sub> $\rightarrow$ A <sub>1</sub>	234.39	0.051		
10 $\rightarrow$ 12	A <sub>2</sub> $\rightarrow$ A <sub>2</sub>	222.78	0.013	231.35	vw
	E $\rightarrow$ E	222.32	0.007		
01 $\rightarrow$ 03	A <sub>2</sub> $\rightarrow$ A <sub>2</sub>	222.67	0.031	228.32	w,h
	E $\rightarrow$ E	222.67	0.058		
02 $\rightarrow$ 04	A <sub>1</sub> $\rightarrow$ A <sub>1</sub>	210.25	0.093	217.13	w,h
	E $\rightarrow$ E	210.25	0.068		

<sup>a</sup> vs = very strong, s = strong, m = medium, w = weak, vw = very weak, h = head.

**TABLE 4**  
**Torsional Frequencies (in  $\text{cm}^{-1}$ ) and Intensities of the Methyl Group in Partially Deuterated Propanal:  $\text{CH}_3\text{-CH}_2\text{-CDO}$  ( $d_1$ )**

Transitions		Theoret.		Experim.[5]	
cis methyl torsion (c-type)					
$\nu \rightarrow \nu'$	symm.	freq.	int. $\times 10^4$	freq.	intens <sup>a</sup> .
00 $\rightarrow$ 10	A $_1\rightarrow$ A $_2$	211.52	0.097	211.53	m
	E $\rightarrow$ E	211.50	0.097		
10 $\rightarrow$ 20	E $\rightarrow$ E	197.00	0.104	198.51	m
	A $_2\rightarrow$ A $_1$	196.69	0.106		
20 $\rightarrow$ 30	A $_1\rightarrow$ A $_2$	182.96	0.075	183.73	w
	E $\rightarrow$ E	180.54	0.078		
cis aldehyde-methyl combination bands (c-type)					
02 $\rightarrow$ 12	A $_1\rightarrow$ A $_2$	199.91	0.020	204.65	w
	E $\rightarrow$ E	199.42	0.019		
11 $\rightarrow$ 21	A $_1\rightarrow$ A $_2$	188.61	0.008	186.92	w
	E $\rightarrow$ E	185.55	0.011		
10 $\rightarrow$ 11	E $\rightarrow$ E	113.98	0.019	113.91	w
	A $_2\rightarrow$ A $_1$	113.77	0.019		
11 $\rightarrow$ 12	A $_1\rightarrow$ A $_2$	109.01	0.154	107.88	w
	E $\rightarrow$ E	108.33	0.150		
20 $\rightarrow$ 21	A $_1\rightarrow$ A $_2$	105.70	0.038	105.57	mw
	E $\rightarrow$ E	102.52	0.033		
12 $\rightarrow$ 13	E $\rightarrow$ E	103.90	0.009	99.55	vw
	A $_2\rightarrow$ A $_1$	102.51	0.008		

<sup>a</sup> m = medium, mw = medium weak, w = weak, vw = very weak.

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

## 4. RESULTS AND DISCUSSIONS

### 4.1. Propanal- $d_0$ Spectrum

The FIR spectra of propanal and isotopomers were recorded by Durig *et al.* in the region 300–100  $\text{cm}^{-1}$  (1, 5). The spectra are complex and consist of a series of linelike features superimposed on a strong absorbing background (1). In addition, a series of very strong bands associated with the  $\nu_{15}$  in-plane bending mode appear in the region 280–250  $\text{cm}^{-1}$ .

The main features of the FIR spectrum, calculated at 0°C for the *a*- or *c*-band types in nondeuterated propanal, were presented in Ref. (3). The frequencies and intensities were recalculated and some bands reassigned. They are given in Tables 1 and 2, for comparison purposes, together with the last experimental data (5).

The frequencies and intensities of the five lowest *c*-type bands assigned to the aldehyde torsion in the *cis* conformer are

gathered in Table 1. They appear in the spectrum region 130–100  $\text{cm}^{-1}$ . The proposed assignment is based on both the frequencies and intensities. A clear progression is observed. In the same table, some experimental values of frequencies and intensities reported recently in this interval by Durig *et al.* are also given (5). Although the calculated frequencies are in general too low, a satisfactory correlation is observed.

The same table 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, 79  $\text{cm}^{-1}$ . Unfortunately no band is reported by Durig *et al.* in this region of the spectrum. These authors report a band at 96.59  $\text{cm}^{-1}$  which can be tentatively assigned to the fundamental *gauche* transition located by Van Nuffel *et al.* at 91.8  $\text{cm}^{-1}$  (2). However, it can be also related to the 05  $\rightarrow$  06 transition of the *cis* conformer.

**TABLE 5**  
**Torsional Frequencies (in  $\text{cm}^{-1}$ ) and Intensities of the Aldehyde Group in Partially Deuterated Propanal:  $\text{CH}_3\text{-CD}_2\text{-CHO}$  ( $d_2$ )**

Transitions		Theoret.		Experim. [5]	
cis aldehyde torsion (c-type)					
$\nu \rightarrow \nu'$	symm.	freq.	int. $\times 10^4$	freq.	intens. <sup>a</sup>
00 $\rightarrow$ 01	$A_1 \rightarrow A_2$	125.21	0.872	126.39	vs
	$E \rightarrow E$	125.21	0.872		
01 $\rightarrow$ 02	$E \rightarrow E$	119.01	0.644	115.40	vs
	$A_2 \rightarrow A_1$	118.99	0.644		
02 $\rightarrow$ 03	$A_1 \rightarrow A_2$	112.64	0.325	112.15	s
	$E \rightarrow E$	112.62	0.324		
03 $\rightarrow$ 04	$E \rightarrow E$	105.40	0.117	104.15	s
	$A_2 \rightarrow A_1$	105.38	0.117		
04 $\rightarrow$ 05	$E \rightarrow E$	96.69	0.007	94.56	mw
	$A_1 \rightarrow A_2$	96.49	0.031		
gauche aldehyde torsion (c-type)					
00 $\rightarrow$ 01	$A_1 \rightarrow A_2$	77.32	0.316		
	$E \rightarrow E$	77.32	0.316		
	$A_2 \rightarrow A_1$	77.31	0.316		
	$E \rightarrow E$	77.31	0.316		
Double quanta cis aldehyde torsion (a-type)					
00 $\rightarrow$ 02	$E \rightarrow E$	244.22	0.035	242.55	w,h
	$A_1 \rightarrow A_1$	244.21	0.055		
10 $\rightarrow$ 12	$A_2 \rightarrow A_2$	230.94	0.001	232.62	vw
	$E \rightarrow E$	230.42	0.007		
01 $\rightarrow$ 03	$E \rightarrow E$	231.63	0.063	228.40	vw,h
	$A_2 \rightarrow A_2$	231.63	0.033		
02 $\rightarrow$ 04	$A_1 \rightarrow A_1$	218.02	0.102	216.40	vw,h
	$E \rightarrow E$	218.02	0.075		

<sup>a</sup> vs = very strong, s = strong, mw = medium weak, w = weak, vw = very weak, h = head.



TABLE 6

**Torsional Frequencies (in  $\text{cm}^{-1}$ ) and Intensities of the Methyl Group in Partially Deuterated Propanal:  $\text{CH}_3\text{-CD}_2\text{-CHO}$  ( $d_2$ )**

Transitions		Theoret.		Experim.[5]	
cis methyl torsion (c-type)					
$\nu \rightarrow \nu'$	symm.	freq.	int. $\times 10^4$	freq.	intens. <sup>a</sup>
00 $\rightarrow$ 10	$A_1\rightarrow A_2$	210.24	0.121	210.20	s
	E $\rightarrow$ E	210.23	0.121		
10 $\rightarrow$ 20	E $\rightarrow$ E	196.52	0.123	196.23	s
	$A_2\rightarrow A_1$	196.24	0.124		
20 $\rightarrow$ 30	$A_1\rightarrow A_2$	183.47	0.083	181.64	ms
	E $\rightarrow$ E	181.53	0.087		

cis aldehyde-methyl combination bands (c-type)					
02 $\rightarrow$ 12	$A_1\rightarrow A_2$	196.98	0.020	203.82	w
	E $\rightarrow$ E	196.43	0.020	200.02	vw
11 $\rightarrow$ 21	$A_1\rightarrow A_2$	186.98	0.010	185.19	w
	E $\rightarrow$ E	184.07	0.013	183.45	vw
10 $\rightarrow$ 11	E $\rightarrow$ E	118.20	0.199	120.37	m
	$A_2\rightarrow A_1$	118.00	0.197		
11 $\rightarrow$ 12	$A_1\rightarrow A_2$	112.94	0.159	111.40	ms
	E $\rightarrow$ E	112.22	0.155		
20 $\rightarrow$ 21	$A_1\rightarrow A_2$	108.74	0.040	109.12	vw
	E $\rightarrow$ E	105.76	0.033		
12 $\rightarrow$ 13	E $\rightarrow$ E	107.71	0.086	106.82	w
	$A_2\rightarrow A_1$	105.96	0.081		

<sup>a</sup> s = strong, ms = medium strong, m = medium, w = weak, vw = very weak.

Some *a*-band-type transitions of the FIR spectrum of propanal are also presented in Table 1. All these transitions are relatively weak. Those of the *cis* conformer appear in the region 250–220  $\text{cm}^{-1}$ . 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 the same table.

The frequencies and intensities of the three lowest *c*-type bands assigned to the methyl torsion in the *cis* conformer are gathered in Table 2. They appear at higher frequencies, 220–190  $\text{cm}^{-1}$ . Here again a clear progression is observed. In the same table, the experimental values of frequencies and intensities reported in this interval by Durig *et al.* are also given for comparison (1). Although Durig *et al.* assigned initially one of these frequencies to the *gauche* conformer, a very good agreement between these three lowest calculated and measured frequencies is observed. The theoretical and experimental fundamental frequencies are located at 219.88 and 219.90  $\text{cm}^{-1}$ , respectively (5).

The frequencies and intensities of some excited *c*-type hot bands assigned to the aldehyde torsion in the *cis* conformer are gathered in Table 2. All these transitions are weak and appear

also in the region 200–190 and 120–100  $\text{cm}^{-1}$ . Clear progressions are again observed. Some weak experimental frequencies reported by Durig *et al.* in these regions are tentatively assigned to these combination bands.

#### 4.2. Propanal- $d_1$ , $-d_2$ , and $-d_5$ Spectra

The calculations, carried out at 0°C for the *a*- or *c*-band types, were extended to all the symmetric isotopomers of propanal. The main features of the FIR spectra of the three symmetric isotopomers measured by Durig *et al.* (5),  $\text{CH}_3\text{-CH}_2\text{-COD}$ ,  $\text{CH}_3\text{-CD}_2\text{-COH}$ , and  $\text{CD}_3\text{-CD}_2\text{-COH}$ , are presented in Tables 3–8, together with the experimental data.

The frequencies and intensities of the five lowest *c*-type bands assigned to the aldehyde torsion in the *cis* conformer are gathered in Tables 3, 5, and 7. They appear also in the spectrum region 130–90  $\text{cm}^{-1}$ . Clear progressions are observed. In

TABLE 7

**Torsional Frequencies (in  $\text{cm}^{-1}$ ) and Intensities of the Aldehyde Group in Partially Deuterated Propanal:  $\text{CD}_3\text{-CD}_2\text{-CHO}$  ( $d_5$ )**

Transitions		Theoret.		Experim.[5]	
cis aldehyde torsion (c-type)					
$\nu \rightarrow \nu'$	symm.	freq.	int. $\times 10^4$	freq.	intens <sup>a</sup> .
00 $\rightarrow$ 01	E $\rightarrow$ E	106.32	0.516	103.53	vs
	$A_1 \rightarrow A_2$	106.26	0.515		
01 $\rightarrow$ 02	E $\rightarrow$ E	103.33	0.501	100.40	vs
	$A_2 \rightarrow A_1$	103.12	0.497		
02 $\rightarrow$ 03	E $\rightarrow$ E	100.78	0.357	98.86	s
	$A_1 \rightarrow A_2$	100.42	0.352		
03 $\rightarrow$ 04	E $\rightarrow$ E	98.42	0.213	95.74	m
	$A_2 \rightarrow A_1$	97.68	0.210		
04 $\rightarrow$ 05	E $\rightarrow$ E	94.79	0.106	86.60	mw
	$A_2 \rightarrow A_1$	94.01	0.103		
gauche aldehyde torsion (c-type)					
00 $\rightarrow$ 01	$A_1 \rightarrow A_2$	75.20	0.326		
	E $\rightarrow$ E	75.20	0.326		
	$A_2 \rightarrow A_1$	75.20	0.326		
	E $\rightarrow$ E	75.20	0.326		
Double quanta cis aldehyde torsion (a-type)					
00 $\rightarrow$ 02	E $\rightarrow$ E	209.64	0.010	213.40	w,h
	$A_1 \rightarrow A_1$	209.37	0.010		
01 $\rightarrow$ 03	E $\rightarrow$ E	204.11	0.021	204.30	vw,h
	$A_2 \rightarrow A_2$	203.44	0.021		
02 $\rightarrow$ 04	E $\rightarrow$ E	199.21	0.031	197.40	vvw
	$A_1 \rightarrow A_1$	198.02	0.027		
10 $\rightarrow$ 12	E $\rightarrow$ E	193.84	0.004		
	$A_2 \rightarrow A_2$	192.48	0.006		

<sup>a</sup> vs = very strong, s = strong, m = medium, w = weak, vw = very weak, vvw = very very weak, h = head.

TABLE 8

**Torsional Frequencies (in  $\text{cm}^{-1}$ ) and Intensities of the Methyl Group in Partially Deuterated Propanal:  $\text{CD}_3\text{-CD}_2\text{-CHO}$  ( $d_5$ )**

Transitions		Theoret.		Experim. [5]	
cis methyl torsion (c-type)					
$\nu \rightarrow \nu'$	symm.	freq.	int. $\times 10^4$	freq.	intens <sup>a</sup> .
00 $\rightarrow$ 10	E $\rightarrow$ E	181.29	0.505	177.12	s
	$A_1\rightarrow A_2$	181.25	0.506	176.27	m
10 $\rightarrow$ 20	E $\rightarrow$ E	174.19	0.310	171.78	s
	$A_2\rightarrow A_1$	174.09	0.312	169.28	m
20 $\rightarrow$ 30	E $\rightarrow$ E	167.10	0.021	166.33	m
	$A_1\rightarrow A_2$	167.00	0.045		
cis aldehyde-methyl combination bands (c-type)					
11 $\rightarrow$ 21	E $\rightarrow$ E	164.96	0.082	162.71	m
	$A_1\rightarrow A_2$	164.53	0.085		
02 $\rightarrow$ 12	E $\rightarrow$ E	164.41	0.018	161.45	mw
	$A_1\rightarrow A_2$	163.57	0.021		
10 $\rightarrow$ 11	E $\rightarrow$ E	98.00	0.111	92.99	m
	$A_2\rightarrow A_1$	97.69	0.110		
11 $\rightarrow$ 12	E $\rightarrow$ E	94.78	0.106	91.18	m
	$A_1\rightarrow A_2$	94.01	0.103		
20 $\rightarrow$ 21	E $\rightarrow$ E	88.75	0.021	84.07	vw
	$A_1\rightarrow A_2$	88.14	0.045		

<sup>a</sup> s = strong, m = medium, mw = medium weak, w = weak, vw = very weak.

the same table, some experimental values of frequencies and intensities reported in this interval by Durig *et al.* are also given for comparison purposes (5). A satisfactory correlation is again observed.

The same tables show the calculated frequencies and intensities of the fundamental c-type bands for the aldehyde torsion in the *gauche* conformer. These also appear at lower frequencies, 77–73  $\text{cm}^{-1}$ .

Some a-band types of the FIR spectrum of these isotopomers of propanal are also presented in Tables 3, 5, and 7. All these transitions are relatively weak. Those of the *cis* conformer appear in the region 250–220  $\text{cm}^{-1}$ . Here again clear progressions are observed. The experimental frequencies and intensities of some broad bands, reported by Durig *et al.* in this interval, are also given in the same tables.

The frequencies and intensities of the three lowest c-type bands assigned to the methyl torsion in the *cis* conformer are gathered in Tables 4, 6, and 8. They appear at higher frequencies, 220–180  $\text{cm}^{-1}$ . Here again clear progressions are observed. In the same table, the experimental values of frequencies and intensities reported in this interval by Durig *et al.* are also given for comparison (5). Very good agreement between the calculated and measured frequencies and intensities is observed when the methyl group is not deuterated. For the

fundamental frequencies, we have 211.52, (211.53), 210.24, (210.20), and 181.29, (177.12  $\text{cm}^{-1}$ ), with the experimental data in parentheses (5).

The frequencies and intensities of some methyl torsionally excited c-type combination bands assigned to the aldehyde torsion in the *cis* conformer are gathered in Tables 4, 6, and 8. All these transitions are relatively weak and appear also in the region 200–190 and 120–100  $\text{cm}^{-1}$  for  $d_1$  and  $d_2$ , and 165–160 and 100–90  $\text{cm}^{-1}$  for  $d_5$ . Clear progressions are observed. Some weak experimental frequencies, reported also by Durig *et al.* (5) in these regions, are also tentatively assigned to these combination bands.

In the deuterated species, some additional weak bands appear which cannot be easily assigned. Some of them appear in the regions of 134–131, 135–133, and 128–125  $\text{cm}^{-1}$  in the  $d_1$ ,  $d_2$ , and  $d_5$  isotopomers, respectively. In the calculated spectra, some weak bands (intensities = 0.015) corresponding to double-quanta aldehyde-torsion transitions in the *gauche* conformers are found at 143, 150, and 147  $\text{cm}^{-1}$ , for the  $d_1$ ,  $d_2$ , and  $d_5$  isotopomers, respectively. Some correlation could be perhaps established between the experimental data and the calculated values.

Finally, concerning the intensities, it can be observed, in both calculated and experimental spectra, that the aldehyde torsion intensities in the *cis* conformer are relatively stronger in the nondeuterated methyl group isotopomers,  $d_0$ ,  $d_1$ , and  $d_2$ . On the contrary, the methyl and aldehyde torsion intensities are relatively stronger and weaker, respectively, in the deuterated methyl isotopomer,  $d_5$ . This behavior could be related to the populations of the methyl and aldehyde torsion energy levels, which are higher and lower, respectively, in the  $d_5$  isotopomer.

## 5. CONCLUSIONS

In Table 9, the fundamental frequencies calculated for the aldehyde and methyl torsions in the *cis*-rotamer of propanal

**TABLE 9**  
**Fundamental Frequencies (in  $\text{cm}^{-1}$ ) Calculated and Observed for the Aldehyde and Methyl Torsions in the *cis*-Rotamers of the Symmetric Isotopomers of Propanal**

Molecules	Aldehyde torsion		Methyl torsion	
	theoret.	exp.	theoret.	exp.
$\text{CH}_3\text{-CH}_2\text{-CHO}$ , $d_0$	128.2	135.1	219.9	219.9
$\text{CH}_3\text{-CH}_2\text{-CDO}$ , $d_1$	120.1	126.4	211.5	211.5
$\text{CH}_3\text{-CD}_2\text{-CHO}$ , $d_2$	125.2	126.9	210.2	210.2
$\text{CH}_3\text{-CD}_2\text{-CDO}$ , $d_{12}$	116.4	–	203.8	–
$\text{CD}_3\text{-CH}_3\text{-CHO}$ , $d_3$	106.5	–	193.5	–
$\text{CD}_3\text{-CH}_2\text{-CDO}$ , $d_4$	102.6	–	180.5	–
$\text{CD}_3\text{-CD}_2\text{-CHO}$ , $d_5$	106.3	103.5	181.3	177.1
$\text{CD}_3\text{-CD}_2\text{-CDO}$ , $d_6$	101.8	–	170.0	–

and all its symmetric isotopomers are gathered. In the same table, the frequencies of the available experimental data are given.

At first glance, it is seen that the theoretical results agree fairly well with the experiment, especially for the methyl torsion whenever this group is not deuterated. When the methyl group is deuterated, the agreement is not so good. There is thus clearly a mass effect which is not considered in the present calculations. This could be the zero-point vibrational energy correction or/and the Coriolis effect.

The deuteration on the central carbon atom,  $C_2$ , produces relatively small effects. In this case, the theoretical results are generally better. In contrast, the deuteration on one of the terminal groups produces drastic changes. This result could be partially explained by taking in account that the molecular center of mass is not too much affected with deuteration in the former case.

The far-infrared spectra of the remaining isotopomers were also predicted. It should be interesting to verify these results, as well as the present theory, by performing their measurements. In the same way, measurements at lower frequencies could be interesting to elucidate the *gauche* conformer spectra.

Because of the observed small irregularities probably due to mass effects, it must be concluded that the zero vibrational point correction should probably be taken into account in the potential energy surface determination.

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