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Ab initio spectroscopic studies of non-rigid molecules: an application to acetic acid

M. L. Senent

Abstract   The torsional levels of various isotopologues of acetic acid are determined from an *ab initio* potential energy surface using a flexible model depending on the OH-torsion and the methyl-torsion coordinates. Previous calculations for CH_3–$COOH$ and CH_3–$COOD$ are review and first theoretical energies of the one-deuterated species CH_2D–$COOH$ are provided. The zero point vibrational energy correction and an exact definition for the methyl-torsional coordinate have been considered. The levels are compared with previous calculations (Senent in Mol Phys 99:1311, 2001) and experimental data (Havey et al. in J Mol Spectrosc 229:151, 2005). Isotopic effects on the torsional barriers and energies are discussed. For CH_2D–$COOD$, the deuteration splits by $25\,cm^{-1}$ the zero vibrational energy level.

Keywords   Non-rigid molecules · Astrochemistry · Acetic acid

1 Introduction

Acetic acid may be classified as an important "complex organic molecule" of astrophysical relevance and an important trace species for atmospheric pollution [1,2]. For many years, it has been the object of meticulous astrophysical searches because combined with NH_2^+, is a precursor of glycine, the first aminoacid. However, its detection is very recent since its abundance in astrophysical sources is relatively low with respect to other species of comparable properties as they are its isomers methyl-formate and glycolaldehyde [3]. Recently, it has been observed in hot molecular clouds toward IRAS 16293-2422 [4].

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Astrophysical and atmospheric observations have motivated many spectroscopic studies in gas phase [5–16,18], although there are still not well explored aspects. Generally, these works focus to the G_6 isotopic varieties like CH_3–COOH, CD_3–COOH, and CH_3–COOD. Regardless of their astrophysical interest, rarely one-deuterated species of G_2 symmetry (i.e. CH_2D–COOH and CHD_2–COOH) are considered [14]. To my knowledge, the cold molecular beam spectrum for the methyl torsion fundamental has not been measured and the corresponding band centre, predicted to lie between 70 and $80\,cm^{-1}$, remains uncertain. Two other large amplitude fundamentals have been measured at $534\,cm^{-1}$ (*OH torsion*) and $581\,cm^{-1}$ (*CCO deformation*), above the methyl torsional barrier which height has been estimated to be $169\,cm^{-1}$ [9]. Focused towards the ALMA project preparation, microwave and millimeter-wave rotational transitions corresponding to the ground, first and second methyl torsional states have been measured by Ilyushin et al. [15,16]. The estimated methyl torsional barriers coincide in all the previous works.

In 2001, I performed an *ab initio* study of the torsional spectra of acetic acid [17]. Later, my calculations were employed by Havey et al. [18] for the interpretation of the infrared spectra measured in 2005. In my previous paper, I determined rotational-torsional levels up to J = 8 for the isotopologues CH_3–COOH, CD_3–COOH, CH_3–COOD and CD_3–COOD. For this purpose, I used a two-dimensional relaxed model depending on the two torsional coordinates, α (OH torsion, ν_{17}) and θ (CH_3 torsion, ν_{18}), and a MP4(DSQ)/cc-pVQZ potential energy surface [17]. The same model was employed successfully for the study o a large list of non-rigid astrophysical molecules [19–27] including the two isomers of acetic acid, glycolaldehyde [25] and methyl-formate [26]. The two fundamentals of the most abundant isotopologue of acetic acid were found to lie at $82.9\,cm^{-1}$ (A) and $77.4\,cm^{-1}$ (E) and $568.5\,cm^{-1}$ (A, E).

In this paper, the torsional levels of CH_3–COOH and CH_3–COOD are re-determined and first theoretical results for the one-deuterated species CH_2D–COOH are provided. All the new vibrational calculations are performed with the original code ENEDIM [28–30]. Some theoretical improvements developed after 2001 [24,27] are now included to search for more accurate results than those of Ref. [17]. For example, these old calculations were performed without the correction of the zero point vibrational energy [27] that now is included. In addition, now a more satisfactory definition of the methyl-torsional coordinate is used [24]. New experimental data allow to discuss the validity of these corrections [15,16,18]. The new *ab initio* calculations are performed with the Gaussian 03 code [31].

2 Theoretical aspects

For J = 0, the vibrational levels of a single molecule may be determined by solving the Hamiltonian depending on 3N-6 internal coordinates [29,30]:

$$\hat{H}_{vib} = - \sum_{i}^{3N-6} \sum_{j}^{3N-6} \left(\frac{\partial}{\partial q_i} \right) B_{ij} \left(\frac{\partial}{\partial q_j} \right) + V(q_1, q_2, \ldots, q_{3N-6})$$
$$+ V'(q_1, q_2, \ldots, q_{3N-6}) \tag{1}$$

where B_{ij} are the kinetic energy parameters, the g_{ij} elements of the G matrix defined in cm^{-1}; V represents the Potential Energy Surface (PES) and V' is the Podolsky pesudopotential arising from the "*Podolsky trick*" application [17]. It may be defined as:

$$V' = \frac{\hbar^2}{8} \sum_i^{3N-6} \sum_j^{3N-6} \left[\left(\frac{\partial}{\partial q_k} \right) gkl \left(\frac{\partial Lng}{\partial q_l} \right) - \left(\frac{\partial Lng}{\partial q_k} \right) gkl \left(\frac{\partial}{\partial q_l} \right) \right]$$
$$+ \frac{\hbar^2}{8} \sum_i^{3N-6} \sum_j^{3N-6} \left(\frac{\partial Lng}{\partial q_k} \right) gkl \left(\frac{\partial Lng}{\partial q_l} \right) \qquad (2)$$

where g represents the G matrix determinant.

Non-rigid molecules, i.e. acetic acid, are defined as those showing various minima in their PES separated by barriers sufficiently low to be overcome in the experimental/observational conditions. Large amplitude vibrations, which are usually really anharmonic, are responsible for the non-rigidity. They inter-transform different conformers trough feasible energy barriers and cannot be treated as small displacements with respect a single equilibrium position as second order perturbation theory does. Usually, their rovibrational levels, which split by tunnelling effect, are calculated variationally.

For medium size molecules such as acetic acid, the variational resolution of the 3N-6 Hamiltonian of Eq. 1 would be computationally extremely demanding. Fortunately, in a non-rigid molecule showing inversion or torsional modes, the separability of variables can be assumed as an adiabatic approximation without losing accuracy. Following this criterion, we have applied in many studies, the following procedure [17,20–27]:

(a)   The n large amplitude vibrations (LAM) are supposed to be independent on the remaining 3N-6-n coordinates

(b)   The PES is determined from the total electronic energies of a grid of M conformations selected for different values of the n coordinates. Accurate results require state-of-the art *ab initio* methods.

(c)   The remaining 3N-6-n internal coordinates are allowed to be relaxed in all the M conformations; the relaxation represents a partial way of taking into consideration their small interactions with the LAM [20].

(d)   As these 3N-6-n modes are expected "to be at the Zero Point Vibrational Energy (ZPVE)" instead "at the PES minima", a V^{ZPVE} correction must be added [27].

Thus, the vibrational Hamiltonian is substituted by an operator depending on n independent variables:

$$\hat{H}_{LAM} = - \sum_i^n \sum_j^n \left(\frac{\partial}{\partial q_i} \right) B_{ij} \left(\frac{\partial}{\partial q_i} \right) + V(q_1 + q_2 +, \ldots, q_n)$$
$$+ V'(q_1 + q_2 +, \ldots, q_n) + V^{ZPVE}(q_1 + q_2 +, \ldots, q_n) \qquad (3)$$

When interactions between LAM and medium (m) and high (h) frequency modes are relatively small, the model "works well". Accurate energies can be derived. However,

if the interactions are too strong, other vibrational modes must be explicitly added to obtain a new operator $H_{LAM'}$,

$$H_{LAM'} = H_{LAM} + H_{mh} + H_{LAM,mh} \qquad (4)$$

An example where a of 2D model fails when the Hamiltonian parameters are calculated theoretically, is dimethyl-ether. Strong Fermi interactions between large modes (the two torsions) and medium amplitude vibrations (the COC bending) displace the bands. A third coordinate, the COC bending, has to be explicitly considered to obtain accurate methyl torsional overtones [21,22]. This problem is also discussed in our series of studies of dimethyl-amine [32–35].

The most important contribution to the ZPVE correction is the harmonic one. For each geometry,

$$E^{ZPVE} = \sum_{i=n+1}^{i=3N-6} \frac{\omega_i}{2} \qquad (5)$$

Once the ZPVE correction and the V' pseudopotential are determined for all the M conformations with Eqs. (2) and (5), they can be fitted to analytical forms (in principle) identical to the one for the PES that transforms as the totally symmetric representation of the Molecular Symmetry Group. If isotopic substitution breaks the symmetry, analytical expressions can be different: whereas the PES is invariant to the isotopic substitution, V' and V^{ZPVE} as well as the B_{ij} kinetic parameters depend on atomic masses.

3 Acetic acid

Acetic acid is a non-rigid molecule which displays two conformers *trans* and *cis* and 6 minima in the PES corresponding to the ground electronic state (see Fig. 1). Two LAMs are responsible for the non-rigidity: the α OH torsion (ν_{17}) and the θ CH$_3$ torsion (ν_{18}). The methyl torsion inter-transforms three equivalent minima separated by energy barriers of 169.8 cm^{-1} (MP4(SDQ)/cc-pVQZ) [17], whereas the OH torsion relates two different conformers which energy difference was evaluated to be $\Delta H = 1882.7$ cm^{-1} [17]. Both structures are separated by a barrier of 4432.1 cm^{-1}. Table 1 summarizes the previously calculated potential parameters and rotational constants, compared with experimental data. For the three isotopologues, isotopic effects on the barriers are evaluated by considering the ZPVE vibrational correction within the harmonic approximations.

From the two-dimensional MP4(SDQ)/cc-pVQZ PES of Ref. [17], the torsional levels of the G_6 symmetry varieties CH$_3$–COOH and CH$_3$–COOD are re-calculated. CH$_2$D–COOH levels are first determined. With respect to the *old model*, two additional aspects are included in the present paper:

(a)   the search for a correct definition of methyl-torsional coordinate, θ
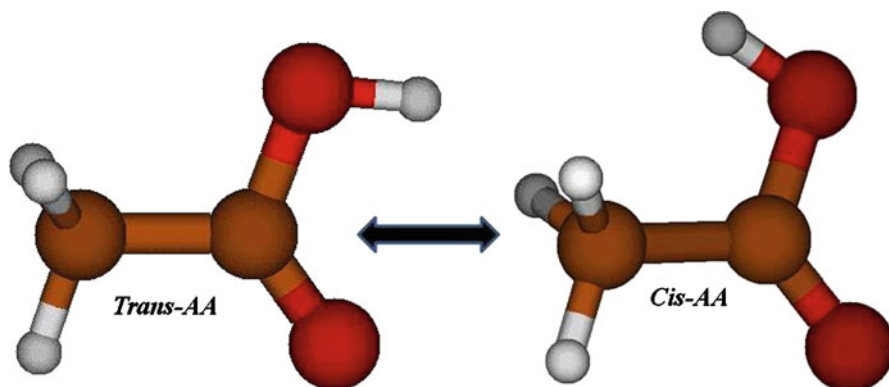(b)   the ZPVE correction.

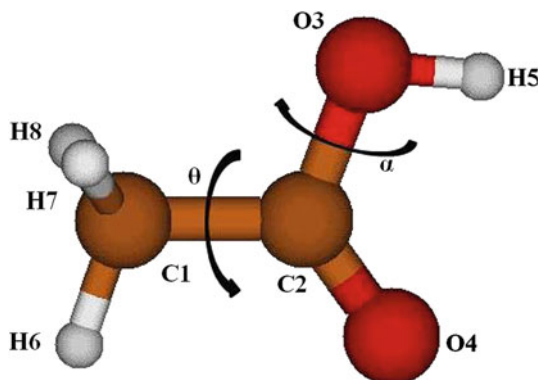**Fig. 1** The two-conformers of acetic-acid, *trans* and *cis*.

Table 1 Rotational constants (in MHZ) and potential parameters (in cm^{-1}) of *trans*-acetic acid

	Calculated	Experimental
A(CH$_3$–COOH)	11,309.84	11,335.50 [8], 11,335.47 [10] 11,335.58 [14]
B(CH$_3$–COOH)	9,534.95	9,478.64 [8], 9,478.60 [10], 9,478.73 [14]
C (CH$_3$–COOH)	5,343.16	5,325.01 [8], 5,324.91 [10], 5,324.99 [14]
V$_3$	169.8	
V$_3$(CH$_3$–COOH)	191.5	168.16 [8,10,14], 168.24 [11]
V$_3$(CH$_3$–COOD)	185.3	165.82 [10]
	V(θ)	**V(θ)** [13]
	V(0.0)=0.0	V(0.0)= 0.0
V($\theta°$)	V(60.0)=222.7	V(61.2)= 190.18
(CH$_2$D–COOH)	V(120.0)=31.4	V(123.0)=21.37
	V(180.0)=191.4	V(180.0)=180.0
V$_{OH}$ ($\alpha = 93°$)	4,432.1	
V$_{OH}$ (CH$_3$–COOH)	4,280.2	
V$_{OH}$ (CH$_3$–COOD)	4,312.1	
V$_{OH}$ (CH$_2$D–COOH)	4,276.7	
ΔH	1,882.7	
ΔH (CH$_3$–COOH)	1,856	
ΔH (CH$_3$–COOD)	1,864.3	
ΔH (CH$_2$D–COOH)	1,855.7	

3.1 The search for a correct definition of the CH$_3$ coordinate

The separation of variables represents an accurate approximation for obtaining very low energies of many molecules but can introduce unexpected inaccuracies that require special attention.

Fig. 2 The two torsional
coordinates θ y α

One of the problems is the artificial deformation of the methyl groups during their internal rotation. Acetic acid methyl groups display a distorted C_{3v} symmetry at the equilibrium geometry ("static symmetry"), but during the internal rotation, a "dynamical C_{3v} symmetry" is preserved since the three H atoms are indistinguishable [35]. The analytical form of the potential energy surface has to be symmetric with respect to the hydrogen exchange.

However, if the relaxed procedure described above is employed to solve the torsional Hamitonian of acetic acid, the "dynamical symmetry" artificially breaks. For working in two dimensions, two internal coordinates (n=2) need to be frozen and 3N-6-2 coordinates need to be optimized in each one of the M conformations. A practical and common tactic is to identify the dihedral angles H5O3C2C1 and H6C1C2O3 with the α and θ coordinates (see Fig. 2). These two angles are frozen. Then, H6C1C2O3 (θ_1), H7C1C2O3 (θ_2), y H8C1C2O3 (θ_3) are not identically treated producing an artificial distortion.

The search for a correct definition of methyl coordinate compatible with relaxed models has been object of various studies. Many solutions have been proposed for the called "symmetry dilemma". For example, Smeyers and Villa [35] have proposed to identify the H6C1C2O3 with the torsional coordinate ($\theta = \theta_1$) after using a well selected set of conformations (H6C1C2O3 = 180.0°, 90.0°, 0.0° and −90.0°). This procedure was followed in my first paper on acetic acid [17]. In a further paper [24], we derived an exact definition of the methyl group coordinate of acetaldehyde,

$$\theta = (\theta_1 + \theta_2 + \theta_3 - 2\pi) \tag{6}$$

By taking into consideration the representation of the C_{3v} group, it is easy to define also the two deformation coordinates:

$$\beta_1 = \frac{1}{2}(\theta_1 - \theta_2)$$
$$\beta_2 = -\frac{1}{4}(\theta_1 - \theta_2) + \frac{1}{2}\theta_3 \tag{7}$$

Each M structure is defined by a pair of values of α and θ, whereas a set of 3N-8 coordinates including the two linear combinations β_1 and β_2, are optimized. However, rarely computers programs are developed for geometry optimization using linear combination of internal coordinates and high levels of *ab initio* theory. To avoid this drawback, a practical procedure can be followed for acetic acid:

(a) Calculations are preformed on a grid of 78 (36 × 3) geometries defined for H6C1C2O3 = 30.0°, 60.0°, 90.0°, 120.0°,…, 300°, 330.0°. H7C1C2O3 and H8C1C2O3 are allowed to be relaxed.

(b) Energies are fitted to the 4D potential:

$$
\begin{aligned}
V\,(\alpha, \theta, \beta_1, \beta_2) \\
= \sum_{M=0} \sum_{L=0} \left[A_{ML}^{cc} \cos{(M\alpha)} \cos{(3L\theta)} + A_{ML}^{ss} \sin{(M\alpha)} \sin{(3L\theta)} \right] \\
+ B_1 \sin{(3\theta)}\,\beta_1 + B_2 \sin{(3\theta)}\,\beta_2 + B_3 \sin{(3\theta)}\,\beta_1\beta_2 \\
+ B_4 \cos{(\alpha)} \cos{(3\theta)}\,\beta_1 + B_5 \cos{(\alpha)} \cos{(3\theta)}\,\beta_2
\end{aligned}
\tag{8}
$$

(c) Rovibrational calculations are performed neglecting the last terms ($B_1 = B_2 = \cdots = B_5 = 0$). Thus, the excess of energy arising from the inexact minimization, is eliminated.

The two first columns of Table 2 summarize the CH_3–COOH results performed with 26 configurations (OLD, procedure of Refs. [17,32]), and the NEW results performed with 78 structures. Bands are displaced less than 1 cm^{-1}. The old procedure which reduces extremely computational expenses, is really powerful, in spite of it fails for non-planar molecules and cannot be applied to the one-deuterated species of low symmetry such as CH_2D–COOH [32].

3.2 Isotopic substitution effects: the ZPVE correction

Whereas, the PES is isotopically invariant and transforms as the totally symmetric representation of the G_6 groups, the V^{ZPVE} corrections as well as the pseudopotential V' and the kinetic B_{ij} parameters depend on the atomic masses.

Whereas, the PES of all the isotopologues may be calculated using only 26 conformations, the remaining parameters of the Hamiltonian require a number of conformations depending on the isotopic species: 26 for the G_6 species and 78 for the G_2 ones such as CH2D-COOH. For this last case, the analytical form of the PES is the following:

$$
V\,(\alpha, \theta) = \sum_{M=0} \sum_{L=0} \left[A_{ML}^{cc} \cos{(M\alpha)} \cos{(L\theta)} + A_{ML}^{ss} \sin{(M\alpha)} \sin{(L\theta)} \right]
\tag{9}
$$

4 Results and discussion

Table 1 shows the rotational constants as well as various potential parameters of CH_3–COOH compared with experimental data. The two potential energy barriers, V_3

Table 2 Calculated energy levels of isotopic species of *trans*-acetic acid (in cm^{-1})

vv'	Sym.	CH_3–$COOH$			CH_3–$COOD$		CH_2D–$COOH$	
		OLD [17]	NEW	NEW (+ZPVE)	OLD [17]	NEW	Sym.	NEW (+ZPVE)
0 0	A_1	0.0	0.0	0.0	0.0	0.0	A'	0.0
	E	0.3	0.3	0.2	0.3	0.3	A'	25.7
							A''	25.9
OH torsion								
01	A_2	568.5	569.6	554.9	422.3	418.2	A''	552.6
	E	568.7	569.8	555.1	422.6	417.8	A''	576.7
							A'	576.8
02	A_1	1, 118.2	1, 120.1	1, 093.6	834.3	826.1	A'	1, 089.4
	E	1, 118.3	1, 120.3	1, 093.6	834.3	826.2	A'	1, 112.4
							A''	1, 112.4
03	A_2	1, 646.6	1, 649.4	1, 612.8	1, 235.7	1, 223.1	A''	1, 607.5
	E	1, 647.3	1, 650.0	1, 613.1	1, 235.8	1, 223.2	A''	1, 629.7
							A'	1, 629.8
CH$_3$ torsion								
1 0	A_2	82.9	82.7	88.2	82.0	85.5	A''	80.4
	E	77.4	77.4	83.9	76.4	81.0	A'	99.8
							A''	102.4
2 0	A_1	129.4	130.5	141.7	127.9	137.3	A'	148.3
	E	149.6	150.4	160.0	148.2	156.0	A'	157.6
							A''	169.2
3 0	A_2	256.3	257.0	265.6	254.7	261.6	A''	203.2
	E	197.9	198.9	208.8	196.4	204.7	A'	205.5
							A''	244.6
4 0	A_1	258.6	259.5	268.8	256.9	264.8	A'	249.9
	E	330.3	331.0	339.6	328.9	335.5	A'	301.8
							A''	302.8
5 0	A_2	511.9	512.6	520.8	509.4	516.0	A''	367.4
	E	415.2	415.9	424.3	413.0	420.6	A'	367.6
							A''	442.2
6 0	A_1	511.9	512.6	520.8	512.1	517.2	A'	442.3
	E	620.6	620.9	629.0	617.5	624.1	A'	526.4
							A''	526.4
Combination bands								
1 1	A_1	657.7	658.2	648.1	506.6	507.2	A'	638.0
	E	653.6	654.2	644.9	504.8	504.7	A''	656.2
							A'	658.0

Table 2 Continued

vv′	Sym.	CH$_3$–COOH			CH$_3$–COOD		CH$_2$D–COOH	
		OLD [17]	NEW	NEW (+ZPVE)	OLD [17]	NEW	Sym.	NEW (+ZPVE)
2 1	A$_2$	711.9	713.8	709.0	561.3	566.5	A″	710.9
	E	730.1	731.6	725.5	579.7	583.2	A″	719.5
							A′	729.5
1 2	A$_2$	1, 213.3	1, 214.4	1, 191.6	925.1	920.7	A′	1, 197.0
	E	1, 210.2	1, 211.4	1, 188.7	922.5	917.7	A″	1, 198.2
							A″	1, 274.0
ZPVE								
		329.5	329.8	326.3	254.1	254.2		321.8

and V^{OH}, and the energy difference between the two conformers *trans* and *cis*, ΔH, are calculated for the different isotopologues considering the ZPVE correction. Without attending to the isotopic effect, V_3 has been determined to be 169.8 cm^{-1} in a very good agreement with the experimental data. If the ZPVE correction is considered, V_3 increases to 191.5 and 185.3 cm^{-1} for CH$_3$–COOH and CH$_3$–COOD, respectively. However, V^{OH} decreases with isotopic effects.

In Table 2, the calculated energy levels (NEW) are compared with the results (OLD) obtained in 2001 [17]. The new results are determined by taking into consideration the pseudopotential (whose effect on the levels is negligible) and the V^{ZPVE} correction. The levels of *trans*-CH$_3$–COOH and *trans*-CH$_3$–COOD are classified following the representations of the G_6 group (A$_1$, A$_2$ and E) and assigned to the modes. v,v′ correspond to ν_{18}, ν_{17}. For the G_2 species, there are only two representations, A′ and A″ because the E degenerate levels split into two components as a consequence of the symmetry breaking. The zero vibrational level, which components lie at 0.0 and 0.2 cm^{-1} in CH$_3$–COOH, are displaced by 0.0, 25.7 and 25.9 cm^{-1} in CH$_2$D–COOH. The (1,0) and (0,1) levels splits in three components: 80.4, 99.8 and 102.4 cm^{-1} (CH$_3$ torsion) and 552.6, 576.7 and 576.8 cm^{-1} (OH torsion).

As generally occurs, the effect of V^{ZPVE} correction is very important. For example, for CH$_3$–COOH, the methyl torsion fundamental are displaced from 82.7 cm^{-1} (A) and 77.4 cm^{-1} (E) to 88.2 cm^{-1} (A) and 83.9 cm^{-1} (E). The OH fundamental changes from 569.6 cm^{-1} (A) and 568.8 cm^{-1} (E) to 554.9 cm^{-1} (A) and 555.1 cm^{-1} (E). This last displacement occurs following the good direction since the experimental value for the ν_{17} fundamental is 534 cm^{-1}. Nothing sure can be asserted for the ν_{18} fundamental because the available experimental values have been determined indirectly (79.1 and 72.8 cm^{-1} [75]). Old papers [6] provide higher frequencies (99 and 66 cm^{-1} for CH$_3$–COOH and CD$_3$–COOH).

Finally, in Table 3, the OH calculated transitions are compared with the experimental values of Havey et al. [18], who use my old results for assignments. New results obtained with the ZPVE corrections are really more accurate for all the considered transitions. Table 3 shows also results for the two deuterated species. In the case of

Table 3 Predicted frequencies (in cm^{-1}) corresponding to the OH torsions compared with experimental data

Assign.	Symm.	CH$_3$COOH			CH$_3$COOD	CDH$_2$COOH	
		OLD [17]	NEW (+ZPVE)	Exp. [18]	NEW (+ZPVE)	NEW (+ZPVE)	
03 ← 02	A$_2$ ← A$_1$	528.4	519.2	525.8	397.0	A″ ←A′	495.1
	E ← E	529.0	519.5		397.0	A″ ←A′	517.3
						A′ ←A″	517.4
						A″ ←A′	518.1
						A″ ←A′	540.3
02 ← 01	A$_1$ ← A$_2$	549.7	538.7	531.1	407.9	A′ ←A″	512.7
	E ← E	549.6	538.5		408.4	A′ ←A″	535.7
						A″ ←A′	535.6
						A′ ←A″	536.8
						A′ ←A″	559.8
12 ← 11	A$_2$ ← A$_1$	555.6	543.5	533.0	413.5	A″ ←A′	616.0
	E ← E	556.3	543.8		413.0	A″ ←A′	636.0
						A″ ←A′	540.2
						A′ ←A″	540.8
						A″ ←A′	560.2
01 ← 00	A$_2$ ← A$_1$	568.5	554.9	534.7	418.2	A″ ←A′	526.9
	E ← E	568.4	554.9		417.5	A′ ←A″	550.9
						A″ ←A′	551.0
						A″ ←A′	552.6
						A″ ←A′	576.7
11 ←10	A$_1$ ← A$_2$	574.8	559.9	535.9	421.7	A′ ←A″	535.6
	E ← E	576.2	561.0		423.7	A′ ←A″	555.6
						A″ ←A′	556.4
						A′ ←A″	557.6
						A′ ←A″	577.6
21 ←20	A$_2$ ← A$_1$	582.5	567.3	537.1	429.2	A″ ←A′	553.6
	E ← E	580.4	565.5		427.2	A′ ←A″	560.3
						A″ ←A′	561.9
						A″ ←A′	562.6
						A″ ←A′	571.2

the one-deuterated species each band splits into 6 components although, it may be expected that tree of the components will shoe very low intensities.

5 Conclusions

The torsional levels of CH$_3$–COOH, CD$_3$–COOH and CH$_2$D–COOH are determined from a MP4(DSQ)/cc-pVQZ potential energy surface and a flexible model depending

on the OH-torsion and the methyl-torsion coordinates. Theoretical results are compared with experimental data and previous calculations. These previous levels were determined using an approximate definition of the methyl torsional coordinate which validity for acetic acid is confirmed.

Isotopic effects are discussed. As generally occurs, the effect of V^{ZPVE} correction is very important. For CH_3–COOH, the methyl torsion fundamental are displaced by $\sim 6\,cm^{-1}$ whereas the OH fundamental $\sim 15\,cm^{-1}$. However, V' is negligible.

For the G_2 species CH_2D–COOH, the E degenerate levels split into two components as a consequence of the symmetry breaking. The zero vibrational level, which components lie at 0.0 and $0.2\,cm^{-1}$ in CH_3–COOH, are displaced to 0.0, 25.7 and $25.9\,cm^{-1}$ in CH_2D–COOH.

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