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REGULAR ARTICLE

Modelization of vibrational spectra beyond the harmonic approximation from an iterative variation–perturbation scheme: the four conformers of the glycolaldehyde

Philippe Carbonniere · Claude Pouchan

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Abstract This paper presents the computed anharmonic frequencies and IR intensities in the mid-infrared region for the four conformers of glycolaldehyde (Cis cis, Trans trans, Trans gauche and Cis trans forms). The fundamental transitions and their connected overtones and combination bands through strong anharmonic couplings (Fermi resonances) are provided. The results are stemmed from an iterative variational–perturbational resolution of the vibrational problem implemented in the VCI-P code. The four potential electronic surfaces are built as a Taylor series truncated to the fourth order around each minimum geometry. The second derivatives with respect to the normal coordinates were computed at the CCSD(T)/cc-pVTZ level, while the third and fourth derivatives were estimated with the B3LYP/6-31 + G(d,p) model chemistry. For the most stable Cc form, an average deviation of about 10 cm^{-1} is obtained with respect to the unambiguous experimental values. Furthermore, some of the transitions observed in the CH stretchings region were reassigned. The theoretical values calculated for the Tt and Tg forms are compared to the experimental data obtained from the irradiation of the Cc conformer isolated in Ar matrix with an IR source.

Keywords Ab initio · DFT · Anharmonic vibrational spectra · Glycolaldehyde · IR intensities

Dedicated to Professor Vincenzo Barone and published as part of the special collection of articles celebrating his 60th birthday.

P. Carbonniere (✉) · C. Pouchan (✉)
Groupe Chimie Théorique et Réactivité, ECP, IPREM UMR CNRS 5254, Université de Pau et des Pays de l'Adour 2, Rue Jules Ferry, 64053 Pau, France
e-mail: philippe.carbonniere@univ-pau.fr

C. Pouchan
e-mail: claude.pouchan@univ-pau.fr

1 Introduction

The vibrational fingerprint of a molecular system that infrared (IR) or Raman spectroscopy allows to observe is a widely used information for substance recognition and for the understanding of its behavior within a chemical environment. Thus, it is also used for applications such as structural and conformational analysis [1–3] reactivity monitoring [4, 5] and molecular design [6].

The subtle interplay between the different effects that induce the experimental picture of such fingerprint makes the identification task non-trivial, particularly when the molecular system presents strong anharmonic couplings giving rise to IR (or Raman)-active overtones and combination bands. From a theoretical point of view, the need to go beyond the harmonic approximation for an accurate modelization of a vibrational spectrum requires to face the computational cost that makes the treatment impracticable in its most complete formalism.

In the framework of the time independent formalism, several models have been developed and implemented to explicitly take into account anharmonicity. For small molecules (3–5 atoms), converged rovibrational levels can be obtained by fully variational methods, *that is,* the discrete variable representation (DVR) [7] or the vibrational configuration interaction (VCI) [8] methods. For larger molecules, four approximate schemes have been proposed. The vibrational self-consistent field (VSCF) approach represents the total vibrational wave function by a separable product of single-mode wave functions optimized separately using an effective mean field potential [9]. For a better accuracy, the correlation between modes is commonly treated by (i) the vibrational Moller–Plesset perturbation theory (VMP) [10] that is computationally cheap but overestimates the strong anharmonic complings, (ii) a vibrational configuration

interaction (VCI) [8] that treats properly the strongest interactions but proves much more time consuming, (iii) the vibrational mean field configuration interaction (VMFCI) [11] that plays on the partitioning of the vibrational modes and encompasses both VSCF and VCI as particular case and (iv) the vibrational coupled cluster (VCC) [12] level of theory. Several strategies to strongly reduce the computational cost of such treatment were proposed in the literature [13–16] (see Ref. [16] for a more detailed description). A possible way which is used in the present study is to take advantage of both perturbative and variational approaches [17]. This variational–perturbational scheme in its most advanced version has been implemented in the VCI-P code [16] that uses small VCI matrices to treat the strongest interactions while the myriads of the weakest interactions are treated perturbationally (see the section computational details and method). Such a recipe was used to investigate the vibrational properties of the four conformers of glycolaldehyde (CH_2OHCHO).

The glycolaldehyde is the first monosaccharide detected in the interstellar medium which has increased the interest in the study of isomerism in interstellar chemistry (see Ref. [18] and therein). Among its four conformers [18, 19] so-called Cc, Tt, Tg and Ct (see Fig. 1), only the Cc conformer was detected from IR/Raman spectroscopy in gas phase [20–23] or in matrix isolation [24, 25], while the Tt form is observed from IR-induced conformer interconversion process in low-temperature matrices.

In the present study, we report the computed anharmonic fundamental transitions and their connected overtones or combination transitions through Fermi resonances of the four conformers of glycolaldehyde at least for two reasons (i) because of the presence of strong anharmonic couplings in the CH stretching region in which the assignment of the vibrational transitions appears non-univocal for the Cc and Tt conformers and (ii) because no experimental data are reported for the Tg and Ct forms.

2 Computational details and method

Computations at the CCSD(T) [26] level of theory were performed with the CFOUR [27] program, while Gaussian 09 [28] was used for the DFT computations. The anharmonic vibrational treatment relies on a hybrid [29] quartic force field in which the second derivatives are computed at the CCSD(T)/cc-pVTZ [30] level of theory, while the third and fourth derivatives are computed at the DFT level using the B3LYP functional [31, 32] with a valence double zeta Pople basis set including diffuse and polarization functions, 6–31+G(d,p) [33]. This model chemistry was chosen since it has been previously shown [34, 35] that for the prediction of harmonic and anharmonic force constants and in the case of small organic systems, it is able to approach the results obtained using the more expensive CCSD(T)/cc-pVTZ level of theory by an average value of 10 cm^{-1} on the fundamental transitions.

The analytic model of the potential functions is determined as follows [36]: from a minimum energy structure of a given system, a quartic force field is built in which the third and fourth derivatives are computed by 6 N–11 (N = number of atoms) numerical differentiation of analytical second derivatives. In the quartic approximation, the potential provided by the Gaussian code is a Taylor series in normal coordinates limited to the 3-mode interactions. From a technical point of view, it can be shown [36] that the best setup is obtained using a step size of 0.01 Å for the numerical differentiation of harmonic frequencies, tight convergence criteria for structural optimizations and fine grids for integral evaluation (that is, at least 99 radial and 590 angular points).

The Hamiltonian used is the pure vibrational Hamiltonian as detailed in Ref. [37]:

$$\hat{H} = \frac{1}{2}\sum_i \omega_i p_i^2 + V_{(q_1,\ldots,q_M)} + \sum_\alpha B_\alpha \left(\sum_{i,j\neq i,k,l\neq k} \zeta_{ij}^\alpha \zeta_{kl}^\alpha q_i p_j q_k p_l \sqrt{\frac{\omega_j \omega_l}{\omega_i \omega_k}} \right) \quad (1)$$

where q_i and p_i are, respectively, the dimensionless normal coordinates and their conjugate momenta. $V(q1,\ldots, qM)$ is a polynomial expansion of the PES in terms of normal coordinates q_i truncated to the fourth order The last term represents the major component of the rotational contribution to the anharmonicity in which B_α is the rotational constant of the system with respect to the Cartesian axis α, and ζ_{ij}^α is the Coriolis constant that couples q_i and q_j through the rotation about the α axis.

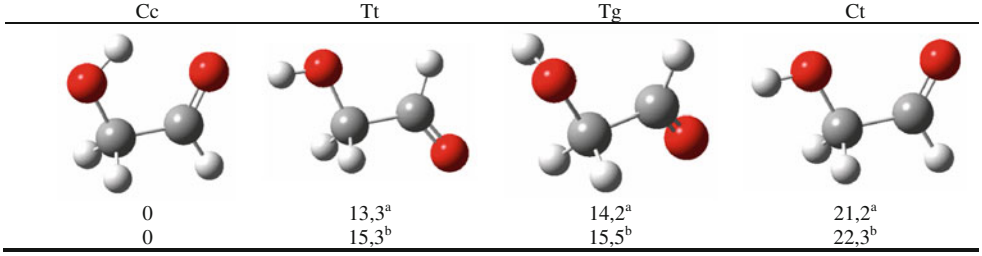

Fig. 1 The four conformers of glycolaldehyde and their corresponding relative energy (in kJ·mol^{-1}) computed at the [a]CCSD(T)/cc-pVTZ level of theory (our work) and [b]MP4(SDTQ)/cc-pVQZ (see Ref. [18])

Table 1 Calculated wavenumbers (cm^{-1}) for the glycolaldehyde in its Cc form with the VCI-P method from a CCSD(T)/cc-pVTZ//B3LYP/6-31G(d,p) hybrid quartic force field

Description	Mode	Experimental			Calculations				
		Gas phase[a]	Ar[b]	Ar[c]	ν^{d}_{VMP2}	ν^{d}_{VCI-P}	$I_{\nu}{}^{d}$	Description[d]	ν^{e}
OH stretch	ν_{18}	3,549	3,541	3,542	3,542	3,570	54	81% ω_{18} + 7% $2\omega_{18}$	3,624
as. CH_2 stretch	ν_{17}	2,881	2,895	2,855	2,876	2,898	13	74% ω_{17} + 16% ω_{16} + ω_{17}	2,921
	$\nu_9 + \nu_{12}$				2,649	2,650	1	83% ω_9 + ω_{12} + 4% ω_{17}	
	$\nu_9 + \nu_{10}$				2,503	2,496	1	83% ω_9 + ω_{10} + 4% ω_{17}	
	$2\nu_{13}$				2,798	2,913	14	58% $2\omega_{13}$ + 15% ω_{16}	
	$\nu_{12} + \nu_{13}$				2,882	2,883	9	54% ω_{12} + ω_{13} + 16% $2\omega_4$ + ω_{12} + 10% ω_{16}	2,836
	$2\nu_4 + \nu_{13}$					2,874	11	32% $2\omega_4$ + ω_{13} + 27% ω_{12} + ω_{13} + 13% ω_{16}	
s. CH_2 stretch	ν_{16}	2,840	2,845	2,895	2,999				2,967
	$2\nu_4 + \nu_{11}$					2,794	6	55% $2\omega_4$ + ω_{11} + 16% $4\omega_4$ + 4% ω_{16}	
	$\nu_{10} + \nu_{12}$				2,689	2,681	2	76% ω_{10} + ω_{12} + 10% ω_{10} + ω_{11} + 4% ω_{16}	
CH stretch	ν_{15}	2,820	2,907	2,845	2,822	2,854	19	49% ω_{15} + 26% ω_{11} + ω_{12}	2,870
	$2\nu_{12}$				2,831	2,816	14	43% $2\omega_{12}$ + 33% ω_{11} + ω_{13} + 4% ω_{15} + 7% ω_{16}	
	$\nu_{11} + \nu_{12}$				2,775	2,767	5	62% ω_{11} + ω_{12} + 16% ω_{15}	
	$2\nu_{11}$	2,710	2,712	2,713	2,720	2,707	6	78% $2\omega_{11}$ + 10% ω_{15}	2,718
C=O stretch	ν_{14}	1,754	1,747	1,747	1,770	1,761	108	64% ω_{14} + 25% $2\omega_6$	1,753
	$2\nu_6$	1,706	1,697	1,707	1,702	1,716	33	58% $2\omega_6$ + 27% ω_{14}	1,711
	$2\nu_4$				1,441	1,412	10	73% $2\omega_4$ + 12% ω_{13} + 9% ω_{11}	
CH_2 scissor	ν_{13}	1,456	1,443	1,430	1,460	1,454	11	81% ω_{13} + 13% $2\omega_4$	1,462
		1,425	1,429	1,424					
			1,421						
CH_2 wag, ip OH bend	ν_{12}	1,378	1,399	1,400	1,426	1,421	27	92% ω_{12}	1,420
ip CH bend	ν_{11}	1,356	1,367	1,366	1,367	1,363	31	94% ω_{11}	1,378
ip OH bend, CH_2 wag,	ν_{10}	1,275	1,267	1,268	1,279	1,273	41	94% ω_{10}	1,265
CH_2 twist	ν_9		1,229	–	1,229	1,225	3	95% ω_9	1,235
	$2\nu_8$			2,209	2,229	2,233	1	86% $2\omega_8$ + 1% ω_8	2,222
C–O stretch	ν_8	1,112	1,110	1,110	1,120	1,120	80	93% ω_8	1,116
CH_2 twist, op CH bend	ν_7		1,130	–	1,087	1,081	0	95% ω_7	1,090
CC stretch	ν_6	859	858	856	865	865	49	91% ω_6	867
O=CC bend, CCO bend	ν_5	752	749	751	757	758	9	95% ω_5	740
CH_2 rock, op CH bend	ν_4		–	–	722	713	0	96% ω_4	715

Comparison with the experimental values obtained in gas phase and in Ar matrix and VPT2 results from a MP2/6-311++G(d,p) quartic force field [24]. Calculated intensities are in $km \cdot mol^{-1}$

[a] Taken from Ref. [23], [b] taken from Ref. [24], [c] taken from Ref. [25], [d] our work, [e] taken from Ref. [24]

The anharmonic vibrational treatment is based on an iterative variational–perturbational scheme implemented in the VCI-P code [16]. This code computes the anharmonic wavenumbers and the anharmonic IR intensities of the fundamental transitions, overtones and combination bands which are IR (or Raman) actives through strong anharmonic couplings (Fermi or Darling Dennisson resonances).

Here, we recall [16] that the VCI-P method consists in 3 N–5 independent VCI computations (one for the fundamental state and one for each mono-excitation). For each VCI computation, an automated procedure builds

iteratively an active space by selecting, through the second-order perturbational formula, the vibrational configurations that lead to the strongest couplings with the states of interest. Each active space gathers from some dozens to some hundreds of configurations while the weakest interactions, up to several hundred of thousands, are discarded from the variational process and contribute perturbationally to the anharmonicity:

$$E_{i,L}^{VCI-P} = E_{i,L}^{VCI} + \sum_{j_{weak}}^{N_{weak}} \frac{\left\langle \Psi_{i,L-1}^{n_i} \middle| \hat{H} \middle| \Phi_{j_{weak},L}^{n_j} \right\rangle^2}{E_i^0 - E_{j_{weak},L}^0} \quad (2)$$

The process is ended at the L^{th} iteration when the convergence on the VCI-P energy of the state i is reached. It has been set to 0.2 cm^{-1} in the present study. Note that in the above expression, $E_{i,n}^{VCI}$ corresponds to the VCI energy obtained by the diagonalization of an active space containing the N_{strong} configurations $\Phi_k^{n_k}$, $\Phi_k^{n_k}$ being the n_kth excitations of the configuration i. The second term represents the perturbational contribution of the weakest configurations $\Phi_j^{n_j}$ interacting with the state $\Psi_i^{n_i}$ determined variationally at the iteration *L-1*.

Thus, any state of interest $\Psi_i^{n_i}$ appears as a linear combination of the most pertinent configurations $\Phi_k^{n_k}$ that belong to the final active space:

$$\Psi_i^{n_i} = \sum_{k}^{Nstrong} c_{ik} \Phi_k^{n_k} \quad (3)$$

Note that any configuration $\Phi_k^{n_k}$ for which c_{ik}^2 is greater than a threshold (4% in the present study) is considered as a strong resonant configuration. As

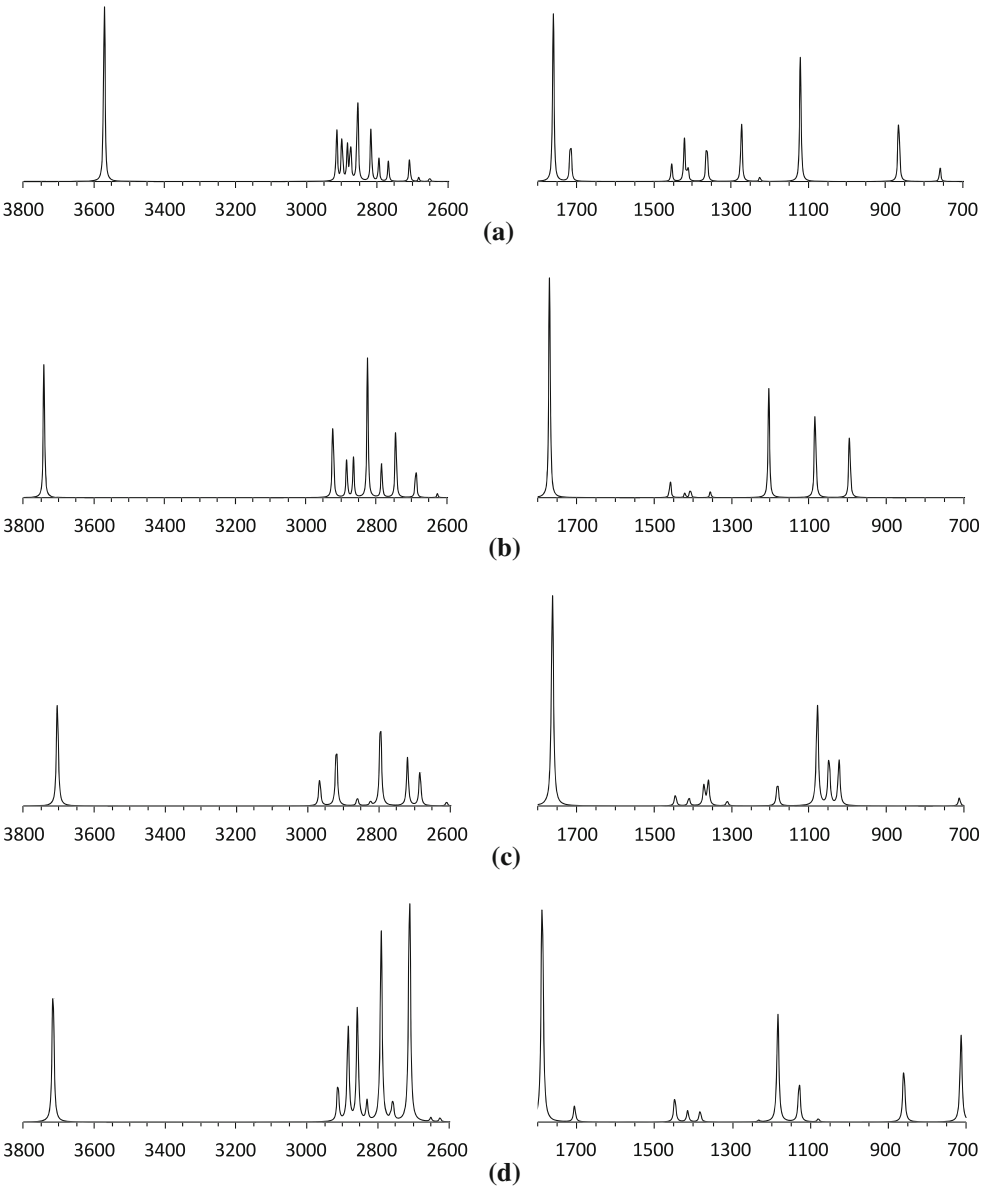

Fig. 2 anharmonic spectra of the four conformers of glycolaldehyde in the 3,800–2,600 cm^{-1} region and the 1,800–700 cm^{-1} region with the VCI-P method from a CCSD(T)/cc-pVTZ//B3LYP/6-31G(d,p) quartic force field. **a** Cc form, **b** Tt form, **c** Tg form, **d** Ct form

consequence, their multiexcitations are generated from the procedure detailed above up to the convergence of their VCI-P energy. This ensures for each CI matrix the orthogonality between the state $\Psi_i^{n_i}$ and its connected states through Fermi resonances for which the corresponding anharmonic intensities can be determined more safely.

Furthermore, this program allows the computation of anharmonic intensities [16]: starting from the quadratic expansion of the dipole surface, the second derivatives of dipole moment, d_{ij} (where α is a Cartesian component of the dipole moment vector d_j referred to the Eckart axes) are calculated in a manner analogous to the cubic and quartic force constants detailed above:

$$D_\alpha = D_\alpha(0) + \sum_i d_{\alpha_i} q_i + \frac{1}{2} d_{\alpha_{ij}} q_i q_j \quad (4)$$

The anharmonic intensity between an initial state i and a final state j is then evaluated as follows:

$$I_{i,j} = \frac{8\pi^3 N_A}{3hc(4\pi\varepsilon_0)} \nu_{i,j} \sum_\alpha \left\langle \Psi_{i,L} \middle| D_\alpha \middle| \Psi_{j,L'} \right\rangle^2 (N_i - N_j). \quad (5)$$

3 Results and discussion

Table 1 reports the vibrational transitions in the mid-infrared region of the glycolaldehyde in its Cc form. The first column corresponds to the description of the modes in terms of functional groups involved in the vibrational transition as reported in Ref. [25]. In the column 3, are reported data stemmed from a gas phase IR spectrum recorded at 300 K [23], while the data in columns 4 and 5 are issuing from low-temperature experiments in Ar matrix [24, 25]. These are compared to our theoretical results comprising the anharmonic wavenumbers, their corresponding anharmonic intensities and their theoretical descriptions. In the last columns are reported the second-order perturbative results available in the literature from a MP2/6-311++G(d,p) quartic force field [25].

Globally, the VCI-P results achieve an average convergence of 11 cm^{-1} with the overall of the non-ambiguous experimental values (values reported in Table 1 excepted ν_7, ν_{13}, ν_{15}, ν_{16}, as discussed). This mean absolute

Table 2 Calculated wavenumbers (cm^{-1}) for the glycolaldehyde in its Tt form with the VCI-P method from a CCSD(T)/cc-pVTZ//B3LYP/6-31G(d,p) hybrid quartic force field

Description	Mode	exp[a]	ν^b_{VMP2}	ν^b_{VCIP}	$I\nu^b$	Description[b]
OH stretch	ν_{18}	3,668	3,707	3,740	36	82% ω_{18} + 6% $2\omega_{18}$
as. CH_2 stretch	ν_{17}	2,940	2,903	2,921	15	74% ω_{17} + 4% ω_{16} + ω_{17}
	$\nu_{10} + \nu_{12}$		2,621	2,625	1	83% ω_{10} + ω_{12} + 4% ω_{17}
	$\nu_8 + \nu_{13}$		2,553	2,534	1	65% ω_8 + ω_{13} + 4% ω_{17}
	$2\nu_{13}$		2,849	2,921	8	64% $2\omega_{13}$ + 19% $2\omega_5$ + ω_{13} + 13% ω_{16}
	$2\nu_5 + \nu_{13}$			2,882	10	34% $2\omega_5$ + ω_{13} + 14% ω_{16}
s. CH_2 stretch	ν_{16}	2,935	2,971	2,863	10	33% ω_{16} + 27% $2\omega_{13}$
CH stretch	ν_{15}	2,810	2,807	2,823	35	34% ω_{15} + 30% $2\omega_{12}$
	$2\nu_{12}$		2,795	2,783	9	52% $2\omega_{12}$ + 21% ω_{15} + 8% ω_{16}
	$\nu_{11} + \nu_{12}$		2,748	2,743	20	67% ω_{11} + ω_{12} + 16% ω_{15} + 6% ω_{16}
	$2\nu_{11}$		2,701	2,686	9	76% $2\omega_{11}$ + 15% ω_{15}
C=O stretch	ν_{14}	1,747	1,767	1,770	145	91% ω_{14}
CH_2 scissor	ν_{13}	1,439	1,472	1,458	12	76% ω_{13} + 16% $2\omega_5$
	$2\nu_5$		1,441	1,420	3	64% $2\omega_5$ + 17% ω_{13}
CH_2 wag, ip OH bend	ν_{12}		1,410	1,406	6	91% ω_{12}
ip CH bend	ν_{11}	1,353	1,357	1,354	4	94% ω_{11}
CH_2 twist	ν_{10}	–	1,220	1,217	0	94% ω_{10}
ip OH bend, CH_2 wag,	ν_9	1,203	1,214	1,203	68	93% ω_9
op CH bend	ν_8	1,129	1,088	1,083	2	95% ω_8
C–O stretch	ν_7	1,065	1,082	1,083	63	90% ω_7
CC stretch	ν_6	998	996	994	46	92% ω_6
CH_2 rock, op CH bend	ν_5	–	728	719	0	95% ω_5
O=CC bend, CCO bend	ν_4	538	539	540	6	91% ω_4

Comparison with the experimental values obtained in Ar matrix. Calculated intensities are in $km \cdot mol^{-1}$

[a] Taken from Ref. [24], [b] our work

deviation (M.A.D) is confronted to the VPT2 results [25] stemmed from a MP2/6-311G(d,p) quartic force field for which a mean deviation of about 17 cm^{-1} is observed on the same set.

The experimental values in the 1,800–700 cm^{-1} region are particularly well reproduced by the VCI-P approach, namely for the remarkable case of Fermi resonance that occurs between the C=O stretching and the first overtone of the C–C stretching mode. Indeed, a gap of 45–50 cm^{-1} is observed between the two transitions both experimentally and theoretically with an intensity ratio $I_{\nu_{C=O}} : I_{2\nu_{C-C}}$ of about 5:1 in gas phase [23], 2:1 in Ar matrix [24] and 3:1 from our calculations.

Here, the most ambiguous assignment concerns the fundamental transition of the CH_2 scissoring mode for which two bands of about the same intensity [23, 24] were observed. From the experiment in gas phase [23], the two values (1,425 and 1,456 cm^{-1}) were assigned to the fundamental transition even though it was pointed out that one of the two positions could correspond to the first overtone of ν_4 (CH_2 rocking mode). From low-temperature experiments in Ar matrix, a triplet is reported in Ref. [24] (1,421–1,429–1,443 cm^{-1}) invoking possible site effects in this material, while the Ref. [25] mentions only a doublet (1,424–1,430 cm^{-1}). These observations are consistent with our calculations concerning both the positions and the intensity ratio. Thus, the values around 1,430 and 1,450 cm^{-1} are assigned to the $2\nu_4$ and ν_{13} (CH_2 scissoring), respectively.

More problems are encountered in the region above 2,600 cm^{-1} since the symmetric CH_2 and CH stretching modes are affected by strong anharmonic couplings, giving rise to several IR-active overtones and combination bands. Starting from the CH stretching mode region, the presence of a Fermi resonance between this mode (ν_{15}) and the first overtone of the op CH bending mode ($2\nu_{11}$) was observed in the three experiments [23–25], but different values of ν_{15} were reported (2,820, 2,907 and 2,845 cm^{-1}), while the

Table 3 Calculated wavenumbers (cm^{-1}) for the glycolaldehyde in its Tg and Ct forms with the VCI-P method from a CCSD(T)/cc-pVTZ//B3LYP/6-31G(d,p) hybrid quartic force field

Tg				Ct		
Description	Mode	CC//B3	Iν	Mode	CC//B3	Iν
OH stretch	ν_{18}	3,703	27	ν_{18}	3,715	36
as. CH_2 stretch	ν_{17}	2,965	7	ν_{17}	2,883	20
				$\nu_{10} + \nu_{12}$	2,650	1
				$\nu_{10} + \nu_{11}$	2,624	1
				$\nu_7 + \nu_{13}$	2,531	1
s. CH_2 stretch	ν_{16}	2,918	16	ν_{16}	2,857	29
	$2\nu_5 + \nu_{13}$	2,859	2	$2\nu_5 + \nu_{13}$	2,884	5
	$\nu_{10} + \nu_{12}$	2,683	9			
	$2\nu_{13}$	2,822	1	$2\nu_{13}$	2,912	10
				$4\nu_5$	2,757	5
				$\nu_{11} + \nu_{12}$	2,830	5
CH stretch	ν_{15}	2,794	23	ν_{15}	2,710	62
	$2\nu_{12}$	2,718	12	$2\nu_{12}$	2,790	49
				$2\nu_{11}$	2,763	1
	$\nu_{10} + \nu_{12}$	2,682	13			
C=O stretch	ν_{14}	1,764	137	ν_{14}	1,790	151
				$2\nu_6$	1,707	10
CH_2 scissor	ν_{13}	1,446	7	ν_{13}	1,449	16
	$2\nu_5$	1,411	5			
CH_2 wag, ip OH bend	ν_{12}	1,372	13	ν_{12}	1,416	7
ip CH bend	ν_{11}	1,361	16	ν_{11}	1,384	7
ip OH bend, CH_2 wag,	ν_{10}	1,312	3	ν_{10}	1,233	1
CH_2 twist	ν_9	1,182	15	ν_9	1,184	68
C–O stretch	ν_8	1,079	66	ν_8	1,129	26
CH_2 twist, op CH bend	ν_7	1,049	32	ν_7	1,080	2
CC stretch	ν_6	1,023	29	ν_6	860	35
O=CC bend, CCO bend	ν_5	712	5	ν_5	718	0
CH_2 rock, op CH bend	ν_4	519	2	ν_4	713	56

Calculated intensities are in $km \cdot mol^{-1}$

value of $2\nu_{11}$ is determined around 2,710 cm^{-1}. The theoretical description reveals a more subtle interplay involving four transitions, in particular between the $2\nu_{12}$ and the ν_{15}, calculated at 2,816 and 2,854 cm^{-1}, respectively, for which the intensities are of the same magnitude. Thus, the experimental value of 2,820 cm^{-1} corresponds probably to the $2\nu_{12}$ transition. Note, therefore, that the deviation between theory and experiment on the $2\nu_{11}$, ν_{15} and $2\nu_{12}$ are of 9, 4 and 3–5 cm^{-1}, respectively.

The assignment of the CH_2 stretching mode (ν_{16}) is not straightforward. According to our theoretical description, the harmonic character ω_{16} is widely spread within the states $2\nu_{13}$, $\nu_{12} + \nu_{13}$ and $2\nu_4 + \nu_{13}$ and no major component of ω_{16} appears, according to the form of the PES used. However, Fig. 2a that displays the anharmonic spectrum of the Cc form shows a multiplet shape in the CH stretching region very close to the pictures reported in Ref. [20, 23].

If we turn our attention on the asymmetric CH_2 and OH stretching modes, the observed deviation is about 3–17 cm^{-1} and 21–29 cm^{-1} with the VCI-P results, respectively, while it is about 5–19 cm^{-1} and 0–7 cm^{-1} with the VMP2 results. Here again [38], in the absence of Fermi resonance, the VMP2 treatment is closer to the experimental counterpart for a mode having a well-defined Morse potential even though the analytical form of the PES used has no Morse behavior far from the local minimum (quartic force field). Nevertheless, the VCI-P wavenumber, based on such a force field, is closer to the experimental value than its VCI counterpart (see Eq. 2) that yields some discrepancies of 20–34 cm^{-1} and 39–50 cm^{-1} for the asymmetric CH_2 stretching mode and OH stretching mode, respectively.

Table 2 reports the anharmonic frequencies and activities calculated in the mid-infrared region for the glycolaldehyde in its Tt form. These results are compared with the experimental data obtained when irradiating the Cc conformer isolated in matrix with an IR source [24]. In the region below 1,800 cm^{-1}, the very strong absorptions (ν_{C-C}, ν_{C-O}, ip OH bending) are in good agreement with the theoretical computations, while the very weak absorption (op CH bending) is too far from its theoretical counterpart. In the region above 2,600 cm^{-1}, the experimental transition observed at 2,935 cm^{-1} probably does not correspond to $\nu_{a,CH2}$ since it appears 72 cm^{-1} higher than the corresponding theoretical value and the observed ν_{OH} mode at 3,668 cm^{-1} is overestimated by 72 cm^{-1} by our computations. According to Table 3, it should be noted that the experimental values pointed out here (2,935 and 3,668 cm^{-1}) are closer to their theoretical counterpart belonging to the Tg form which is expected very close in energy to the Tt form.

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