Spectroscopic properties of formaldehyde in aqueous solution: insights from Car-Parrinello and TDDFT/CASPT2 calculations

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Supporting Information Available

1. Absorption spectra of formaldehyde in aqueous solution: a brief summary of reported studies.

Abbreviations used: MD = molecular dynamics, MC = Monte Carlo. If MD or MC is specified, then the configurations of formaldehyde in water were generated at room temperature (i.e., either 298 or 300 K).

Notice that in all of the QM/MM schemes mentioned, the QM and the MM regions are electrostatically coupled.

Table S1: Summary of full QM approaches applied on formaldehyde in gas phase and in aqueous solution. The basis set used is specified in parenthesis.

Ref.	Scheme	Gas phase geometry	Method
1	QM, MC	INDO	CIS
2	QM, MC	MP2 (aug-cc-pVDZ)	TDDFT (6-311++G(d,p))
3	FMO, MD	HF (6-31G)	CIS(D) (6-31G*)

Table S2: Summary of QM/MM approaches applied on formaldehyde in gas phase and in aqueous solution. The basis set used is specified in parenthesis.

Ref.	Scheme	Gas phase geometry	Method
4	QM/MM, MD	RHF (6-31G+d)	RHF(6-31G+d)
5	QM + effective potential	HF(DZP)	MRD-CI(DZP)
6	QM/MM, MD, ASEP	RHF (6-31G+d)	CIS(D), CASPT2 (6-21++G, 6-311+G/G**)
7	QM/MM, MC	CCSD (TZ+2P)	CASSCF (cc-pVTZ)
8	QM/MM, MD, ASEP	experim.	CASSCF (ANO)
9	RISM-SCF	RHF (DZP)	CASSCF (DZP)
10	RISM-SCF	CASSCF (DZP)	CASSCF (DZP)
11	QM/MMpol, MD	AM1	CI
12	QM/MM, MD	B3LYP (cc-pVTZ)	LR-CCSD (aug-cc-pVTZ)
13	QM/MM, MD	B3LYP (cc-pVTZ)	LR-HF, LR-B3LYP, LR-CCSD (6-31++G)
14	QM/MM, MC	MP2 (ANO)	CASSI (ANO)
15	QM/MM, MD, ASEP	MP2 (cc-pvtz)	MRCI, SA-MCSCF (cc-pvtz, aug-cc-pvtz, 6-31++G**)

Table S3: Summary of the implicit solvent based methods applied on formaldehyde in aqueous solution. The basis set used is specified in parenthesis.

Ref.	Scheme	Gas phase geometry	Method
[16]	QM, (IVC)-PCM	PBE0 (6-311G(d,p))	TDDFT, PBE0 (6-311++G(d,p))
[17]	QM, PCM (IEF)	SCF, CASSCF, CI, MR-CI (6-31G**)	SCF, CASSCF, CI, MR-CI (6-31G**)
[18]	QM, PBF	RHF (6-31G+d)	PBF, CIS (6-31G**)

2. Further computational details on CASPT2 calculations

The CASPT2 calculations performed in this work exploited a zeroth order CASSCF wavefunction with no IPEA shift. Here, the complete active space included 4 electrons and 3 orbitals (n, π and π^*). Several tests with different active spaces have been performed: we did not observe large variation on the absorption value, while, with large active spaces, we had problems on the stability of the wave function. In particular, performing single point calculation on a sample of distorted geometries, we noticed, on each calculation, that the active spaces change leading to unreliable results. The choice of the small active space was the best compromise between accuracy and reliability.

3. HOMO and LUMO electronic density

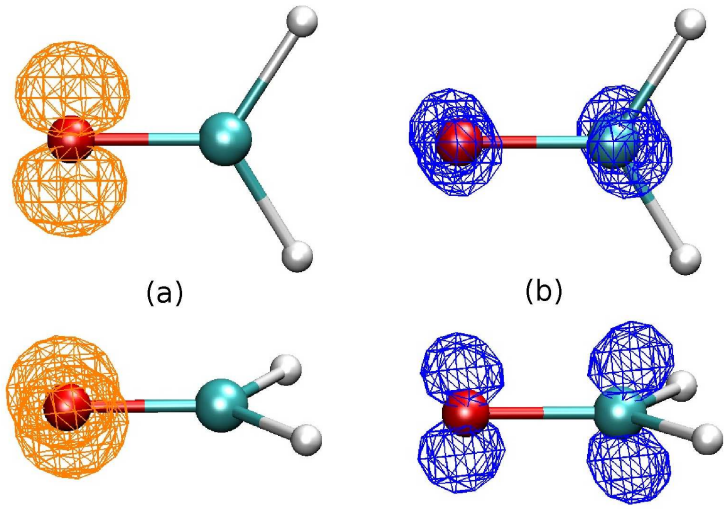

Figure S1: Electronic density contours (isovalue 0.08 a.u.) of the HOMO (a) and LUMO (b), as obtained from our DFT-BLYP calculations of formaldehyde *in vacuo*.

4. Geometrical parameters of formaldehyde from the literature

Table S4: Geometrical features of formaldehyde *in vacuo* from the literature (theoretical values). Bond lengths are in Å and angles in degrees.

Ref.	d(C=O)	d(C-H)	<(HCH)
[7]	1.2	1.1	116.6
[9]	1.198	1.093	116.2
[10]	1.234	1.08	118.0
[15]	1.210	1.101	116.1
[19]	1.198	1.106	116.0
[20]	1.1985	1.1059	116.07

Table S5: Calculated values of formaldehyde's dipole moments in gas phase at 0 K and in water solution at room temperature, taken from the literature. All values are in D. The last columns reports the elongation of the C=O bond (in Å) in formaldehyde or in acetone (last line). The '-' symbol refers to the fact that the carbonyl elongation has not been reported.

Ref.	gas phase μ	water solution μ	carbonyl elongation
[2]	2.38	3.38	-
[6]	2.4	3.4	-
[7]	2.1	3.4	-
[8]	2.35	3.0	-
[9]	2.8	3.2	-
[10]	2.4	3.3	0.025
[11]	2.3	3.1	-
[12]	2.2	3.6	-
[13]	2.6	4.0	-
[15]	2.34	2.89	-
[21]	3.08	4.09	0.02

5. Radial distribution function of formaldehyde in water

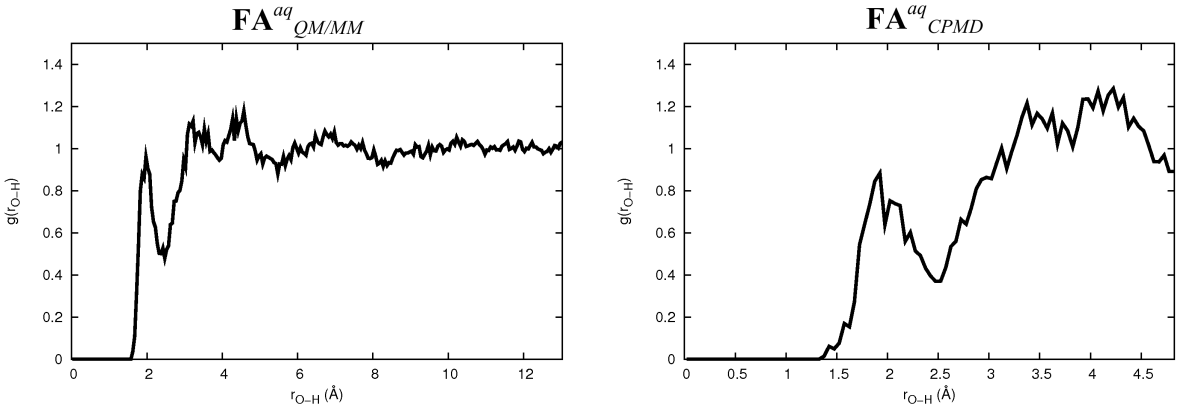

Figure S2: Radial distribution function between formaldehyde oxygen and water hydrogen atoms from QM/MM (left) ad QM (right) calculations.

Table S6: Radial distribution function between formaldehyde oxygen and water oxygen atoms, and relative coordination numbers. The results from the calculations performed here are compared.

		QM in solution	QM/MM
O_{FA}-H_W	Peak (Å)	1.92 ± 0.05	1.97 ± 0.05
	First minimum (Å)	2.47 ± 0.05	2.47 ± 0.05
	♯ H atoms in 1st shell	1.96	1.93
O_{FA}-O_W	Peak (Å)	3.02 ± 0.05	2.92 ± 0.05
	First minimum (Å)	3.22 ± 0.05	3.12 ± 0.05
	♯ O atoms in 1st shell	2.9	2.5

6. Vibrational analysis of formaldehyde in water

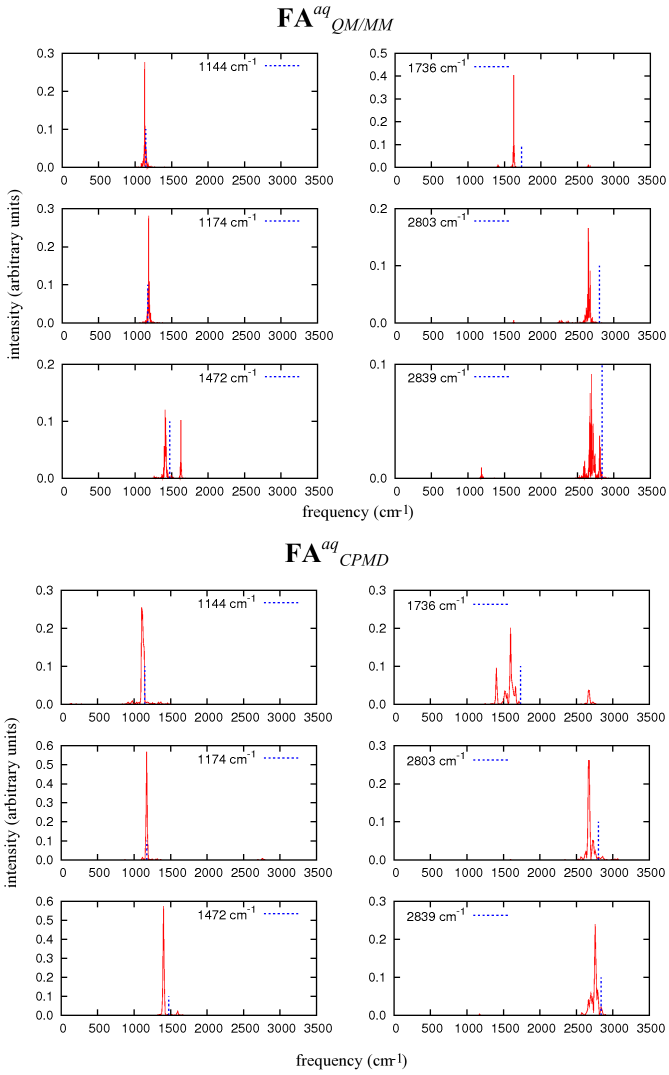

Figure S3: Normal mode analysis for $\mathbf{FA}^{aq}_{QM/MM}$ (top) and $\mathbf{FA}^{aq}_{CPMD}$(bottom). Normal modes associated to each graph, up to down, left: ν_4, ν_6, ν_3; right: ν_2, ν_1, ν_5. The reference normal mode frequencies in gas phase ($\mathbf{FA}_{opt}$) are shown in blue.

7. Simulation of formaldehyde in gas phase at 300 K

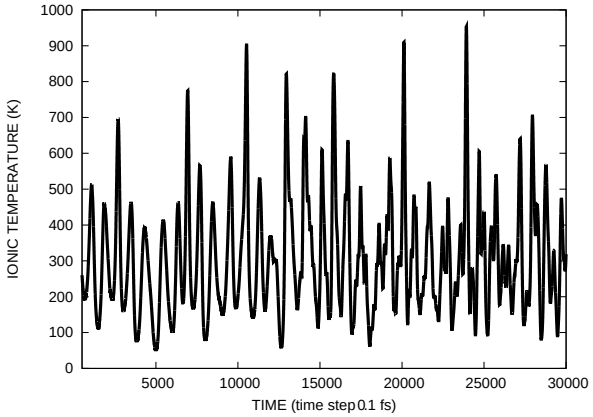

Figure S4: Temperature fluctuations of formaldehyde in gas phase during the CP simulation in the canonical ensemble, obtained by coupling the system to a chain of Nosé-Hoover thermostats.[22]

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