Supplementary Material for Semiclassical Vibrational Spectroscopy of Biological Molecules using Force Fields

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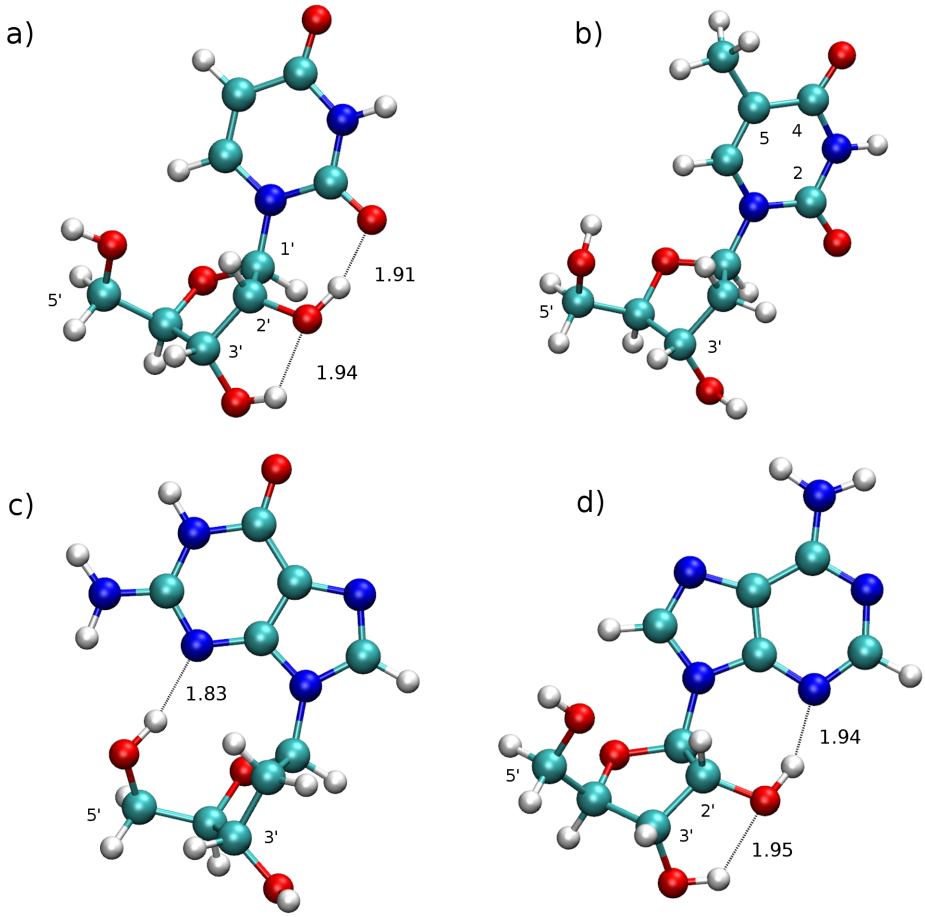

Figure S1. Global minimum structures of uridine (a), thymidine (b), deoxyguanosine, c) adenosine, (d) as predicted by AMBER14SB force field. Colors stand for: oxygen(red); hydrogen (grey); carbon (light blue); nitrogen (dark blue). The positions of some relevant carbon atoms are labeled according to the standard numbering and all the internal hydrogen bonds are reported, together with the corresponding distances in Angstrom.

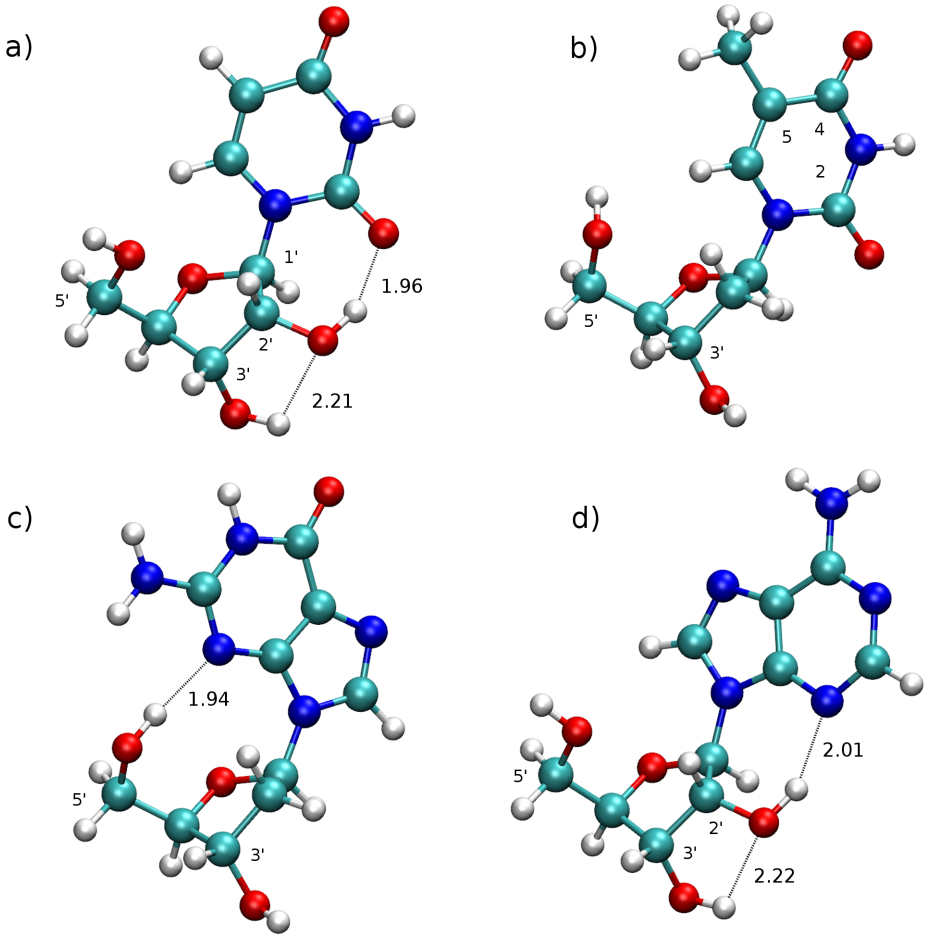

Figure S2. Global minimum structures of uridine (a), thymidine (b), deoxyguanosine, c) adenosine, (d) as predicted by AMOEBABIO18 force field. Colors stand for: oxygen(red); hydrogen (grey); carbon (light blue); nitrogen (dark blue). The positions of some relevant carbon atoms are labeled according to the standard numbering and all the internal hydrogen bonds are reported, together with the corresponding distances in Angstrom.

	AMBER14SB	Δ_{Amb14}	AMOEBABIO18	Δ_{Amo18}	DFT B3LYP	Δ_{DFT}	EXP.
Uridine							
5OH	3668	3	3897	232	3763	98	3665
3OH	3580	-4	3862	278	3642	58	3584
NH	3402	-25	3615	188	3600	173	3427
2OH	3496	38	3729	271	3570	112	3458
Thymidine							
5OH	3696	31	3897	232	3761	96	3665
3OH	3675	33	3890	248	3742	100	3642
NH	3407	-23	3612	182	3604	174	3430
C2O	1714	-13	1606	-121	1809	82	1727
C4O	1884	170	1688	-26	1790	76	1714
C5C6	1786	124	1578	-84	1712	50	1662
Deoxyguanosine							
3OH	3678	16	3892	230	3739	77	3662
NH_2 asym	3425	-120	3715	170	3669	124	3545
NH	3441	3	3612	174	3587	149	3438
NH_2 sym	3288	-157	3598	153	3554	109	3445
5OH	3395	165	3782	552	3417	187	3230
Adenosine							
5OH	3676	40	3900	264	3732	96	3636
NH_2 asym	3437	-118	3747	192	3727	172	3555
3OH	3580	-7	3863	276	3677	90	3587
NH_2 sym	3312	-127	3619	180	3602	163	3439
2OH	3473	208	3727	462	3452	187	3265

Table S1. Harmonic frequencies for each nucleoside and adopted theoretical method compared to the experiment.[S1–S5] The Δ columns represent the distance of each value with respect to experimental findings. All the frequencies values are reported in cm^{-1}.

	AMBER14SB	Δ_{Amb14}	AMOEBABIO18	Δ_{Amo18}	DFT B3LYP	Δ_{DFT}	EXP.
Uridine							
5OH	3560	-105	3730	65	3680	15	3665
3OH	3480	-104	3640	56	3560	-24	3584
NH	3340	-87	3490	63	3340	-87	3427
2OH	3480	22	3580	122	3490	32	3458
MAE		80		77		40	
Thymidine							
5OH	3580	-85	3700	35	3680	15	3665
3OH	3560	-82	3660	18	3650	8	3642
NH	3270	-160	3450	20	3380	-50	3430
C2O	1690	-37	1600	-127	1780	53	1727
C4O	1850	136	1670	-44	1770	56	1714
C5C6	1760	98	1600	-62	1680	18	1662
MAE		90		51		33	

Table S2. Semiclassical frequencies for Uridine and Thymidine compared to the experiment.[S1,S3] The Δ columns represent the distance of each value with respect to experimental findings, while the MAE label stands for Mean Absolute Error. All the frequencies values are reported in cm^{-1}.

	AMBER14SB	Δ_{Amb14}	AMOEBABIO18	Δ_{Amo18}	DFT B3LYP	Δ_{DFT}	EXP.
Deoxyguanosine							
3OH	3580	-82	3700	38	3650	4	3662
NH_2 asym	3400	-145	3530	-15	3560	5	3545
NH	3370	-68	3470	32	3470	23	3438
NH_2 sym	3190	-255	3400	-45	3460	11	3445
5OH	3280	50	3590	360	3280	-65	3230
MAE		120		98		25	
Adenosine							
5OH	3570	-66	3730	94	3640	-12	3636
NH_2 asym	3330	-225	3540	-15	3560	15	3555
3OH	3490	-97	3630	43	3610	32	3587
NH_2 sym	3190	-249	3400	-39	3450	15	3439
2OH	3210	-55	3550	285	3200	50	3265
MAE		157		95		26	

Table S3. Semiclassical frequencies for Adenosine and Deoxyguanosine compared to the experiment.[S2,S4,S5] The Δ columns represent the distance of each value with respect to the experimental findings, while the MAE label stands for Mean Absolute Error. All the frequencies values are reported in cm^{-1}.

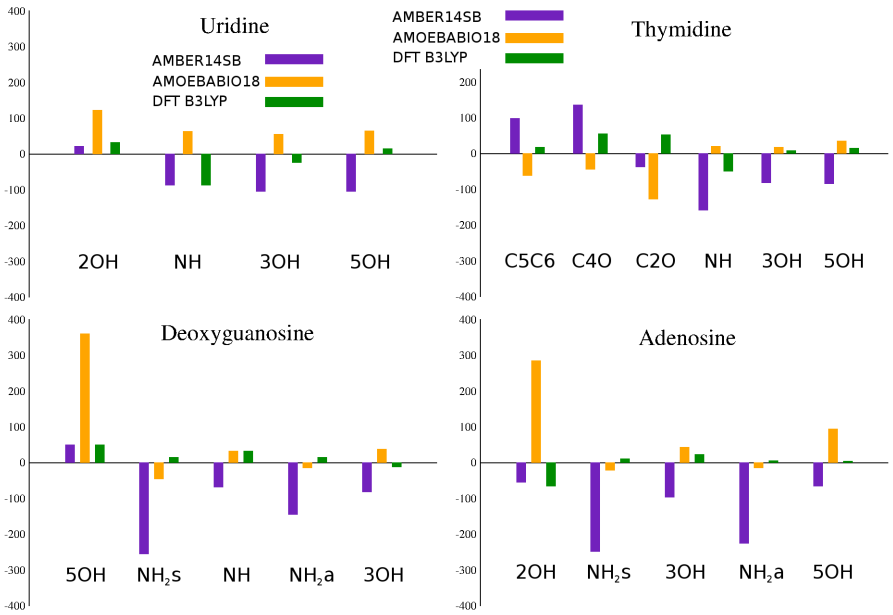

Figure S3. Difference (cm^{-1}) between all calculated semiclassical frequencies and experimental values for each nucleoside and theoretical method.

	Num. Hess.	Cutoff
Uridine zpe traj	245	0.15
Thymidine zpe traj	234	0.15
Deoxyguanosine zpe traj	256	0.15
Adenosine zpe traj	244	0.15
Uridine refinement traj	285	0.15
Thymidine refinement traj	274	0.15
Deoxyguanosine refinement traj	211	0.07
Adenosine refinement traj	262	0.15

Table S4. Number of Hessian matrices calculated and corresponding Hessian database cutoff adopted for each nucleoside analysis, in case of DFT semiclassical simulations.

	AMBER14SB		AMOEBABIO18		DFT B3LYP	
Uridine	Sub Dim	Thr.	Sub Dim	Thr.	Sub Dim	Thr.
5OH	1	$\geqslant 7 \cdot 10^{-6}$	3	$1 \cdot 10^{-6}$	5	$4 \cdot 10^{-6}$
3OH	11[a]	$4 \cdot 10^{-6}$	1	$\geqslant 2 \cdot 10^{-6}$	1	$\geqslant 9 \cdot 10^{-6}$
NH	2	$6 \cdot 10^{-6}$	1	$\geqslant 2 \cdot 10^{-6}$	2	$5 \cdot 10^{-6}$
2OH	1	$\geqslant 3 \cdot 10^{-6}$	1	$\geqslant 4 \cdot 10^{-6}$	3	$5 \cdot 10^{-6}$

Thymidine	Sub Dim	Thr.	Sub Dim	Thr.	Sub Dim	Thr.
5OH	9	$3 \cdot 10^{-6}$	1	$\geqslant 7 \cdot 10^{-6}$	23	$1 \cdot 10^{-6}$
3OH	9	$3 \cdot 10^{-6}$	2	$7 \cdot 10^{-6}$	23	$1 \cdot 10^{-6}$
NH	2	$3 \cdot 10^{-6}$	1	$\geqslant 7 \cdot 10^{-6}$	1	$\geqslant 2 \cdot 10^{-6}$
C2O	1	$\geqslant 2 \cdot 10^{-6}$	1	$\geqslant 2 \cdot 10^{-6}$	1	$\geqslant 2 \cdot 10^{-5}$
C4O	1	$\geqslant 1 \cdot 10^{-6}$	1	$\geqslant 9 \cdot 10^{-7}$	1	$\geqslant 2 \cdot 10^{-5}$
C5C6	1	$\geqslant 1 \cdot 10^{-6}$	1	$\geqslant 2 \cdot 10^{-6}$	1	$\geqslant 2 \cdot 10^{-5}$

Deoxyguanosine	Sub Dim	Thr.	Sub Dim	Thr.	Sub Dim	Thr.
3OH	1	$\geqslant 1 \cdot 10^{-5}$	1	$\geqslant 4 \cdot 10^{-6}$	20	$2 \cdot 10^{-6}$
NH_2 asym	1	$\geqslant 3 \cdot 10^{-6}$	1	$\geqslant 3 \cdot 10^{-6}$	20	$2 \cdot 10^{-6}$
NH	1	$\geqslant 2 \cdot 10^{-6}$	1	$\geqslant 9 \cdot 10^{-6}$	20	$2 \cdot 10^{-6}$
NH_2 sym	1	$\geqslant 2 \cdot 10^{-6}$	1	$\geqslant 8 \cdot 10^{-6}$	20	$2 \cdot 10^{-6}$
5OH	1	$\geqslant 1 \cdot 10^{-6}$	1	$\geqslant 3 \cdot 10^{-6}$	3	$1 \cdot 10^{-6}$

Adenosine	Sub Dim	Thr.	Sub Dim	Thr.	Sub Dim	Thr.
5OH	1	$\geqslant 2 \cdot 10^{-5}$	3	$7 \cdot 10^{-6}$	12	$8 \cdot 10^{-6}$
NH_2 asym	13	$2 \cdot 10^{-6}$	1	$\geqslant 4 \cdot 10^{-6}$	1	$\geqslant 3 \cdot 10^{-5}$
3OH	13	$2 \cdot 10^{-6}$	1	$\geqslant 5 \cdot 10^{-6}$	1	$\geqslant 6 \cdot 10^{-6}$
NH_2 sym	13	$2 \cdot 10^{-6}$	3	$3 \cdot 10^{-6}$	4	$8 \cdot 10^{-6}$
2OH	2	$2 \cdot 10^{-6}$	1	$\geqslant 4 \cdot 10^{-6}$	3	$5 \cdot 10^{-6}$

Table S5. Subspace dimensionality employed in the DC-SCIVR analysis for each nuleoside and method and corresponding threshold for the average Hessian partition criterion. a) In this case a 4-dimensional subspace has been added to a 7-dimensional one to get well defined signals.

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