Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Pitfall in simulations of vibronic TD-DFT spectra: Diagnosis and assessment

SUPPORTING INFORMATION

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During the RRMSE calculations (which required many single–point–type calculations) the following convergence criteria in Gaussian 16 were used: 10^{-11} in SCF (DIIS error), 10^{-11} in CP-KS, and 10^{-7} (10^{-8} for formaldehyde) during the TD–DFT computations. Geometries were optimized using the VeryTight convergence criterion. For the optimization procedures and the frequency calculations (which are required for the numerical evaluation of high order energy–derivatives necessary for the simulation of anharmonic vibronic spectra), we used a respective set of criteria: 10^{-10} in SCF, 10^{-11} in CP-KS, and 10^{-7} in TD–DFT. In all of the computations, the threshold for two–electron integral screening was set to 10^{-14}.

Table S1: Average RRMSE for $\mathrm{d}^3E/\mathrm{d}Q^3$ (averaging over all available normal modes) and different electronic states of formaldehyde, pyridine, and furan, computed with tested DFAs and several unpruned integration grids. For all molecular systems, $1^1\mathrm{A}_1$ denotes the electronic ground–state, and other states are the selected bright excited states. In the case of furan, $1^2\mathrm{A}_2$ corresponds to the lowest electronic state of its ionized form, i.e. the electronic ground–state of furan cation.

		FORMALDEHYDE			PYRIDINE		FURAN	
		$1^1\mathrm{A}_1$	$1^1\mathrm{A}_2$	$1^1\mathrm{B}_2$	$1^1\mathrm{A}_1$	$1^1\mathrm{B}_1$	$1^1\mathrm{A}_1$	$1^2\mathrm{A}_2$
LC-BLYP	(99,590)	0	0	0	4	1	5	0
	(250,974)	0	0	0	1	0	0	0
	(750,974)	0	0	0	1	0	0	0
CAM-B3LYP	(99,590)	0	0	1	4	1	3	0
	(250,974)	0	0	0	1	0	1	0
	(750,974)	0	0	0	1	0	1	0
ωB97X	(99,590)	2	9	9	90	52	65	15
	(250,974)	0	1	0	33	22	32	7
	(750,974)	0	1	0	32	16	32	7
M06-2X	(99,590)	17	16	22	81	21	59	13
	(250,974)	4	11	23	22	10	37	4
	(750,974)	4	11	23	22	10	37	4

Table S2: Average arithmetic mean of RRMSEs of different components of transition dipole moment (calculated as $1/3\sum_{i=x,y,z}\mathrm{RRMSE}[\mathrm{d}^2\langle 1^1A_1|\hat{\mu}_i|X\rangle/\mathrm{d}Q^2]$) from ground electronic state $1^1\mathrm{A}_1$ to different electronic state X of formaldehyde and pyridine (averaging over all available normal modes). Normal modes corresponded to the optimized geometry of the ground electronic states. Results for furan are not shown, due to the fact that for furan, the vertical photoionization from $1^1\mathrm{A}_1$ to $1^2\mathrm{A}_2$ is dipole forbidden.

		FORMALDEHYDE		PYRIDINE
		$1^1\mathrm{A}_2$	$1^1\mathrm{B}_2$	$1^1\mathrm{B}_1$
LC-BLYP	(99,590)	0	0	2
	(250,974)	0	0	2
	(750,974)	0	0	2
CAM-B3LYP	(99,590)	0	4	1
	(250,974)	0	0	1
	(750,974)	0	0	1
ωB97X	(99,590)	4	1	2
	(250,974)	0	0	2
	(750,974)	0	0	1
M06-2X	(99,590)	16	3	4
	(250,974)	1	0	3
	(750,974)	1	0	3

Table S3: Average RRMSE for $\mathrm{d}^3\langle 1^1A_1|\bar{\hat{\mu}}|X\rangle/\mathrm{d}Q^3$, where $\bar{\hat{\mu}} = \frac{1}{3}(\hat{\mu}_x + \hat{\mu}_y + \hat{\mu}_z)$ from ground electronic state $1^1\mathrm{A}_1$ to different electronic state X of formaldehyde and pyridine (averaging over all available normal modes). Normal modes corresponded to the optimized geometry of the ground electronic states. Results for furan are not shown, due to the fact that for furan, the vertical photoionization from $1^1\mathrm{A}_1$ to $1^2\mathrm{A}_2$ is dipole forbidden.

		FORMALDEHYDE		PYRIDINE
		$1^1\mathrm{A}_2$	$1^1\mathrm{B}_2$	$1^1\mathrm{B}_1$
LC-BLYP	(99,590)	0	0	4
	(250,974)	0	0	8
	(750,974)	0	0	2
CAM-B3LYP	(99,590)	0	7	3
	(250,974)	0	1	5
	(750,974)	0	1	3
WB97X	(99,590)	5	4	36
	(250,974)	0	1	20
	(750,974)	0	1	11
M06-2X	(99,590)	24	78	288
	(250,974)	2	10	18
	(750,974)	2	10	20

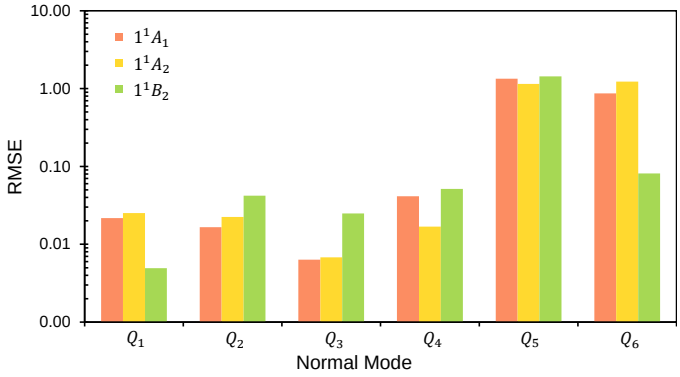

Figure S1: RMSE for $\mathrm{d}^4E/\mathrm{d}{Q_n}^4$ for different normal modes Q_n of formaldehyde corresponding to the optimized geometries of the selected electronic states of formaldehyde, computed with M06-2X and the (99,590) integration grid.

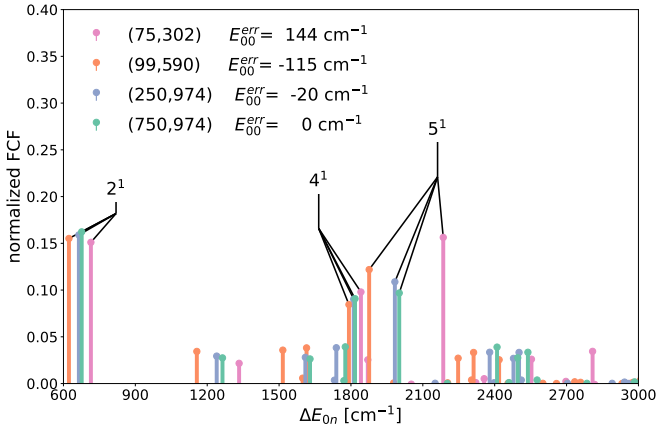

Figure S2: Normalized PT2 FC spectra of the $1^1\mathrm{A}_1 \rightarrow 1^1\mathrm{B}_2$ ($S_0 \rightarrow S_2$) transition of formaldehyde obtained with ωB97–X using various integration grids and $0.02|Q|$ step size for numerical differentiation. On the horizontal axis, differences with respect to the anharmonic 0-0 band are shown ($\Delta E_{0n} = E_{0n} - E_{00}$). On the legend, next to the grid labels, the corresponding errors in the anharmonic transition energies of 0-0 band, when compared to the reference (750,974) grid, are given ($E_{00}^{\mathrm{err}} = E_{00} - E_{00}^{(750,974)}$).

Optimized geometries

```
formaldehyde 1^1A_1 state, LC-BLYP(250,974)/6-311++G**
O 0.000000    0.000000    0.595619
C 0.000000    0.000000   -0.596307
H 0.000000    0.939677   -1.176385
H 0.000000   -0.939677   -1.176385

formaldehyde 1^1A_1 state, M06-2X(250,974)/6-311++G**
O 0.000000    0.000000    0.597941
C 0.000000    0.000000   -0.598713
H 0.000000    0.939401   -1.180490
H 0.000000   -0.939401   -1.180490

formaldehyde 1^1A_1 state,  wB97X(250,974)/6-311++G**
O 0.000000    0.000000    0.599246
C 0.000000    0.000000   -0.599891
H 0.000000    0.940493   -1.183834
H 0.000000   -0.940493   -1.183834

formaldehyde 1^1A_2 state,  LC-BLYP(250,974)/6-311++G**
O  0.627015    0.006654    0.000000
C -0.639214   -0.030025    0.000000
H -1.170085    0.125946    0.943797
H -1.170085    0.125946   -0.943797

formaldehyde 1^1A_2 state,  M06-2X(250,974)/6-311++G**
O  0.631462    0.011004    0.000000
C -0.648254   -0.051961    0.000000
H -1.151553    0.222027    0.933687
H -1.151553    0.222027   -0.933687

formaldehyde 1^1A_2 state,  wB97X(250,974)/6-311++G**
O  0.632854    0.010067    0.000000
C -0.648508   -0.046964    0.000000
H -1.161086    0.199708    0.938452
H -1.161086    0.199708   -0.938452

formaldehyde 1^1B_2 state,  LC-BLYP(250,974)/6-311++G**
O 0.000000    0.000000    0.581260
C 0.000000    0.000000   -0.581071
H 0.000000    0.979031   -1.153157
H 0.000000   -0.979031   -1.153157

formaldehyde 1^1B_2 state,  M06-2X(250,974)/6-311++G**
O 0.000000    0.000000    0.584188
C 0.000000    0.000000   -0.580836
H 0.000000    0.964089   -1.177786
H 0.000000   -0.964089   -1.177786
```

formaldehyde 1^1B_2 state, wB97X(250,974)/6-311++G**
O 0.000000   -0.000000   0.585755
C 0.000000   0.000000   -0.587958
H 0.000000   0.988764   -1.147816
H 0.000000   -0.988764   -1.147816

furan 1^1A_1 state, LC-BLYP(250,974)/6-311++G**
C 0.000000   0.713407   -0.973576
C 0.000000   -0.713407   -0.973576
C 0.000000   -1.082669   0.315702
O 0.000000   0.000000   1.115277
C 0.000000   1.082669   0.315702
H 0.000000   1.370780   -1.827511
H 0.000000   -1.370780   -1.827511
H 0.000000   -2.039130   0.810585
H 0.000000   2.039130   0.810585

furan 1^1A_1 state, M06-2X(250,974)/6-311++G**
C 0.000000   0.717566   -0.982925
C 0.000000   -0.717566   -0.982925
C 0.000000   -1.088799   0.319772
O 0.000000   0.000000   1.123367
C 0.000000   1.088799   0.319772
H 0.000000   1.375596   -1.836126
H 0.000000   -1.375596   -1.836126
H 0.000000   -2.043264   0.817848
H 0.000000   2.043264   0.817848

furan 1^1A_1 state, wB97X(250,974)/6-311++G**
C 0.000000   0.717363   -0.982419
C 0.000000   -0.717363   -0.982419
C 0.000000   -1.088970   0.318334
O 0.000000   0.000000   1.124991
C 0.000000   1.088970   0.318334
H 0.000000   1.376274   -1.837553
H 0.000000   -1.376274   -1.837553
H 0.000000   -2.044929   0.817488
H 0.000000   2.044929   0.817488

furan 1^2A_2 state, ULC-BLYP(250,974)/6-311++G**
C 0.000000   0.682104   -1.006280
C 0.000000   -0.682104   -1.006280
C 0.000000   -1.069124   0.339990
O 0.000000   0.000000   1.128954
C 0.000000   1.069124   0.339990
H 0.000000   1.355780   -1.851083
H 0.000000   -1.355780   -1.851083
H 0.000000   -2.037107   0.825833
H 0.000000   2.037107   0.825833

```
furan 1^2A_2 state,  UM06-2X(250,974)/6-311++G**
C 0.000000    0.688284   -1.014992
C 0.000000   -0.688284   -1.014992
C 0.000000   -1.075733    0.343089
O 0.000000    0.000000    1.137517
C 0.000000    1.075733    0.343089
H 0.000000    1.363904   -1.857491
H 0.000000   -1.363904   -1.857491
H 0.000000   -2.041028    0.831108
H 0.000000    2.041028    0.831108

furan 1^2A_2 state,  UwB97X(250,974)/6-311++G**
C 0.000000    0.687772   -1.014431
C 0.000000   -0.687772   -1.014431
C 0.000000   -1.075170    0.341539
O 0.000000    0.000000    1.139273
C 0.000000    1.075170    0.341539
H 0.000000    1.363143   -1.858789
H 0.000000   -1.363143   -1.858789
H 0.000000   -2.041701    0.830252
H 0.000000    2.041701    0.830252

pyridine 1^1A_1 state,  LC-BLYP(250,974)/6-311++G**
C 0.000000    0.000000   -1.393935
C 0.000000    1.184580   -0.691279
C 0.000000    1.131029    0.686842
N 0.000000    0.000000    1.369886
C 0.000000   -1.131029    0.686842
C 0.000000   -1.184580   -0.691279
H 0.000000    0.000000   -2.477349
H 0.000000    2.140611   -1.198585
H 0.000000    2.045309    1.271924
H 0.000000   -2.045309    1.271924
H 0.000000   -2.140611   -1.198585

pyridine 1^1A_1 state,  M06-2X(250,974)/6-311++G**
C 0.000000    0.000000   -1.408201
C 0.000000    1.193884   -0.698270
C 0.000000    1.137720    0.692320
N 0.000000    0.000000    1.385847
C 0.000000   -1.137720    0.692320
C 0.000000   -1.193884   -0.698270
H 0.000000    0.000000   -2.491991
H 0.000000    2.150914   -1.204695
H 0.000000    2.052286    1.277417
H 0.000000   -2.052286    1.277417
H 0.000000   -2.150914   -1.204695
```

pyridine 1^1A_1 state, wB97X(250,974)/6-311++G**
C 0.000000 0.000000 -1.406996
C 0.000000 1.193302 -0.697577
C 0.000000 1.137405 0.691478
N 0.000000 0.000000 1.385094
C 0.000000 -1.137405 0.691478
C 0.000000 -1.193302 -0.697577
H 0.000000 0.000000 -2.492557
H 0.000000 2.151714 -1.205205
H 0.000000 2.053206 1.278036
H 0.000000 -2.053206 1.278036
H 0.000000 -2.151714 -1.205205

pyridine 1^1B_1 state, LC-BLYP(250,974)/6-311++G**
C 0.108854 1.345637 0.000000
C -0.037600 0.658665 1.211036
C -0.104173 -0.707580 1.203686
N 0.223255 -1.223160 0.000000
C -0.104173 -0.707580 -1.203686
C -0.037600 0.658665 -1.211036
H 0.139531 2.426468 0.000000
H -0.198730 1.188485 2.142553
H -0.382017 -1.332923 2.041678
H -0.382017 -1.332923 -2.041678
H -0.198730 1.188485 -2.142553

pyridine 1^1B_1 state, M06-2X(250,974)/6-311++G**
C 0.096041 1.368896 0.000000
C -0.032432 0.666293 1.218368
C -0.085898 -0.711243 1.220440
N 0.182895 -1.250376 0.000000
C -0.085898 -0.711243 -1.220440
C -0.032432 0.666293 -1.218368
H 0.114472 2.449472 0.000000
H -0.182565 1.184329 2.158909
H -0.308112 -1.336875 2.073283
H -0.308112 -1.336875 -2.073283
H -0.182565 1.184329 -2.158909

pyridine 1^1B_1 state, wB97X(250,974)/6-311++G**
C 0.109518 1.360236 0.000000
C -0.037379 0.664676 1.220802
C -0.100227 -0.711473 1.211672
N 0.214474 -1.239946 0.000000
C -0.100227 -0.711473 -1.211672
C -0.037379 0.664676 -1.220802
H 0.132920 2.443416 0.000000
H -0.204825 1.189773 2.156513
H -0.365175 -1.338208 2.055125
H -0.365175 -1.338208 -2.055125
H -0.204825 1.189773 -2.156513