

# Supporting Information:

## Describing nuclear quantum effects in vibrational properties using molecular dynamics with Wigner sampling

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# 1 Calculations

## 1.1 $\text{H}_2^+$

To simplify simulations, we calculated potential energy at the HF/aug-cc-pV6Z level using ORCA software<sup>S1</sup> and then approximated it with Morse potential  $E(r) = E_e + D_e \cdot (1 - \exp(-\beta \cdot (r - r_e)))^2$ , where  $E_e = -0.606674$  Ha is the equilibrium electronic energy,  $D_e = 0.103666$  Ha is the equilibrium dissociation energy,  $r_e = 1.07691$  Å is the equilibrium distance, and  $\beta = 1.46583$  Å<sup>-1</sup> is the parameter, that controls the steepness of the potential. The one-dimensional stationary Schrödinger equation for the vibrational motion was solved with help of the MOLINC package,<sup>S2</sup> employing sinc-DVR kinetic energy representation.<sup>S3</sup>

Simulations were performed using three sampling routines: (a) MBS at various initial temperatures, (b) WS and (c) SWS with different  $\tau$  parameters ranging from 0.1 to 100 fs. 150 trajectories were ran in each case. The total time of each simulation was 0.5 ps with the time step of 0.5 fs.

## 1.2 Rotational constants for $\text{H}_2\text{O}$ , $\text{C}_2\text{H}_4$ , $\text{CH}_2\text{F}_2$ , $\text{C}_2\text{H}_2\text{F}_2$ , $\text{C}_6\text{H}_{12}\text{N}_2$ , $\text{C}_{26}\text{H}_{34}\text{O}_2$

VPT2 computations were done using Gaussian 16<sup>S4</sup> software.

MD simulations for these molecules were done for 0.5 ps. The slowest harmonic vibration among the test molecules was in cis -  $\text{C}_2\text{H}_2\text{F}_2$  with the frequency of 219 cm<sup>-1</sup>, which corresponds to the vibrational period of 0.15 ps. Thus during 0.5 ps this motion was likely sampled three times. The time step was 0.5 fs. For each of the molecules, 50 MD trajectories with WS and SWS initial conditions were started. The gradients for the molecules were obtained using ORCA 5.<sup>S1</sup> The used quantum-chemical approximation for the electronic problem in all cases was PBE/def2-SVP.<sup>S5,S6</sup> The WS procedure was performed using scripts from the SHARC-MD package.<sup>S7-S9</sup> Rotational and translational motions in the molecules at the beginning of the simulations were frozen. MD simulations were run with the BOMoND script from the PyRAMD repository.<sup>S10,S11</sup> Obtained MD trajectories were processed with scripts from the MOLINC repository.<sup>S2</sup>

For determination of  $\tau$  in the SWS procedure, we obtained 30 trajectories with 1 fs time step and 0.5 ps of total duration for three molecules:  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_4$ , and  $\text{CH}_2\text{F}_2$ . For each  $\tau$  30 independent trajectories were obtained. The minimal vibrational energies were reached at  $\tau = 3$  fs, however with a flat plato-like well in the range of 2-4 fs. Because of that, in SWS+MD simulations, the  $\tau$  parameter was not scanned but fixed at the optimal value found for the  $\text{H}_2^+$  ion ( $\tau = 2$  fs).

For 6,6-dimethyl-1,5-diazabicyclo[3.1.0]hexane ( $C_6H_{12}N_2$ ) and *syn*-conformer of 6,6'-bis(3-oxadamantane) ( $C_{26}H_{34}O_2$ ) we used D3BJ empirical corrections,<sup>S12</sup> so the complete quantum-chemical approximation was PBE-D3BJ/def2-SVP. The lowest and the highest harmonic frequencies among vibrations in both molecules were 78 and 3110  $cm^{-1}$ , which correspond to the vibrational periods of 430 and 11 fs, respectively. To provide an approximate coverage of at least three vibrational periods for each of the modes, the total duration of MD trajectories was set to 1.5 ps. The time step for the simulation was chosen to be 1 fs, to be at least ten times smaller than the period of the fastest vibration. For  $C_6H_{12}N_2$  and  $C_{26}H_{34}O_2$  35 and 46 WS+MD trajectories were obtained, respectively.

### 1.3 Vibrational spectra of $CH_2F_2$

Calculations were done using PBE/def2-SVP quantum-chemical level of theory. Simulations for difluoromethane  $CH_2F_2$  were performed using a combination of SWS and Andersen thermostat (abbreviated as SWS-AT+MD) with the collision period of 300 fs, time step of 1 fs and total trajectory duration of 10 ps. These calculations were done for two different temperatures,  $T = 0$  K and  $T = 300$  K. Three and four trajectories were collected in simulations for  $T = 0$  K and  $T = 300$  K, respectively. For comparison, we also performed classical constant temperature MD simulations with the Andersen thermostat applying the MBS scheme (MBS-AT+MD).

### 1.4 Benzene $C_6H_6$

MD simulations for benzene were performed at the PBEh-3c level of theory<sup>S13</sup> using BOMoND and ORCA 5. The following numbers of trajectories were obtained: 50 for WS+MD, 24 for SWS-AT+MD at  $T = 0$  K, 47 for SWS-AT+MD at  $T = 300$  K and 35 for MBS-AT+MD at  $T = 300$  K. The time step in all cases was 1 fs, the total lengths of each trajectory were 2 ps, collision period for AT was 300 fs.

IR spectra from all the MD simulations were calculated for each trajectory separately. The spectra were then averaged for each simulation type set. First 0.5 ps in each trajectory were considered as equilibration phase and therefore ignored. The resulting spectra were convoluted using Gaussian function with the full width at half maximum (FWHM) parameter of 50  $cm^{-1}$ .

Harmonic and VPT2 frequency calculations have been performed in ORCA 5. At present, the VPT2 module of ORCA does not compute anharmonic IR intensities. Thus, we assumed equal IR intensities for harmonic and VPT2 normal modes.

In modeling photoelectron spectra (PES), conventional Franck-Condon factors were computed for the ground electronic states of the neutral benzene and for its cation using the ezFCS software.<sup>S14</sup> To account for vibrational motions 150 structures of benzene were sampled by the WS procedure and harmonic vibrational modes at the PBEh-3c level. For these structures ionization potentials (IPs) were calculated using ADC(2)/cc-pVTZ method. Binning the obtained IPs allowed us to compute an approximate PE spectrum. For anharmonic treatment of vibrational motions, 5 structures were randomly taken from each of 24 SWS-AT+MD ( $T = 0$  K) trajectories, providing 120 structures in total. For them single-point IPs were computed at the ADC(2)/cc-pVTZ level. Then, doing a similar binning, we obtained the corresponding PE spectrum. Experimental photoelectron spectra (PES) of benzene<sup>S15</sup> were digitized using the WebPlotDigitizer software.<sup>S16</sup>

## 1.5 Protonated methane cation $\text{CH}_5^+$

Four sets of MD simulations were performed, MBS-AT+MD at  $T = 300$  K (29 trajectories), WS+MD (45 trajectories), SWS-AT+MD at  $T = 0$  K (21 trajectories) and  $T = 300$  K (23 trajectories). The gradients were calculated at the PBEh-3c level of theory. The time step was 1 fs for each trajectory. The total time span for each trajectory was set to 4 ps, except for WS+MD with 2 ps. First 0.5 ps were removed from each trajectory due to equilibration. Calculations of IR spectra from trajectories were performed in the same way as for benzene. To compare with standard models, harmonic and VPT2 frequencies were computed in ORCA 5.

Gibbs free energy of the probing reactions has been computed in the following hybrid scheme. Geometry optimizations and frequency calculations were done at the PBEh-3c level of theory for 298 K, whereas single point energies were computed using the ae-CCSD(T) theory applying complete basis set (CBS) extrapolation technique based on the cc-pVTZ and cc-pVQZ sets.<sup>S17-S19</sup>

Experimental spectrum<sup>S20</sup> has been digitized using WebPlotDigitizer.<sup>S16</sup>

## 1.6 Protonated serine octamer $\text{Ser}_8\text{H}^+$

### 1.6.1 IR vibrational spectra

Two MD simulations have been performed, MBS-AT+MD at  $T = 300$  K and SWS-AT+MD at  $T = 0$  K. Gradients were calculated at the BLYP-D3BJ/6-31G level of theory. The lengths of trajectories in both simulations were 3 ps. Of these, first 100 fs were discarded due to equilibration.

The helium detachment energy  $D$  in the  $\text{He} - \text{Ser}_8\text{H}^+$  complex was calculated to be  $379 \text{ cm}^{-1}$ .

For this, the initial structures were generated using the CoalescenceKick software.<sup>S21,S22</sup> Structure optimization, and single point energy calculations were done using the GFN2-xTB<sup>S23</sup> semi-empirical approximation.

### 1.6.2 Benchmark of computational times

For comparing computational effectiveness of VPT2 and MD we have performed two numerical tests at the BLYP-D3BJ/6-31G and PBE-D3BJ/6-31G levels of theory. Two subsequent ORCA calculations were started at the same computational node to evaluate the computational time.

- Single point energy calculation + analytical gradient ( $t_{\text{Grad}}$ ).
- Single point energy calculation + analytical Hessian ( $t_{\text{Hess}}$ ).

**Table S1** Computational times (in seconds) required for analytical gradient ( $t_{\text{Grad}}$ ) and Hessian ( $t_{\text{Hess}}$ ) of protonated serine octamer.

Level of theory	$t_{\text{Grad}}$	$t_{\text{Hess}}$	$667 \times t_{\text{Hess}}/t_{\text{Grad}}$
BLYP-D3BJ/6-31G	91.81	892.18	6482
PBE-D3BJ/6-31G	89.68	1628.20	12110

Both calculations started from the same default initial guess. The timings are shown in the table S1. The VPT2 method for the protonated serine octamer (113 atoms) with  $3 \times 113 - 6 = 333$  vibrational degrees of freedom requires calculation in total 667 Hessians – for two displaced structures along each of the 333 modes plus for the equilibrium structure. Therefore, the total duration of the VPT2 calculations for  $\text{Ser}_8\text{H}^+$  we can estimate as  $t_{\text{VPT2}} \approx 667 \times t_{\text{Hess}}$ .

The limiting stage of the *ab initio* MD simulation is the gradient evaluation ( $t_{\text{Grad}}$ ). Thus, the total computational time of the MD trajectory we can estimate as  $t_{\text{MD}} \approx t_{\text{Grad}} \times N_{\text{MD}}$ , where  $N_{\text{MD}}$  is the number of steps in the MD trajectory.

We can now evaluate the number of MD steps ( $N_{\text{MD}}$ ) that we can perform to keep the computational time of the MD simulation the same as the for the VPT2 calculation. This number is given by equation  $t_{\text{MD}} = t_{\text{VPT2}}$ , which provides us with the estimation

$$N_{\text{MD}} = \frac{667 \times t_{\text{Hess}}}{t_{\text{Grad}}}.$$

As it can be seen for the  $\text{Ser}_8\text{H}^+$  from Table S1, the total number of steps at the GGA level with 6-31G basis set is about  $N_{\text{MD}} \sim 6 - 12 \times 10^3$  steps.

## 2 MD jobs submission data

### 2.1 Submission script

To submit an MD job of a given type, we used Bash scripts that allowed tracking options of the BOMoND<sup>S10,S11</sup> script, given below:

**Table S2** Bash script to start BOMoND simulations.

```
1 #!/bin/bash
2
3 #SBATCH --time=3-20:00:00
4 #SBATCH --nodes=1
5 #SBATCH --job-name BOMoND!
6 #SBATCH --output job.out # File to which STDOUT will be written
7 #SBATCH --error job.err # File to which STDERR will be written
8
9 # this is the path to the location of the PyRAMD code
10 PYRPATH="/home/homedir/pyramd"
11
12 # time step in fs
13 DT=1.0
14 # simulation time in ps
15 ST=4.0
16 # charge of the system
17 Q=1
18 # multiplicity of the system
19 M=1
20
21 ADDOPT="--FreezeTranslation --FreezeRotation "
22 ADDOPT+=" --charge $Q --mult $M "
23 ADDOPT+=" --dt $DT --QCInterface orca5 "
24 ADDOPT+=" --SaveDipoles --SimTime $ST --ThermoT 0.0 --tau 2.0 "
25 # uncommenting option below
26 #ADDOPT+=" --ThermoType Andersen --CollPeriod 300.0 "
27 # uncommenting option below would turn off SWS and switch to MBS
28 #ADDOPT+=" --UseClassicalSampling "
29 # this is the actual command to start the simulation
30 $PYRPATH/bomond.py --infile mol.eqg $ADDOPT
```

This submission requires two additional files:



- XYZ geometry file with the name `mol.eqg` (examples are provided in Section 2.2),
- template for ORCA initiation with BOMoND, with the filename `orca.template` (see Table S3).

The latter has the form

**Table S3** Example of `orca.template` file for dynamics at the BLYP-D3BJ/6-31G level of theory.

```
method blyp d3bj
basis 6-31g
nprocs 16
maxcore 10
```

More information can be found in the manual for PyRAMD (Ref.<sup>S11</sup>), and with the `--help` option from the BOMoND script.<sup>S10</sup>

## 2.2 Structures of the molecules

Here, we provide the XYZ coordinates of the molecules that were optimized at the levels of theory used for the MD, harmonic, and VPT2 simulations.

**Table S4** XYZ coordinates of  $\text{H}_2^+$  used in the parametrization of the Morse-type potential. The can be accessed for simulations with BOMoND by replacing `--QCInterface orca5` option with `--QCInterface diatomic` in script S2.

```
2
H 0.0 0.0 0.0
H 0.0 0.0 1.07691
```

**Table S5**  $\text{H}_2\text{O}$  at the PBE/def2-SVP level of theory.

```
3
PBE/def2-SVP
O 0.09705862731988 0.00000000000000 0.00000000000000
H 0.71007268634005 0.00000000000000 0.75772089182253
H 0.71007268634006 0.00000000000000 -0.75772089182252
```

**Table S6**  $\text{C}_2\text{H}_4$  at the PBE/def2-SVP level of theory.

```
6
PBE/def2-SVP
C 0.00000000042893 0.00000000007856 0.67036663022628
C 0.00000000044712 -0.00000000071689 -0.67036662984861
H -0.00000000040079 0.93765747445985 -1.25029086268085
H -0.0000000004210 -0.93765747555995 -1.25029086651837
H -0.0000000003723 0.93765747467858 1.25029086466883
H -0.00000000039592 -0.93765747294015 1.25029086415272
```

**Table S7**  $\text{CH}_2\text{F}_2$  at the PBE/def2-SVP level of theory.

5

PBE/def2-SVP

C	-0.00000000071881	-0.00000000012728	0.49516112953972
H	-0.92252225473455	0.00000000085942	1.12230597725551
H	0.92252225267286	-0.00000000042326	1.12230597348823
F	0.00000000085747	1.11049747677907	-0.28977503990941
F	0.00000000192302	-1.11049747708795	-0.28977504037405

**Table S8** C<sub>2</sub>H<sub>2</sub>F<sub>2</sub> at the PBE/def2-SVP level of theory. The first and the second structures correspond to the trans- and cis-isomers, respectively.

6

PBE/def2-SVP (trans)

C	-0.33062128447250	0.58415731011038	0.00000000096466
C	0.33062128319808	-0.58415731041137	-0.00000000011277
F	0.33064823352720	1.75160703970318	-0.00000000053804
H	-1.42960288765556	0.66927088121440	-0.00000000016188
H	1.42960288529225	-0.66927087662899	0.00000000014341
F	-0.33064822988947	-1.75160704398760	-0.00000000029538

6

PBE/def2-SVP (cis)

C	-0.00000000014727	0.67150245173288	0.57053189625352
C	-0.00000000066489	-0.67150245246746	0.57053189636336
F	-0.00000000150201	1.40734746797390	-0.54783771801674
H	0.00000000198009	1.25069403773160	1.50765882095368
F	0.00000000187224	-1.40734746669697	-0.54783771817640
H	-0.00000000153817	-1.25069403827396	1.50765882262258

**Table S9** C<sub>6</sub>H<sub>12</sub>N<sub>2</sub> at the PBE-D3(BJ)/def2-SVP level of theory.

20

PBE-D3(BJ)/def2-SVP

C	-0.73124394437269	-0.97135833231599	1.21930537658642
C	0.48586059782019	0.83146121904552	0.00000001968739
C	-0.73124393975220	-0.97135830643496	-1.21930540155648
C	-0.61142049992845	-1.91899246984534	-0.00000002083857
H	0.34505090924913	-2.47712954356539	-0.00000003143964
H	-1.69964254365690	-1.11247923771536	1.74065722627732
H	0.06989082904469	-1.13525124746159	-1.97077176966021
H	-1.69964253660523	-1.11247921803672	-1.74065725811594
H	-1.41832204491429	-2.67789767691387	-0.00000002737737
H	0.06989081316788	-1.13525127897226	1.97077175166949
N	-0.70191903796567	0.42822857467568	0.75264502720738
N	-0.70191905278838	0.42822859534787	-0.75264499132586
C	1.78089840488853	0.04138683007817	0.00000001149984
H	1.65880769731399	-1.05461765480708	0.00000021853888
H	2.38293143291544	0.31339410220863	-0.89166180687851
H	2.38293161508570	0.31339443026189	0.89166160621664
C	0.71201790102901	2.33274217361037	0.00000002055673
H	1.28415367695697	2.64081311112395	0.89922548510555
H	1.28415371758782	2.64081306982189	-0.89922542842940
H	-0.26256399507555	2.85275285989458	-0.00000000772365

**Table S10** C<sub>26</sub>H<sub>34</sub>O<sub>2</sub> at the PBE-D3(BJ)/def2-SVP level of theory.

62

PBE-D3(BJ)/def2-SVP

C	0.16325195972425	-0.80600044690196	-0.33292585834949
C	-0.16325251177401	0.80600054492823	-0.33292589529139
C	0.64345269451679	-1.48004153015816	1.00915680558718
C	-0.64345300343354	1.48004180547569	1.00915673848011
C	1.09726792785756	-2.95483063834384	0.75297400195188
C	-1.09726771348461	2.95483104328177	0.75297386469683
C	-0.11762363731450	-3.79397739767039	0.29450092134178
C	0.11762414310550	3.79397738331534	0.29450081187950
C	-0.60044081697990	-3.15470113881257	-1.01862241822024
C	0.60044109603665	3.15470096611951	-1.01862253378100
C	-1.06473941540137	-1.69370195277587	-0.76467043448109
C	1.06473913380909	1.69370161736623	-0.76467048193773
C	-1.24376427634771	1.03625106670723	-1.42597483873929
C	1.24376380062044	-1.03625065509543	-1.42597475959828
C	-0.45537049799236	-1.55541607939352	2.09652190319806
C	0.45537020216180	1.55541596670100	2.09652184783798
C	2.17455580754252	-3.06473968736082	-0.32905160703664
C	-2.1745554012713	3.06474040629954	-0.32905176727769
C	-1.24308481358616	-3.80052193127330	1.33171608401914
C	1.24308529794716	3.80052151195782	1.33171600995722
O	0.41185486996632	-3.23609484107785	-2.01937886384905
O	-0.41185455104087	3.23609502149394	-2.01937900854154
C	-2.18607581972029	-1.72346643281521	0.29107631405102
C	2.18607556837145	1.72346567135694	0.29107625669524
C	1.58087644515550	-2.50972217731032	-1.62759894101199
C	-1.58087635843031	2.50972271928674	-1.62759910403341
C	-1.67124055618134	-2.35209873901377	1.59751417430106
C	1.67124057133543	2.35209818176051	1.59751413759556
H	-1.52442043997561	0.93013534877487	1.39938942695738
H	1.52441992938230	-0.93013471712441	1.39938949746752
H	1.48185028109115	-3.35484382998619	1.71713928153752
H	-1.48184996192369	3.35484440388249	1.71713911663683
H	0.21374934494009	-4.83128923971842	0.07397260271355
H	-0.21374847056644	4.83128934804843	0.07397250623359
H	-1.46011328715709	-3.72842604615212	-1.42724426956894
H	1.46011378399866	3.72842555168448	-1.42724437817273
H	-1.46335163469562	-1.33708331507930	-1.73203676486039
H	1.46335121870054	1.33708273390353	-1.73203677998493
H	-0.88735018072210	0.61815763319404	-2.38932687258456
H	0.88734950904118	-0.61815750589384	-2.38932685378573
H	-2.18257034620562	0.51113955360504	-1.16656811916877
H	2.18256963215233	-0.51113866138788	-1.16656813428398
H	-0.02614988290720	-2.05344784228117	2.99344775587528
H	0.02614974441794	2.05344788421191	2.99344769104764
H	-0.78480575423179	-0.55827853587064	2.43047009560848
H	0.78480502656285	0.55827826590191	2.43047000569015
H	-3.08208465765486	2.48568220107536	-0.05532585698175

H	3.08208478873090	-2.48568126115672	-0.05532570322485
H	2.47900470465793	-4.12307672021750	-0.46485874498427
H	-2.47900416328961	4.12307751526169	-0.46485888245058
H	-2.10156778791071	-4.40136359209520	0.96056896805172
H	2.10156848028051	4.40136291735303	0.96056895911080
H	-0.89216677034181	-4.27835848679826	2.27165387327652
H	0.89216738196515	4.27835818069483	2.27165378862365
H	-2.57186474397453	-0.70116352047666	0.48304402139457
H	2.57186412634208	0.70116260490077	0.48304393178359
H	-3.04494255968499	-2.31314450822294	-0.09754677238210
H	3.04494252686656	2.31314343390811	-0.09754683942463
H	2.29172049879918	-2.62507274690355	-2.47174628548984
H	-2.29172036196047	2.62507350345397	-2.47174646076684
H	-2.47195770560367	-2.32738377727498	2.36671142791392
H	2.47195772454014	2.32738296873783	2.36671140874842

**Table S11** C<sub>6</sub>H<sub>6</sub> at the PBEh-3c level of theory.

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PBEh-3c

C	0.7744893677	-1.1514007596	-0.0000044086
C	1.3846213015	0.0949091000	0.0000392895
C	-0.6100272244	-1.2462835192	-0.0000163949
C	0.6100272278	1.2462834851	0.0000161969
C	-1.3846213117	-0.0949091074	-0.0000390909
C	-0.7744893667	1.1514007814	0.0000044844
H	1.3783419963	-2.0494536781	0.0000057404
H	2.4642560124	0.1691158062	-0.0002382659
H	-1.0859511926	-2.2182476250	0.0001325330
H	1.0859511072	2.2182476534	-0.0001332835
H	-2.4642560159	-0.1691157442	0.0002382845
H	-1.3783418372	2.0494538222	-0.0000059183

**Table S12** CH<sub>5</sub><sup>+</sup> at the PBEh-3c level of theory.

6

PBEh-3c

C	0.00072698120085	0.08976780484499	-0.01089760735797
H	0.22597154973230	-0.84453406418798	0.64222672737998
H	0.77115623218234	0.73750293566914	0.40163390457156
H	0.28827277460307	-0.98821743315196	-0.35127077734960
H	0.09790926442288	0.17435763828012	-1.10930055585348
H	-1.03953680214143	0.26612311854570	0.24410830860951

**Table S13** C<sub>24</sub>H<sub>57</sub>N<sub>8</sub>O<sub>24</sub><sup>+</sup> at the BLYP-D3(BJ)/6-31G level of theory.

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BLYP-D3(BJ)/6-31G

H	2.79486550573463	4.16081961660193	-2.10457576778304
C	3.40365053150081	3.88802634861621	-1.23333977213480
N	3.96919379895745	2.48896165939716	-1.47371274563828
H	4.35119072640170	2.03133467865615	-0.56780970046525

H	3.24585100943815	1.80541075125552	-1.82156330253135
C	4.60315879657888	4.83551591670559	-1.08777013190750
O	5.46462460005452	4.53522881660444	-2.25305030200471
C	2.51922200744524	3.85437212795414	0.03754025848226
O	1.29749025925049	4.24712564358292	-0.09371438951007
O	3.09602210270638	3.40260097482621	1.10984233581462
H	4.74651111766218	2.60047802345021	-2.15060251071056
H	5.12418264306792	4.62951715839588	-0.13651311740035
H	4.25344739973625	5.88135569153239	-1.09858772283771
H	6.30643572659648	5.04921489347942	-2.20441188482910
H	3.50284736610221	0.26521097537977	3.49499595647227
C	3.47761055966863	0.23218982605543	2.39161858109897
N	2.27712568781884	1.03306450549071	1.93178744993477
H	1.91350774800048	0.71547563133331	0.99339607230266
H	1.44425676073119	0.94832794706605	2.56788973764819
C	4.79731037660940	0.84847150177258	1.86945829321647
O	4.85606513452983	0.87648026642065	0.40973206219960
C	3.31379944186530	-1.24195712494658	1.94114715998634
O	4.40307780252570	-1.95729266882687	1.96556240425809
O	2.16268408995040	-1.66683275983476	1.55199948407294
H	2.53425169612667	2.06347065279857	1.80623076869572
H	5.62935222991534	0.25233947670300	2.27325754853091
H	4.88554251047900	1.89477983271620	2.18871575277549
H	4.71942669264793	-0.04158135158427	-0.02016630028047
H	4.40284910550330	-4.50418810460652	-1.63395296578670
H	4.60882747619105	-2.34434178901833	-2.59844743988790
O	1.78205570147272	-4.54958594810133	-0.55557886301849
C	2.44275755885394	-3.69415564903575	-1.29752943071809
H	0.42845627044847	-4.65276593207960	-0.82084817670286
O	1.97649876974063	-2.93698077097928	-2.21708182885525
C	3.96915502680288	-3.67574392688084	-1.04351469927081
H	5.71258276833407	-2.37693979292309	-1.18811052616021
C	4.65585782911946	-2.37252753336461	-1.49767544720654
N	4.17377706074535	-4.02018261179405	0.43206518620461
O	4.07059009601777	-1.16784030612679	-0.93298660882014
H	4.25407060148321	-3.10391080848615	1.11217205914471
H	3.25640754704374	-0.81437074575596	-1.42025907554489
H	3.31542399691157	-4.54702597163738	0.70581132144613
H	-1.56278383501991	-0.39218869509724	-1.17641427374157
N	-1.50731667920261	0.34276223946717	-1.91515686443707
H	0.42208991832017	-2.60697471944792	-2.42505645862744
H	-2.28731173317596	0.16708993241163	-2.60396095616766
O	-0.42843747602796	-2.08905903361307	-2.65665689178098
H	-1.71391929735452	1.29459663790450	-1.49920925478429
O	2.17775154714185	0.39650748960356	-1.98908943122694
C	0.95986485717192	0.46515412292292	-1.52383349324389
C	-0.15997048493499	0.34836296158195	-2.58346965984200
O	0.62532944898783	0.65153463807311	-0.28822061838840
C	-0.05859751164492	-0.91732074190889	-3.45815067925499
H	-0.76312273435748	-0.84466475083406	-4.30236307794432
H	-0.10986136049338	1.24329310847062	-3.22672335983119
H	0.96784055671559	-1.02623786879830	-3.83434792425820

H	-6.62601923118368	0.76622029684352	-1.92850033086802
O	-3.84345627681283	0.21188635420975	-3.23493330066050
O	-4.87828177478172	-1.41425104738592	-1.94760712311792
C	-4.70577606018281	-0.20374565772374	-2.35112417697699
H	-5.93085329030988	-0.08707726270772	0.20987892413158
H	-4.62980755166826	2.92880323062399	-1.47169344907876
C	-5.56683112376972	0.90575685891792	-1.66051679067716
C	-5.42824515610699	0.83302453164458	-0.12750679771969
H	-5.90749555068060	1.70416151790798	0.34777059097323
H	-1.69622713906683	4.91927693448503	0.94508162940491
O	-4.01395050692292	0.80493517730253	0.25660233420024
H	-2.40998938481212	3.86730477106691	3.14361910757772
C	-2.91941718311749	3.63376270733575	2.19389977631573
H	-3.79200455228970	4.28888315217926	2.07203470321961
N	-5.08679651711285	2.24740508546316	-2.22426386359902
C	-1.98545697267913	3.85598525414812	0.99071646405485
H	-4.33630233647567	1.96823147467835	-2.90958511457766
H	-3.81025329861018	1.45535891320015	1.05688717341730
C	-2.70202749164061	3.47515104068634	-0.33680872628607
O	-3.95017639526205	3.81370707513490	-0.44046942766360
O	-2.01705786776495	2.82686677657792	-1.21809576721798
H	0.15796121399146	3.63055573497979	0.83711176789504
H	-5.83762510991563	2.75218116491808	-2.71474056526309
N	-0.70767578786292	3.03204174197150	1.09289512295935
H	-0.70780048556421	2.30859850822145	0.34309356366114
O	-3.38496931950527	2.24572525360377	2.22680371580187
H	-1.86950888690759	-2.66815710268554	-2.20251849962444
H	-2.97959813988201	1.67581656628185	2.98316272373920
N	-2.79089548239411	-3.17078499577524	-1.95199457424998
H	-3.15320343541378	-0.44027648344059	0.27974294447574
H	-3.62838976564834	-2.51663920954730	-2.12233006284786
H	-0.59320706424990	2.52987640267986	2.00877434865429
O	-2.50338240940013	-1.26094740048569	0.23883680268897
H	-2.83649592180184	-3.99034745261162	-2.57391826309588
C	-2.79750635573342	-3.61667708221096	-0.48785776732138
O	-0.64488641305451	-4.53733665656757	-1.09105419781143
C	-1.40608794368479	-4.13163143528421	-0.06867203346425
H	0.51814898097467	-1.38174042364782	1.69492651900820
C	-3.31352515250063	-2.49778749100605	0.42580987918502
H	-4.35513109004214	-2.26823685885476	0.16267486819165
O	-1.06790831831622	-4.16520150474248	1.14827998824623
O	-2.33107227778787	0.49731899620232	3.74405931977776
H	-3.50710135303418	-4.45908852998893	-0.40222946515339
N	-0.44518253949906	-1.66243199135812	2.02609803794628
C	-1.08872643843109	0.24004481902123	3.46262415277432
H	-3.24185598994292	-2.80844267797608	1.47889144606242
O	-0.21337660667991	1.12319548499413	3.09295387105134
C	-1.67555553813585	-2.18125899167488	4.16124847862288
C	-0.65127580068963	-1.24822799100706	3.48148398249500
H	-1.21504451702270	-1.30855231020428	1.38530391328531
H	-0.49674920056925	-2.70366851283944	1.93131088168534
H	-1.73906589792495	-1.91495723873521	5.23152753248645

H	0.32968554886947	-1.33875034759949	3.97512754099919
H	5.01062023202094	-4.60140753763520	0.58086129674649
O	-2.98864491384326	-2.10735268106229	3.51372461020639
H	-1.35363130591503	-3.22855803787906	4.07508102510118
H	-3.26863020014818	-1.15238535419124	3.62569448148207

### 3 Optimization of the $\tau$ -parameter for the SWS procedure

In the tables below the following parameters are listed:  $T$  is the simulation temperature,  $\tau$  is the SWS parameter,  $\tau_{\text{eff}} = h/(k_{\text{B}}T)$ ,  $\langle r \rangle - r_e$  is the anharmonic shift of the mean H...H distance ( $\langle r \rangle$ ) from from the equilibrium position ( $r_e$ ),  $l$  is the vibrational amplitude, KE is the mean kinetic energy,  $E_{\text{tot}}$  is the mean total energy, relative to the electronic energy at equilibrium,  $N$  is the number of points in the MD simulations.

#### 3.1 The case of $\text{H}_2^+$

**Table S14** Results of the MBS+MD simulations of  $\text{H}_2^+$ .

$T$ , K	$\tau_{\text{eff}}$ , fs	$\langle r \rangle - r_e$ , Å	$l$ , Å	$N$
30	1599.7	0.0002	0.009	149850
60	799.9	0.0005	0.015	149850
300	160.0	0.0024	0.033	149850
600	80.0	0.0051	0.049	149850
3000	16.0	0.0273	0.119	149850
3600	13.3	0.0341	0.136	149850
4200	11.4	0.0443	0.155	149850
6000	8.0	0.0581	0.177	148851
30000	1.6	0.2116	0.460	114885
36000	1.3	0.1457	0.327	116883
60000	0.8	0.1609	0.356	98901

**Table S15** Results of the SWS+MD simulations of  $\text{H}_2^+$ .

$\tau$ , fs	$\langle r \rangle - r_e$ , Å	$l$ , Å	KE, K	$E_{\text{tot}}$ , $\text{cm}^{-1}$	$N$
0.1	0.172	0.418	2910	4898	111888
0.5	0.078	0.248	1630	2572	145854
1	0.036	0.135	996	1440	149850
2	0.030	0.120	881	1244	148851
3	0.033	0.128	945	1352	149850
4	0.034	0.129	968	1373	148851
5	0.040	0.142	1141	1635	148851
10	0.057	0.172	1536	2219	141858
50	0.200	0.352	3860	6365	127872
100	0.252	0.491	4046	6975	126873

## 3.2 Polyatomic molecules

**Table S16** Results of the SWS+MD simulations of water (H<sub>2</sub>O). Harmonic ZPVE energy is 6537 K.

$\tau$ , fs	$E_{\text{tot}}$ , K	$N$
1	8868 $\pm$ 1428	31
2	8407 $\pm$ 1388	31
3	6661 $\pm$ 599	31
4	7919 $\pm$ 850	31
5	13570 $\pm$ 2897	31

**Table S17** Results of the SWS+MD simulations of CH<sub>2</sub>F<sub>2</sub>. Harmonic ZPVE energy is 10014 K.

$\tau$ , fs	$E_{\text{tot}}$ , K	$N$
1	18611 $\pm$ 1521	31
2	12593 $\pm$ 788	31
3	11953 $\pm$ 1118	31
4	11631 $\pm$ 1017	31
5	13163 $\pm$ 2521	31
6	13000 $\pm$ 1050	31
7	17649 $\pm$ 1648	31

**Table S18** Results of the SWS+MD simulations of C<sub>2</sub>H<sub>4</sub>. Harmonic ZPVE energy is 15595 K.

$\tau$ , fs	$E_{\text{tot}}$ , K	$N$
1	28245 $\pm$ 1936	31
2	18362 $\pm$ 1073	31
3	17112 $\pm$ 939	31
4	18464 $\pm$ 1225	31
5	23008 $\pm$ 3429	31

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