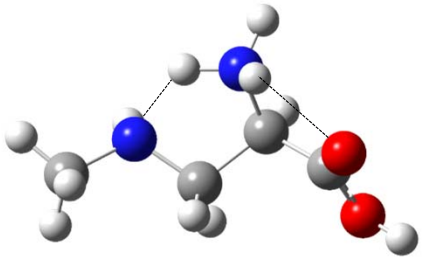
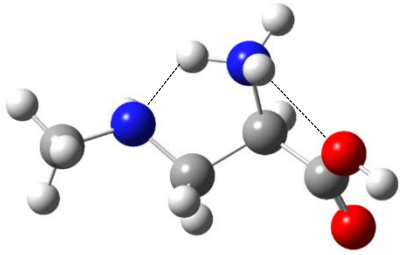


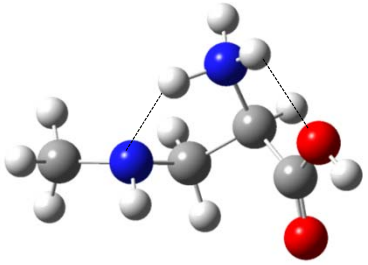
VII

$\Delta_{rel}H$ = 26.5
$\Delta_{rel}G$ = 26.1



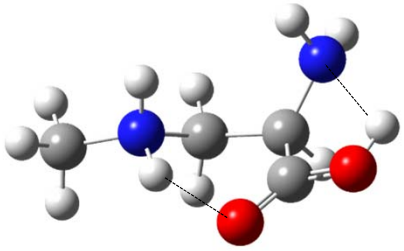
VIII

$\Delta_{rel}H$ = 40.1
$\Delta_{rel}G$ = 38.7



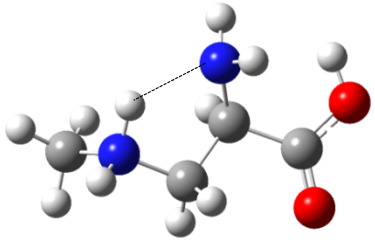
IX

$\Delta_{rel}H$ = 38.7
$\Delta_{rel}G$ = 37.5



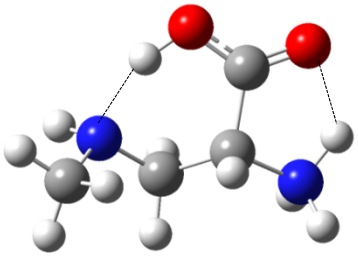
X

$\Delta_{rel}H$ = 39.7
$\Delta_{rel}G$ = 40.2



XI

$\Delta_{rel}H$ = 57.3
$\Delta_{rel}G$ = 54.4



XII

$\Delta_{rel}H$ = 58.2
$\Delta_{rel}G$ = 60.3

Figure S1: Higher energy structures of $[H(BMAA)]^+$ from DFT calculations using the B3LYP functional and 6-311++G(d,p) basis set. Energies are relative to the lowest energy structure, I.

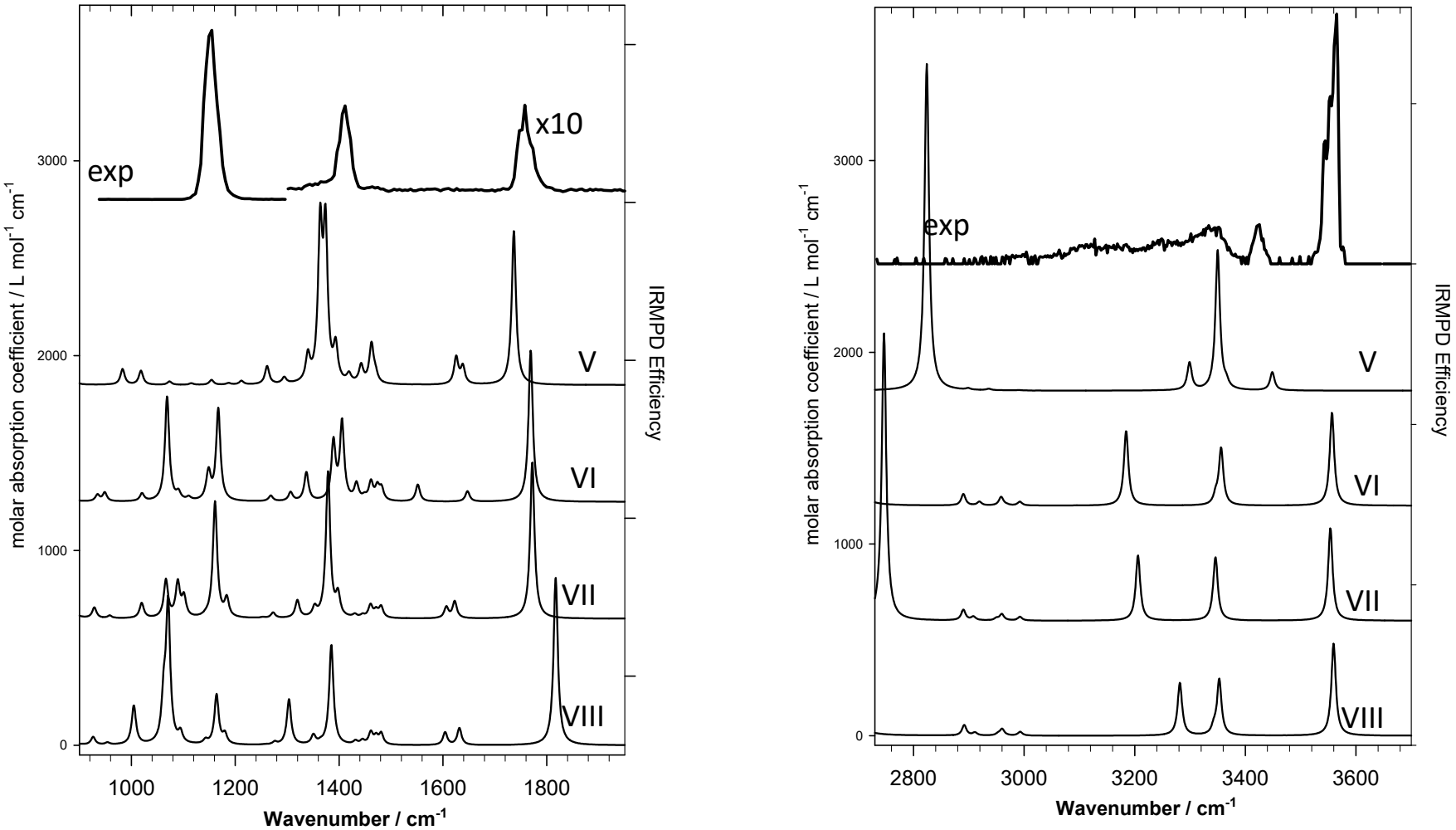

exp
x10
V
VI
VII
VIII
molar absorption coefficient / L mol-1 cm-1
IRMPD Efficiency
Wavenumber / cm-1
0
1000
2000
3000
1000
1200
1400
1600
1800
2800
3000
3200
3400
3600

Figure S2

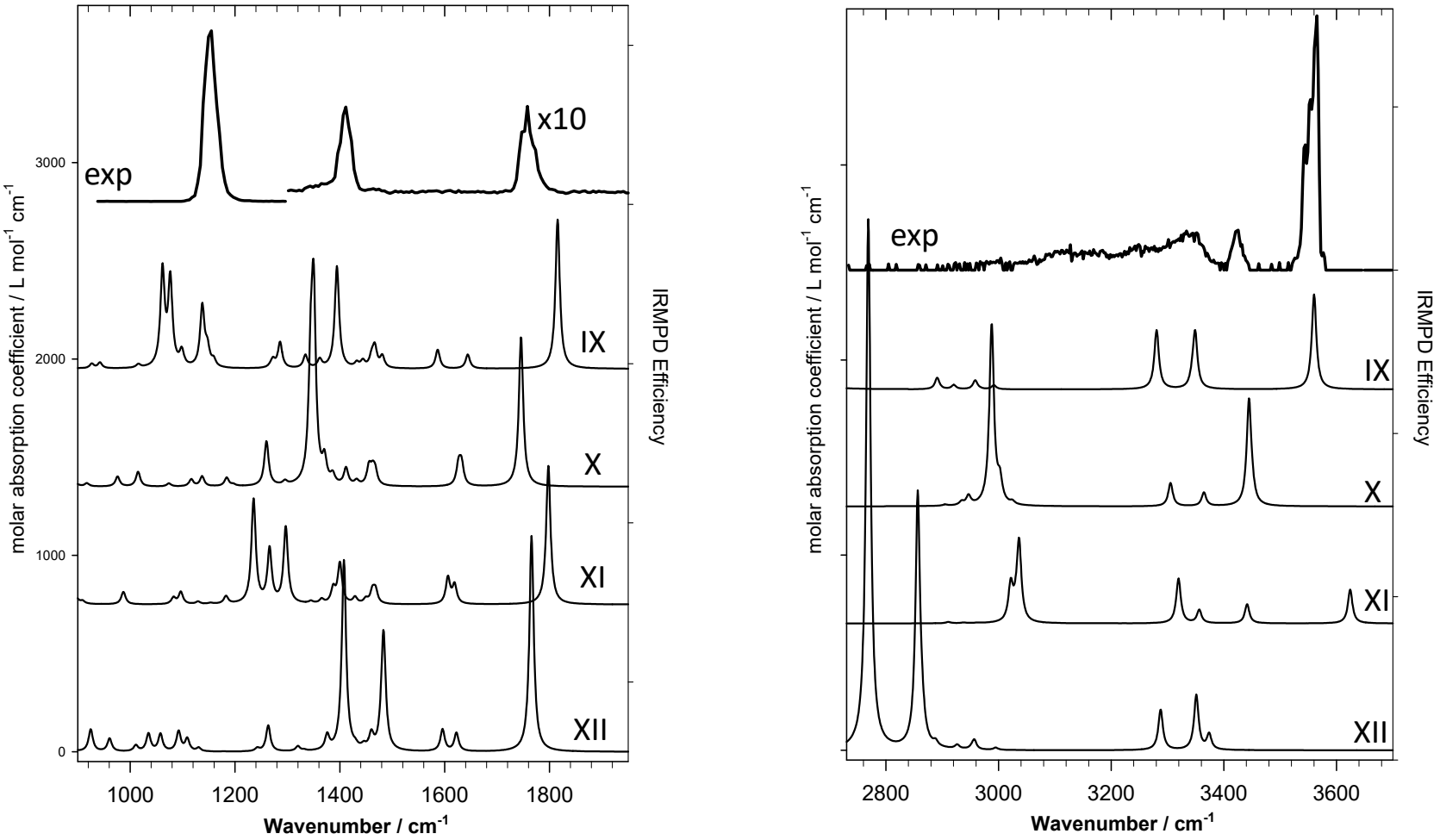

exp
x10
IX
X
XI
XII
molar absorption coefficient / L mol-1 cm-1
IRMPD Efficiency
Wavenumber / cm-1
0
1000
2000
3000
1000
1200
1400
1600
1800
2800
3000
3200
3400
3600

Figure S3

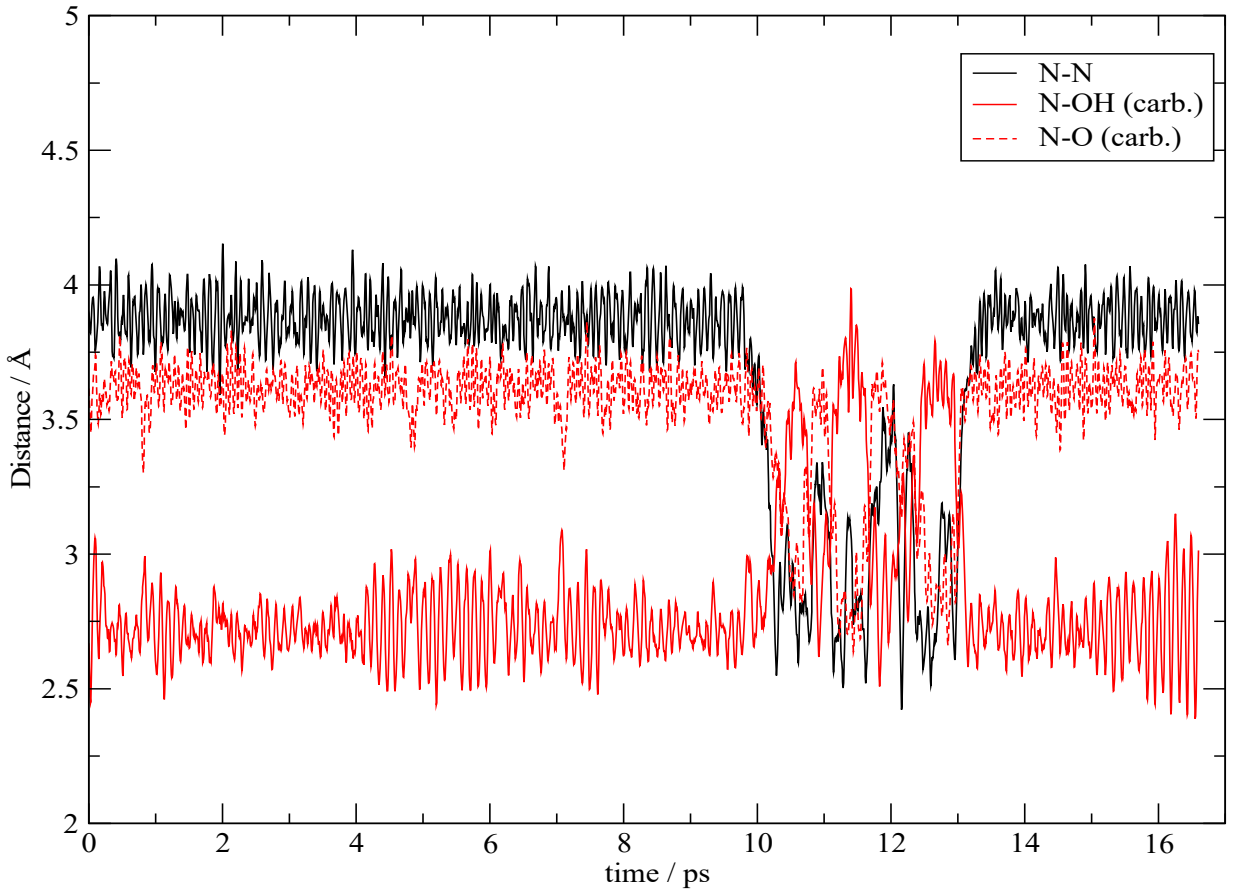


Figure S4: MD results for the non-Hbonded conformer: N—N, N—OH and N—O (carbonyl) distances as functions of time.

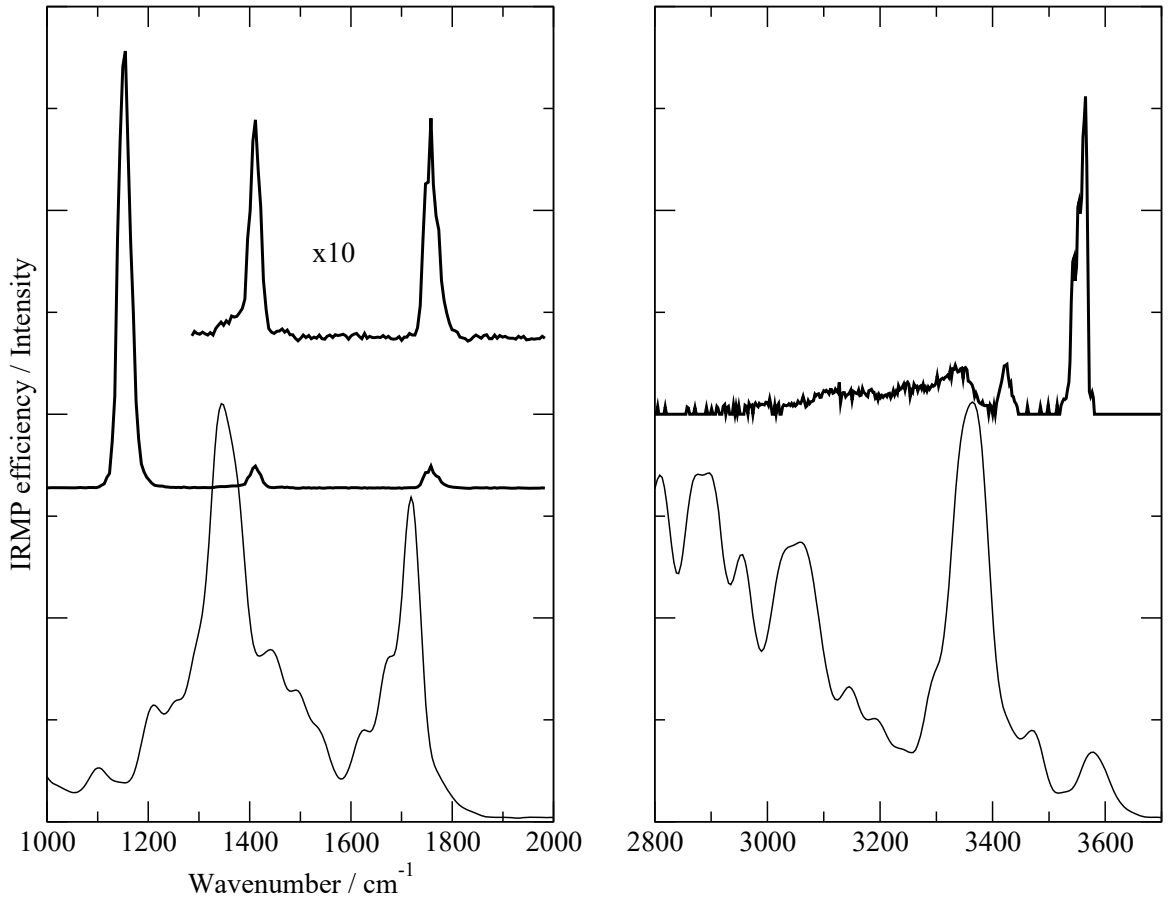


Figure S5: Computed MD spectra of the non-H-bonded conformer (bottom) compared to experimental IRMPD data (top).

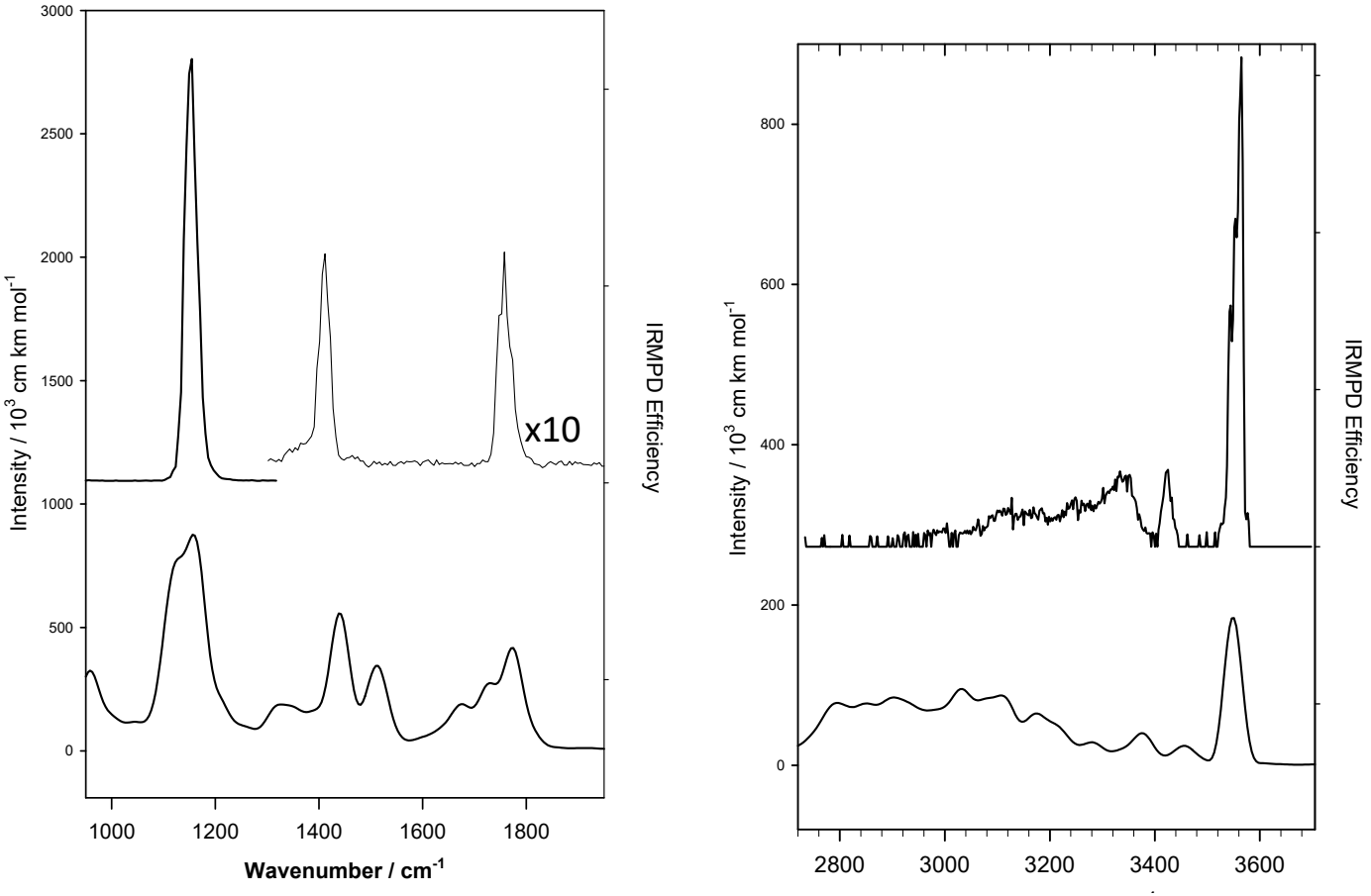


Figure S6: Comparison of the experimental IRMPD spectra (top) with the calculated spectra generated using molecular dynamics with the lowest energy structure as the starting point (bottom).

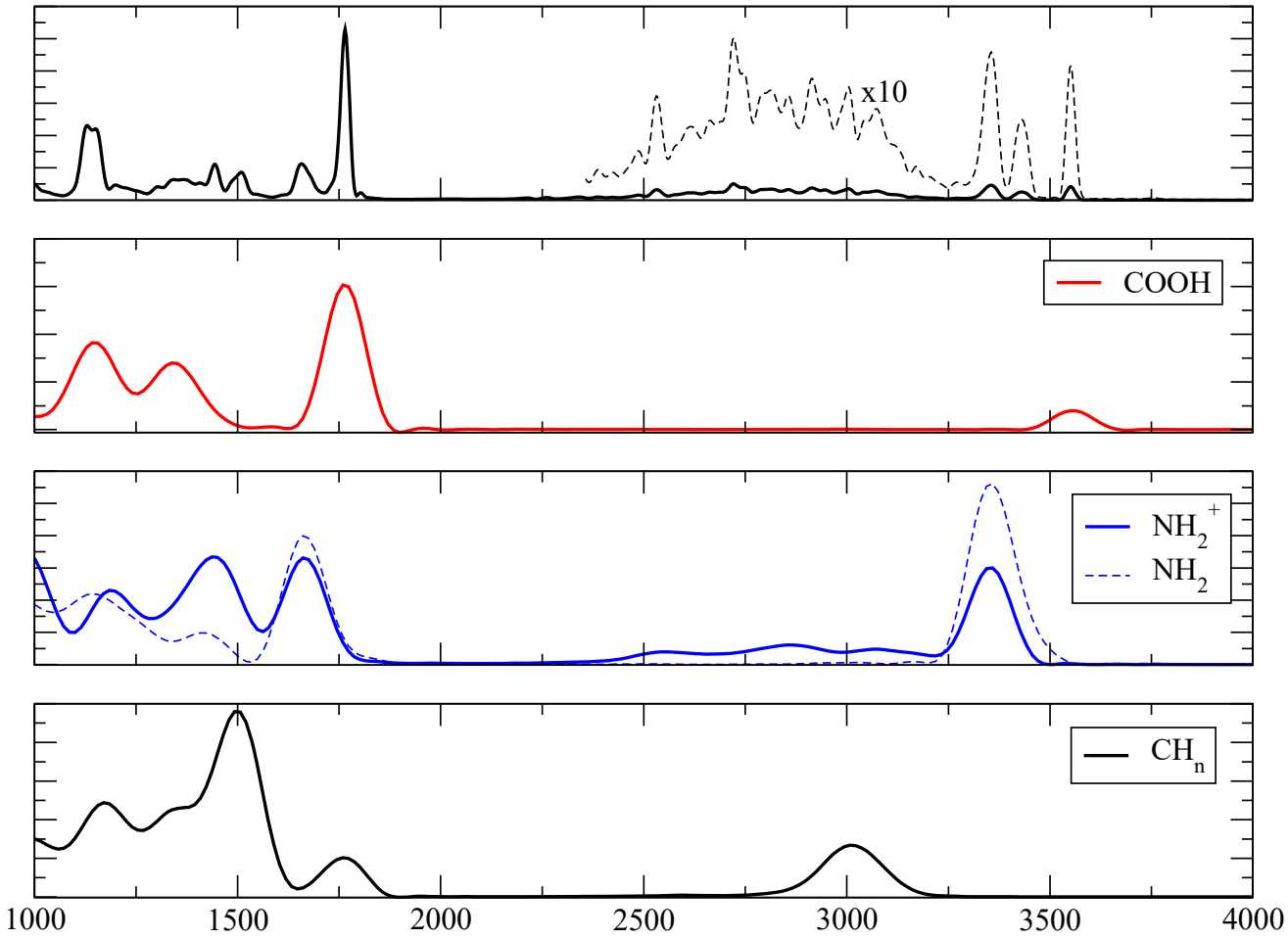


Figure S7: Top: computed IR spectra from MD of the H-bonded conformer with an enlargement of the high energy region. Bottom panels: power spectra as decomposed into the contribution of the indicated functional groups.

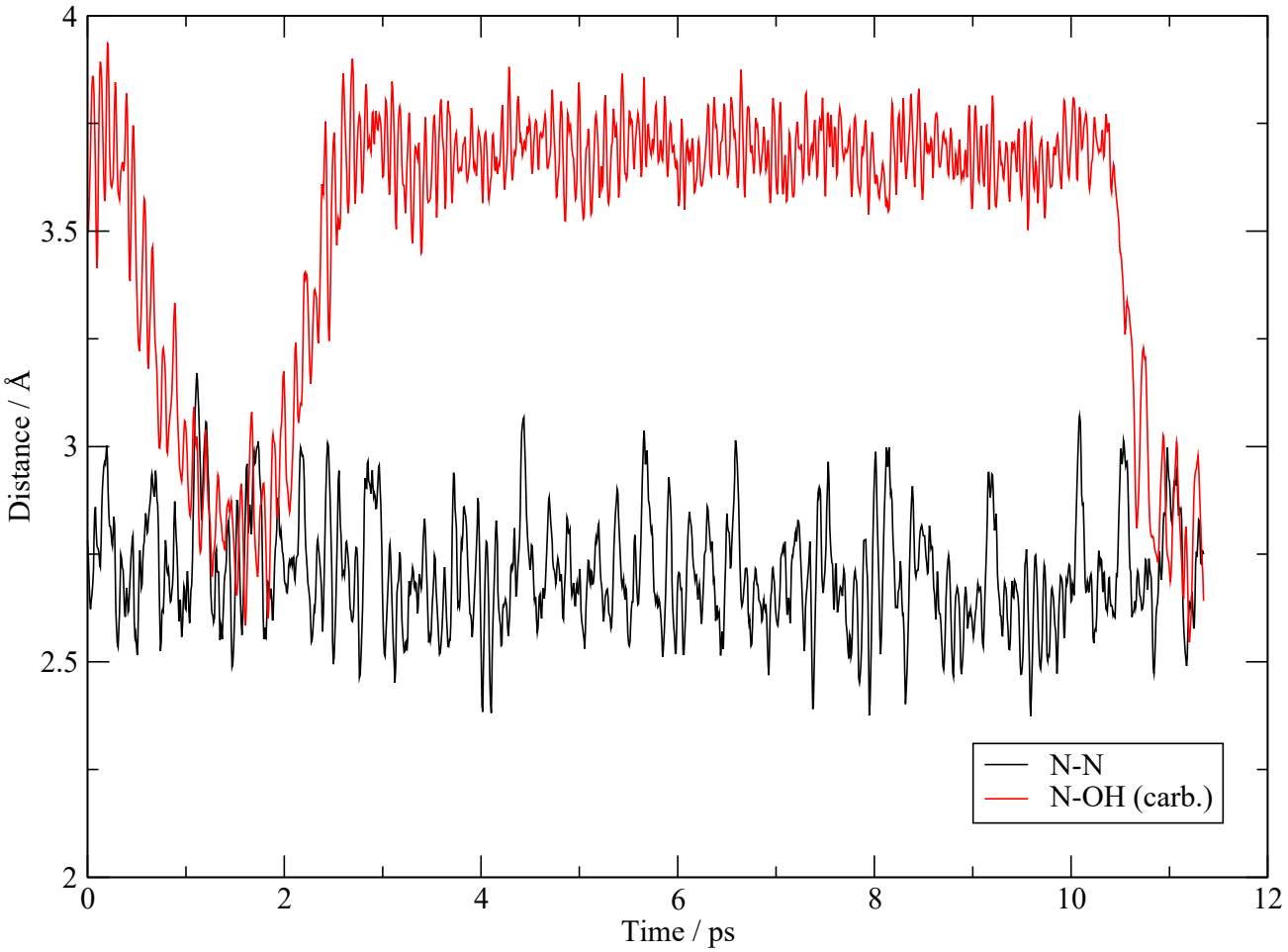


Figure S8: MD results for the Hbonded conformer: N—N, N—OH distances as functions of time.

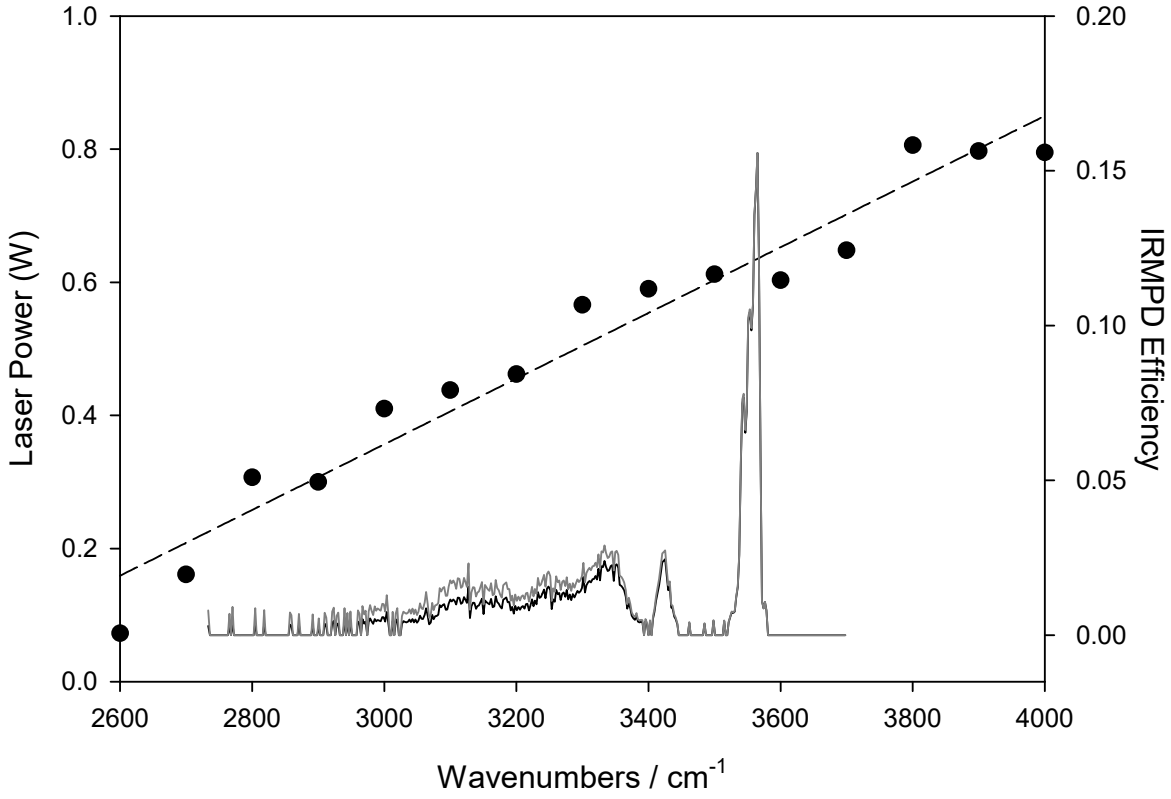
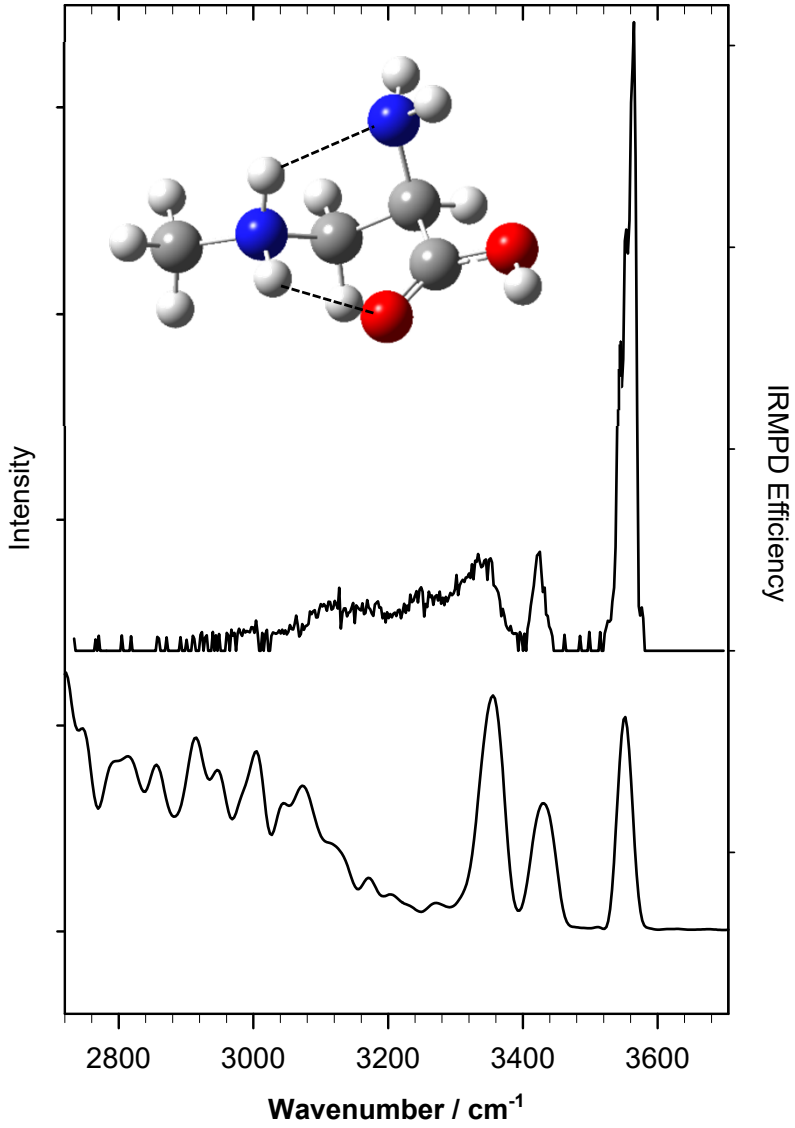


Figure S9: Plot of OPO laser power vs wavenumber (black circles and best fit dashed line. The experimental IRMPD efficiency spectrum (black trace) as well as that with a linear correction applied for the decreasing power vs wavenumber (grey trace) are also shown.


Intensity
IRMPD Efficiency
2800
3000
3200
3400
3600
Wavenumber / cm-1