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

Two color delay dependent IR probing of torsional isomerization in a $[AgL_1L_2]^+$ complex

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Supplementary information

1. Details on the electrospray - mass spectra

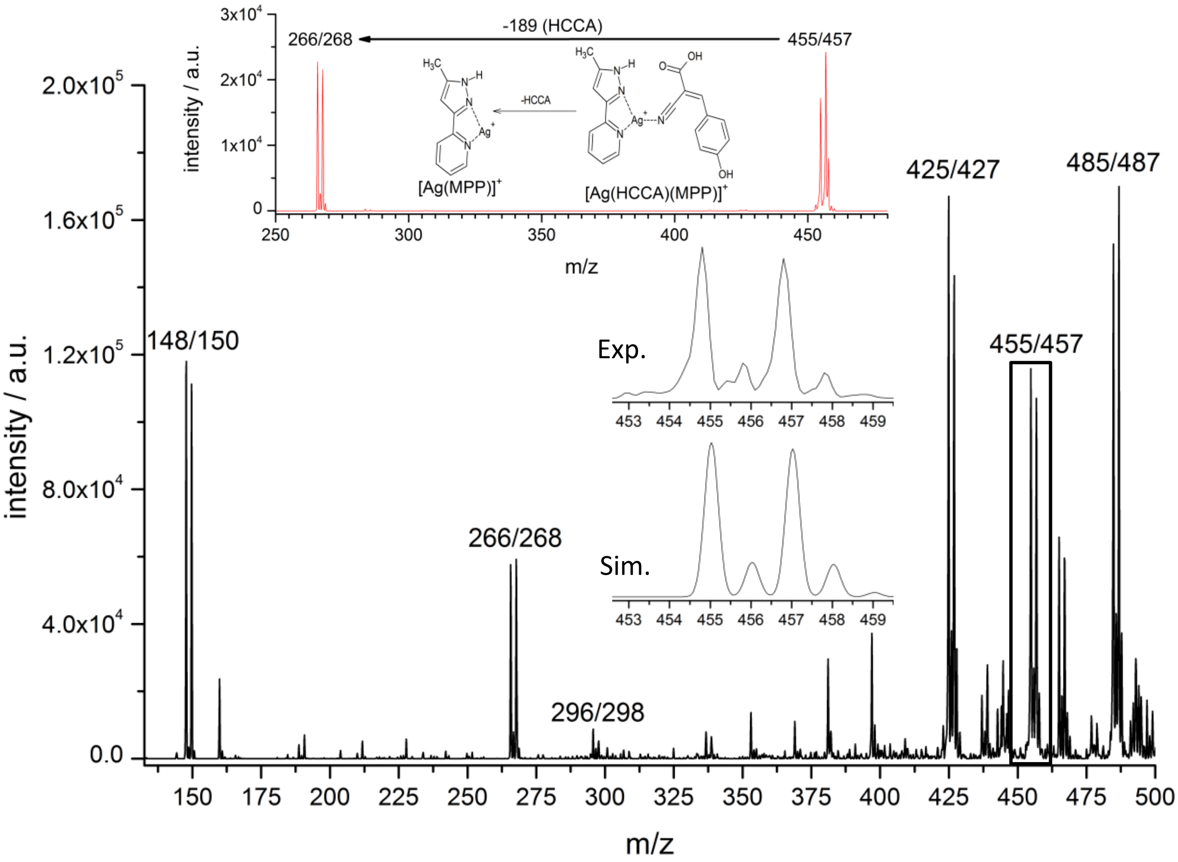


Figure S-1: Cationic ESI-MS of a solution of $AgNO_3$, MPP and HCCA in acetonitrile. **Inset (middle)**: Simulated isotopic distribution of the $[Ag(HCCA)(MPP)]^+$ complex in comparison to the mass spectrum. **Inset (top)**: CID fragmentation of $[Ag(HCCA)(MPP)]^+$. Dissociation of the HCCA ligand is the exclusive fragmentation channel. The mass labeling refers to isotopomers of the two most abundant silver isotopes ^{107}Ag and ^{109}Ag.

Table S-1: Assignment of mass peaks in the experimental spectrum. The mass labeling refers to isotopomers of the two most abundant silver isotopes ^{107}Ag and ^{109}Ag.

m/z	assigned formula	abbreviation
148/150	$[Ag(CH_3CN)]^+$	-
266/268	$[Ag(C_9H_9N_3)]^+$	$[Ag(MPP)]^+$
296/298	$[Ag(C_{10}H_7NO_3)]^+$	$[Ag(HCCA)]^+$
425/427	$[Ag(C_9H_9N_3)_2]^+$	$[Ag(MPP)_2]^+$
455/457	$[(C_9H_9N_3)Ag(C_{10}H_7NO_3)]^+$	$[Ag(HCCA)(MPP)]^+$
485/487	$[(C_{10}H_7NO_3)Ag(C_{10}H_7NO_3)]^+$	$[Ag(HCCA)_2]^+$

ESI-MS was performed using a modified Paul-type quadrupole ion trap instrument (AmaZon SL, Bruker Daltonics). The ion source was used in positive electrospray ionization mode. Scan speed was 32 500 m/z per s (0.3 FWHM per m/z) with a scan range of at least 100 to 500 m/z. The sample solutions were continuously infused into the ESI chamber by a syringe pump at a flow rate of 2 mL min^{-1}. Nitrogen was used as drying gas with a flow rate of 3.0 L min^{-1} at 210 °C. The solutions were sprayed at a nebulizer pressure of 280 mbar and the electrospray needle was held at 4.5 kV. The instrument was controlled by Bruker Esquire Control 5.3 software and data analysis was performed using Bruker Data Analysis 3.4 software.

2. IR-MPD Spectra

An experimental IRMPD spectrum arises from a plot of the fragmentation efficiency as a function of laser frequency. The fragmentation efficiency (frag. eff.) is defined as:

$$frag.eff. = \left(\frac{\sum_i I_{fragment\ ion}(i)}{\sum_i I_{parent\ ion}(i) + \sum_i I_{fragment\ ion}(i)}\right)$$

With $I_{fragment\ ion}$= intensity of the fragment ion and $I_{precursor}$= intensity of the parent ion.

The monitored parent ion (MP) masses are:

$$\left.\begin{array}{l} \text{MP(0)=454.9} \\ \text{MP(1)=455.9} \\ \text{MP(2)=456.9} \\ \text{MP(3)=457.9} \\ \text{MP(4)=459.1} \end{array}\right\} [\text{Ag(HCCA)(MPP)}]^+$$

The monitored fragment ion (MF) masses are:

$$\left.\begin{array}{l} \text{MF(0)=265.9} \\ \text{MF(1)=266.9} \\ \text{MF(2)=267.9} \\ \text{MF(3)=268.9} \end{array}\right\} [\text{Ag(MPP)}]^+$$

3. Laser system

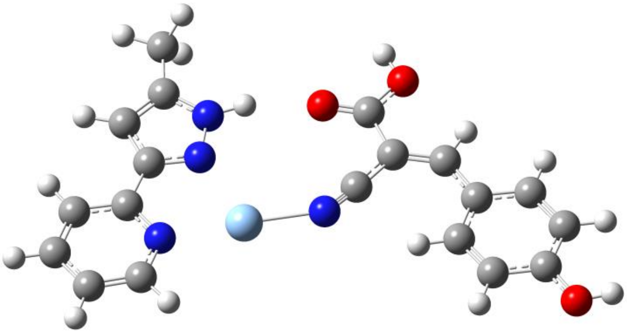
A KTP/KTA optical parametric oscillator/amplifier (OPO/A, LaserVision) system pumped with a pulsed 10 Hz injection seeded $Nd^{3+:}$YAG laser (PL8000, Continuum) was used as a source of tunable IR radiation (δn = 0.9 cm^{-1}, δt = 7 ns) for recording the vibrational spectra (IR_{scan}). The OPA idler wave (≤ 10 mJ per pulse) was used to record spectra within 2600–3900 cm^{-1}.The difference frequency (DF) between the OPA signal and idler waves generated in a $AgGaSe_2$ crystal (≤ 2 mJ per pulse) was applied in the range of 1200–2100 cm^{-1}. After passing through the chamber the IR beam was directed onto a power meter sensor. The idler beam was focused by a 50 cm CaF_2 lens. The DF radiation was focused tighter, by a 90° off-axis parabolic silver mirror with an effective focal length of 15 cm. Optionally, the two-color IR-MPD as facilitated using a second IR OPO/A laser system (IR_{fix}) set to a selected vibrational resonance frequency. Its idler output was focused by a f = 75 cm CaF_2 lens being aligned counter-propagating with respect to the scanning laser beam. Each trapped and isolated portion of ions was irradiated by 2–4 laser pulses (or pulse pairs in two-laser experiments) to produce a sufficient amount of fragment ions. The IR spectra were recorded as ion chromatograms while continuously scanning the IR wavelength. The IR-MPD signal was evaluated as $F_k/(F_k + P_i)$, where F_k and P_i are the sums of the fragment and the parent ion signals, respectively. The IR frequency was calibrated using a wave meter. Despite the online IR power measurement the recorded spectra were not normalized. This is so because of the intrinsically nonlinear power dependence of IR-MPD yields.

4. XYZ-Matrices of the discussed $[Ag(HCCA)(MPP)]^+$ isomers

(B3LYP/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Ag))

Isomer A:

43



C	7.68622	3.85189	3.68348
C	6.75584	2.84091	3.85432
C	6.99262	1.58129	3.30532
C	8.84398	3.58910	2.96412
C	9.01855	2.31766	2.44562
N	8.12371	1.33489	2.60677
H	9.90539	2.07063	1.87940
H	9.59748	4.34586	2.80462
H	7.50976	4.83139	4.10578
H	5.84769	3.02039	4.40938
C	6.02669	0.48705	3.46661
N	6.28355	-0.70341	2.92734
C	4.78425	0.45638	4.13484
H	4.29094	1.24777	4.66939
C	4.30496	-0.82868	3.96630
N	5.24229	-1.48066	3.23578
H	5.24823	-2.44147	2.91328
Ag	8.38037	-0.73189	1.77718
C	11.63608	-5.58292	-1.41371
H	12.37467	-4.81622	-1.59756
C	10.47911	-5.30899	-0.72756
H	10.31989	-4.30306	-0.37239
C	9.51450	-6.31553	-0.49034
C	11.87978	-6.87950	-1.89281
C	10.94312	-7.89508	-1.67245
H	11.12907	-8.89563	-2.04143
C	9.78535	-7.61015	-0.98428
H	9.06358	-8.39861	-0.81699
O	13.03060	-7.07638	-2.55421
H	13.11355	-7.99233	-2.84526
C	8.28196	-6.13379	0.20793
H	7.67343	-7.02650	0.27664
C	7.71528	-5.04205	0.81302
C	6.39731	-5.11285	1.48361
O	5.86560	-4.17197	2.03744
O	5.83510	-6.32974	1.42300
C	8.29427	-3.75338	0.87966
N	8.70285	-2.67940	0.97581
C	3.05012	-1.48100	4.43529
H	2.43898	-0.76711	4.98194
H	2.46083	-1.85763	3.59779
H	3.26280	-2.32045	5.09921
H	4.98411	-6.28543	1.88279

Isomer B:

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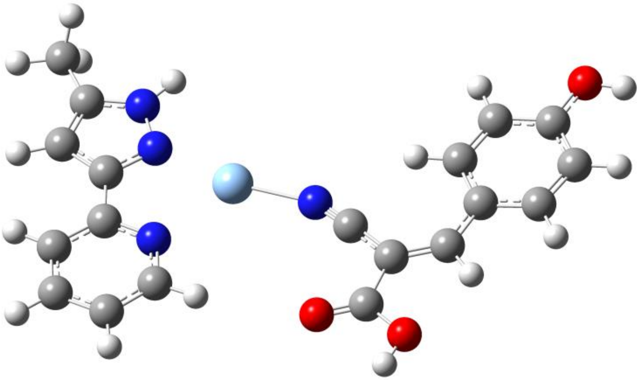
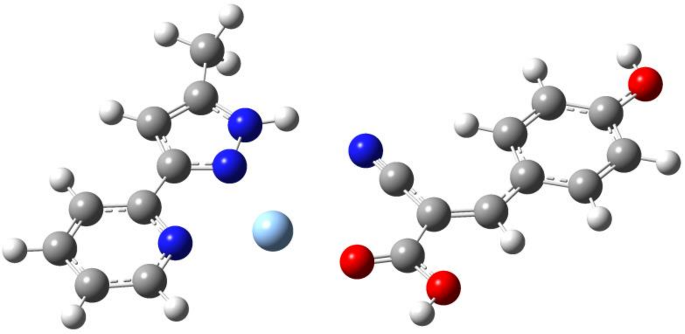


C	9.01373	1.17592	6.08202
C	7.94247	1.58731	5.30259
C	7.53793	0.78852	4.23629
C	9.65192	-0.01787	5.77865
C	9.18970	-0.75834	4.69832
N	8.16059	-0.36608	3.94703
H	9.65625	-1.69614	4.42364
H	10.48922	-0.37376	6.36070
H	9.34419	1.78121	6.91474
H	7.43063	2.51316	5.51889
C	6.40962	1.16238	3.37010
N	6.05883	0.37439	2.34938
C	5.56151	2.28473	3.42233
H	5.58327	3.09867	4.12374
C	4.67137	2.14012	2.37691
N	5.01032	0.98124	1.76482
H	4.57556	0.55948	0.96169
Ag	7.19517	-1.49657	2.00708
C	8.51130	-8.20297	-2.56885
H	8.77984	-9.11237	-3.09125
C	9.19718	-7.82222	-1.43622
H	10.00707	-8.44257	-1.07569
C	8.87179	-6.64352	-0.73311
C	7.46454	-7.40509	-3.04038
C	7.11942	-6.22793	-2.36028
H	6.30685	-5.62819	-2.74401
C	7.80908	-5.85738	-1.23151
H	7.52024	-4.94666	-0.73084
O	6.74962	-7.70753	-4.13744
H	7.05896	-8.52920	-4.53658
C	9.65204	-6.34257	0.42870
H	10.42655	-7.06756	0.64466
C	9.61268	-5.31080	1.32531
C	10.55448	-5.21285	2.47069
O	10.54378	-4.30619	3.26893
O	11.42298	-6.23954	2.52702
C	8.70482	-4.22775	1.28951
N	7.99738	-3.31902	1.32202
C	3.54278	2.99517	1.91484
H	3.70415	3.35028	0.89576
H	2.59703	2.45144	1.93609
H	3.44548	3.86344	2.56142
H	11.99200	-6.09335	3.29693

Isomer C:

43



C	7.44235	2.15758	6.76086
C	6.58634	1.67650	5.78336
C	7.04152	0.70752	4.89110
C	8.73655	1.66094	6.82807
C	9.11872	0.69805	5.90683
N	8.30003	0.22942	4.96159
H	10.11830	0.28509	5.92473
H	9.43766	2.00656	7.57325
H	7.10331	2.90925	7.46015
H	5.57424	2.04517	5.70974
C	6.17453	0.16380	3.83744
N	6.65407	-0.76658	3.01344
C	4.83691	0.45432	3.50261
H	4.16901	1.15529	3.96951
C	4.53689	-0.35839	2.42456
N	5.66068	-1.06945	2.17215
H	5.84470	-1.77157	1.46440
Ag	8.81721	-1.40687	3.33083
C	7.48693	-6.29921	-2.62895
H	6.45558	-6.11934	-2.90535
C	8.06001	-5.58375	-1.60403
H	7.46045	-4.84899	-1.09144
C	9.40414	-5.80411	-1.22836
C	8.23392	-7.26482	-3.32102
C	9.56805	-7.50305	-2.97003
H	10.12796	-8.24983	-3.51364
C	10.13254	-6.78422	-1.94523
H	11.16375	-6.97107	-1.67599
O	7.72553	-7.99131	-4.32723
H	6.80466	-7.75920	-4.49601
C	10.09783	-5.12442	-0.18359
H	11.12398	-5.44456	-0.05865
C	9.71831	-4.14133	0.69893
C	10.66389	-3.62358	1.69244
O	10.42413	-2.75727	2.52959
O	11.87692	-4.17845	1.63545
C	8.42458	-3.55653	0.73063
N	7.37833	-3.07255	0.76507
C	3.28769	-0.51420	1.62756
H	2.52774	0.17592	1.98553
H	3.46171	-0.30608	0.57081
H	2.88860	-1.52658	1.70824
H	12.42430	-3.77470	2.32533

Isomer D:

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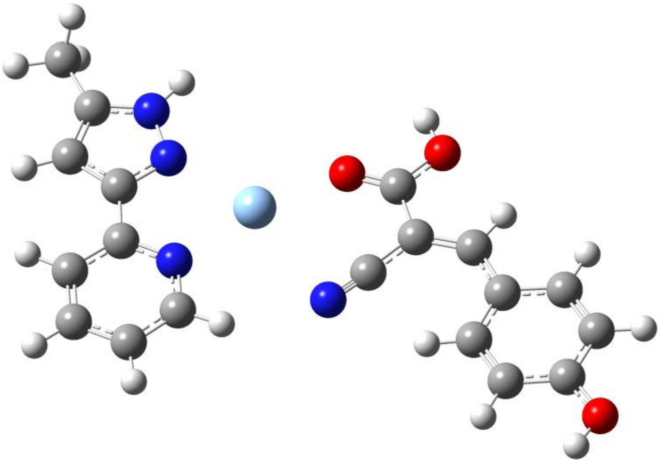
C	6.90806	2.38907	6.82609
C	6.21457	1.80635	5.77741
C	6.84524	0.84747	4.98718
C	8.21880	2.00259	7.06472
C	8.78544	1.04286	6.23980
N	8.11815	0.47858	5.22790
H	9.80338	0.70800	6.38263
H	8.79712	2.43034	7.87022
H	6.43027	3.13461	7.44650
H	5.19424	2.09140	5.57076
C	6.14709	0.20629	3.86423
N	6.77098	-0.69962	3.11030
C	4.82599	0.39754	3.40646
H	4.07267	1.05551	3.79943
C	4.67682	-0.44627	2.32600
N	5.86892	-1.07870	2.19247
H	6.12331	-1.76702	1.50428
Ag	9.03128	-1.10433	3.85389
C	16.10796	-1.71510	6.59916
H	16.11642	-1.00115	7.41320
C	14.96669	-1.89437	5.85302
H	14.09347	-1.31143	6.09919
C	14.93531	-2.82113	4.78721
C	17.26449	-2.45509	6.31025
C	17.26066	-3.38036	5.25975
H	18.16006	-3.94122	5.05183
C	16.11664	-3.55346	4.51980
H	16.11708	-4.26930	3.70839
O	18.40441	-2.32046	7.00504
H	18.31050	-1.66453	7.70594
C	13.80901	-3.08343	3.95140
H	13.98779	-3.83241	3.19080
C	12.53842	-2.56376	3.92805
C	11.55525	-3.01699	2.94199
O	10.40057	-2.60555	2.84775
O	12.00372	-3.95340	2.10260
C	12.05455	-1.56977	4.81901
N	11.61228	-0.76423	5.51736
C	3.52077	-0.70334	1.42228
H	2.67494	-0.08614	1.71445
H	3.76554	-0.46878	0.38503
H	3.20574	-1.74726	1.46527
H	11.28389	-4.18228	1.49642



5. Tables of experimental and calculated vibrational frequencies

Table S-2: Experimentally observed IR-MPD bands.

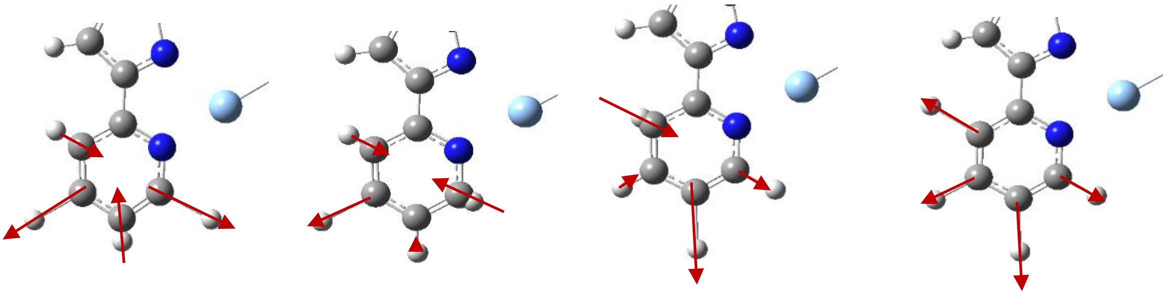
	OH-stretching vibrations / cm^{-1}	NH- stretching vibrations / cm^{-1}	CO- stretching vibrations / cm^{-1}	C=C- skeletal vibrations / cm^{-1}
$[\mathrm{Ag(HCCA)(MPP)}]^+$	3639 (st), 3581 (st)	3490 (m), 3400 (w)	1785 (w), 1763 (m), 1743 (w)	1583 (st), 1522(w)

Table S-3: Calculated vibration frequencies of isomers A-D (theory level: B3LYP/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Ag)). Frequencies above 2000 cm^{-1} are scaled with 0.96. Below 2000 cm^{-1} no scaling factor was applied.

A: ΔE(DFT) = **0** kJ/mol						
$\tilde{\nu}$/ cm^{-1}	3639	3606	3392	2948	1749	1584
assignment	$\nu(\mathrm{Ph\underline{OH}})$	$\nu(\mathrm{CO\underline{OH}})$	$\nu(\mathrm{NH})$	$\nu(\mathrm{CH_3})$	$\nu(\mathrm{\underline{CO}OH})$	C=C
B: ΔE(DFT) = **8** kJ/mol						
$\tilde{\nu}$/ cm^{-1}	3641	3603	3518	2948	1770	1586
assignment	$\nu(\mathrm{Ph\underline{OH}})$	$\nu(\mathrm{CO\underline{OH}})$	$\nu(\mathrm{NH})$	$\nu(\mathrm{CH_3})$	$\nu(\mathrm{\underline{CO}OH})$	C=C
C: ΔE(DFT) = **21** kJ/mol						
$\tilde{\nu}$/ cm^{-1}	3640	3597	3389	2947	1684	1581
assignment	$\nu(\mathrm{Ph\underline{OH}})$	$\nu(\mathrm{CO\underline{OH}})$	$\nu(\mathrm{NH})$	$\nu(\mathrm{CH_3})$	$\nu(\mathrm{\underline{CO}OH})$	C=C
D: ΔE(DFT) = **33** kJ/mol						
$\tilde{\nu}$/ cm^{-1}	3640	3602	3516	2946	1677	1589
assignment	$\nu(\mathrm{Ph\underline{OH}})$	$\nu(\mathrm{CO\underline{OH}})$	$\nu(\mathrm{NH})$	$\nu(\mathrm{CH_3})$	$\nu(\mathrm{\underline{CO}OH})$	C=C

6. CH stretching vibrations of the pyridine ring

In the range 3045-3090 cm^{-1} four vibrational modes can be assigned to the aromatic CH groups of the pyridine ring (MPP ligand L_2, cf. Fig S-2). The frequency and intensity of these 4 modes depends on the torsional isomerization of the complex (cf. Fig.S-3).



CH mode 1 CH mode 2 CH mode 3 CH mode 4

Figure S-2: Definition of selected CH normal modes of the pyridine ring. Note: Arrows represent the directions of motion, the arrow lengths are not concurrent to the lengths of displacement vectors.

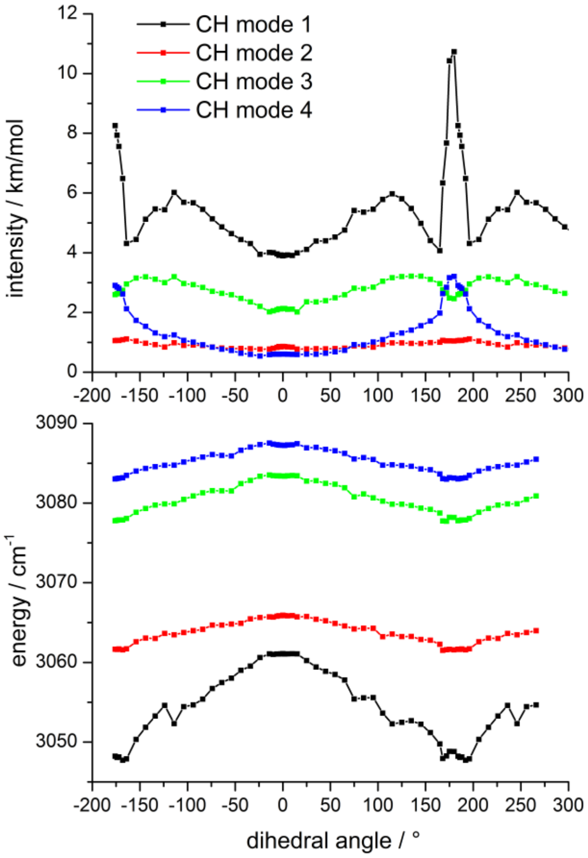


Figure S-3: Intensities (top) and frequencies (bottom) of four selected CH normal modes of the pyridine ring in dependence of the dihedral angle (cf. Fig. S-2 for definition of modes). All calculations at the B3LYP/cc-pVTZ (H, C, N, O) and Stuttgart 1997 ECP (Ag) level of theory, scaling factor 0.96 .