Journal Name

Dynamic Article Links ▶

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Photofragmentation spectroscopy of cold protonated aromatic amines in the gas phase: Supplementary Information

Géraldine Féraud,[a] Michel Broquier,[b,c] Claude Dedonder-Lardeux,[a] Gilles Grégoire,[d] Satchin Soorkia[b] and Christophe Jouvet*[a]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

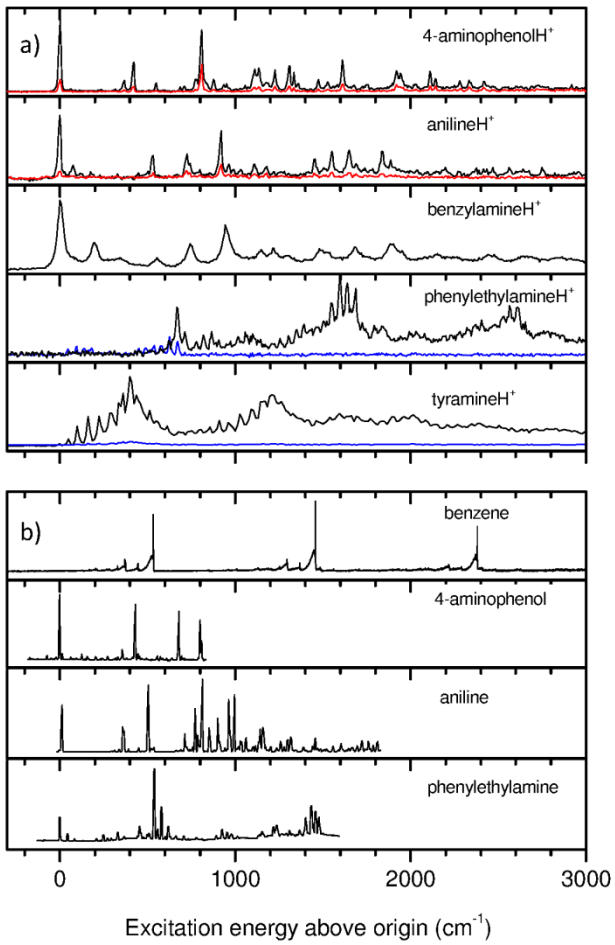

Fig. SI1 Comparison of the electronic spectra of protonated aromatic amines with that of neutral molecules. a) Photofragmentation spectra of protonated aromatic amines (S_1 state) within the main fragmentation channels: NH_3 loss in black, Cα-Cβ bond breaking in blue and H-loss in red. Photofragments are the following: for 4-aminophenolH$^+$, m/z 93 and m/z 109; for anilineH$^+$, m/z 77 and m/z 93; for benzylamineH$^+$, m/z 91; for phenylethylamineH$^+$, m/z 91 and 92 (blue) and m/z 105 (black); for tyramineH$^+$, m/z 108 and m/z 121. b) Neutral benzene UV absorption spectrum (in a cell);[1] jet-cooled neutral p-aminophenol and phenylethylamine fluorescence excitation spectrum from Mori et al.[2] and Yamomoto et al.,[3] respectively; jet-cooled neutral aniline R2PI spectrum.[4]

The 6a mode (around 500 cm^{-1}) is active in both phenylethylamineH$^+$ and neutral phenylethylamine.

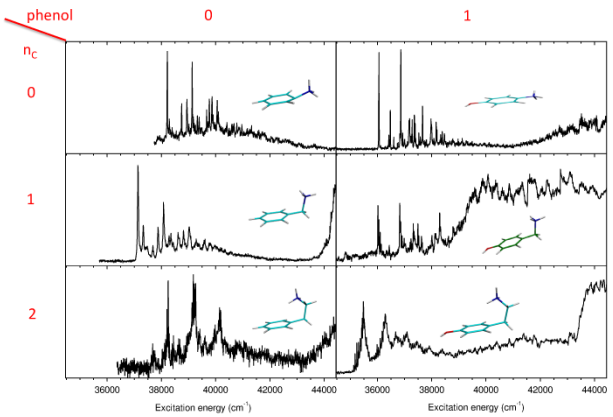

Fig.SI2 Photo-fragmentation spectra of anilineH$^+$, benzylamineH$^+$, phenylethylamineH$^+$, 4-aminophenolH$^+$, 4-hydroxybenzylamineH$^+$ and tyramineH$^+$, in which all the fragments have been added. The absence (0) or the presence (1) of the phenol chromophore is indicated, together with the number of carbon atoms in the substituent chain (0,1 or 2).

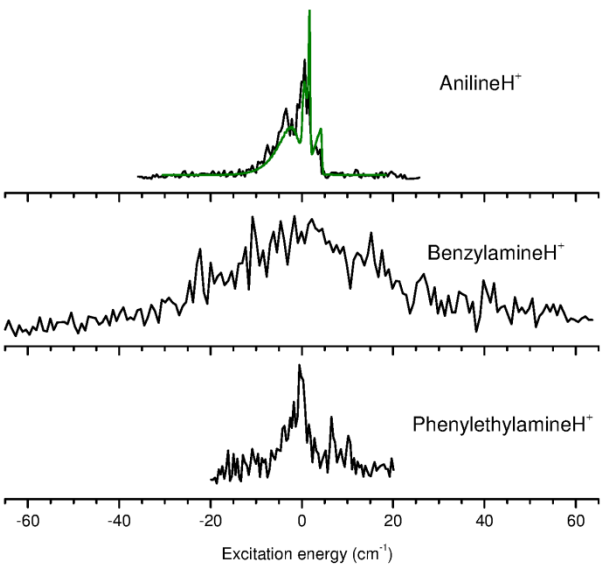

Fig. SI3 High resolution spectra (laser width 0.2 cm^{-1}) recorded on the 0-0 band of anilineH$^+$, benzylamineH$^+$ and phenylethylamineH$^+$ recorded on NH_3-loss fragments. The rotational contour for anilineH$^+$, simulated with pgopher[5] at a rotational temperature of 40 K, is reproduced in green (upper panel). For benzylamineH$^+$ the band contour is very large implying a very short lifetime.

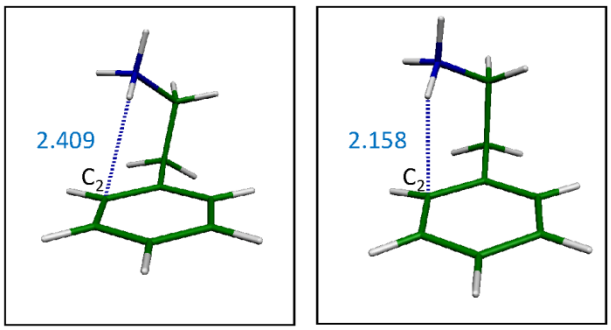

Fig. SI4 Ground state (left panel) and excited state (right panel) geometries of phenylethylamineH$^+$. Like in tyrosineH$^+$,[6] the proton pointing to the aromatic ring is much closer to the C_2 carbon in the excited state (distances are indicated in Å). This change of geometry in the amino chain leads to low frequency active modes in the electronic spectrum. This induces also a change in the planarity of the aromatic ring: the H atom linked to C_2 gets out of plane by 10°.

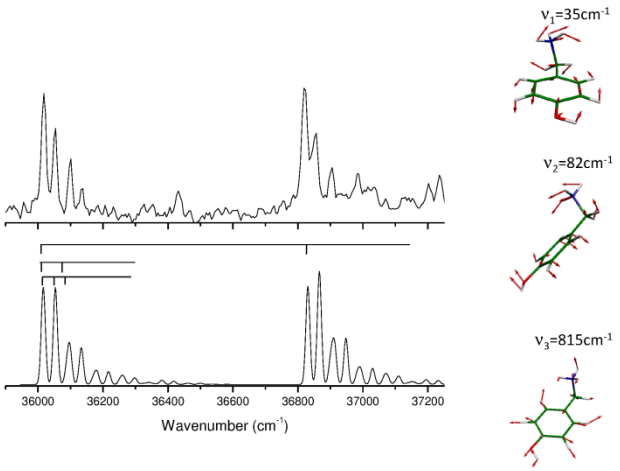

Fig. SI5 Enlarged view of the 4-hydroxybenzylamineH$^+$ spectrum (upper panel) and the calculated one (lower panel). The vibrational active modes are represented. One can note that the bands are not broad as in benzylamineH$^+$ and that, in the excited state, the CH_2NH_3 tail is bent leading to low frequency progression well reproduced by the calculation.

Table SI1 Calculated geometries of anilineH$^+$ at the RI-MP2/aug-cc-pVTZ level of theory for the S_0 ground state and at the RI-CC2/aug-cc-pVTZ level for the S_1 excited state.

S_0			
Atom	Cartesian Coordinates		
1 c	2.25340429327541	2.28879823484277	-0.01635997155765
2 c	3.55715747143058	0.00161279267455	0.02512454876011
3 c	2.25067680008153	-2.28741360997074	-0.01557456939624
4 c	-0.38024839674517	-2.30994054777985	-0.09856694012074
5 c	-1.61655113467474	0.00049306404331	-0.13778963136666
6 c	-0.38008249464208	2.30751175735163	-0.09938322996312
7 n	-4.41951561021840	-0.00426109823415	-0.22780407209485
8 h	-5.10321600171676	1.80311727337405	-0.22409901208637
9 h	-5.17201854948717	-0.92022065157148	1.29991809893095
10h	3.27019000942064	-4.05731981598073	0.01716262768857
11h	5.59900578961591	0.00050029795746	0.08953244840801
12h	3.27187019560563	4.05918951323264	0.01551440459973
13h	-1.41169469804072	4.07623275611799	-0.13206290791384
14h	-1.41300857647498	-4.07730503894346	-0.13055700212432
15h	-5.07275035530202	-0.87685642688296	-1.82508365819683

S_1			
Atom	Cartesian Coordinates		
1 c	2.29994369493288	2.33780082600769	-0.11282358350790
2 c	3.64208499999674	-0.00275857813609	-0.03831431107340
3 c	2.28863454779778	-2.33636652187453	0.03637851515532
4 c	-0.41699479165265	-2.35335679946573	0.08104890026822
5 c	-1.69436279331119	0.01219161988517	0.13830696227415
6 c	-0.40042137518932	2.36435546005508	-0.06808794213035
7 n	-4.44815309695124	-0.00264459448238	-0.27056218297588
8 h	-5.21683192853234	1.71860500515319	0.16809236775392
9 h	-5.30638729324699	-1.33056938284858	0.84862781110778
10h	3.29104982595089	-4.11496340157583	0.07906909874624
11h	5.68282508265236	-0.00902730743115	-0.04108889641613
12h	3.30895867997147	4.11172735820931	-0.17802426782599
13h	-1.42744435061310	4.13470222635329	-0.12108843618272
14h	-1.45083826392855	-4.11897828566400	0.13772865501450
15h	-4.91884419574889	-0.40657912395441	-2.11929155664111

Table SI2 Calculated geometries of benzylamineH$^+$ at the RI-MP2/aug-cc-pVDZ level of theory for the S_0 ground state and at the RI-CC2/aug-cc-pVDZ level for the S_1 excited state.

S_0			
Atom	Cartesian Coordinates		
1 n	-1.61950241263567	2.36939827357116	2.64066224456268
2 c	0.17273344474778	3.91462097824585	4.32837692818479
3 h	1.93801185293990	2.82406473469342	4.42690703888532
4 h	0.49490332927897	5.70362854155653	3.32294459009716
5 c	-1.08178048061450	4.25200399936830	6.84815827957396
6 c	-0.73624503013141	2.41909161392732	8.76028294509050
7 h	0.56949401233339	0.83670177297383	8.46683007029399
8 c	-2.70076405287416	6.33681075090655	7.25757881031694
9 h	-2.91878585600683	7.79256706343268	5.79872073153027
10c	-2.02174744637712	2.66815140012826	11.07510927694817
11h	-1.74053995929941	1.26594082954555	12.56657515491879
12c	-3.98213303508696	6.57758093087002	9.57556957913491
13h	-5.21799347831040	8.20014715720757	9.90671904990831
14c	-3.64908549134787	4.73935836350386	11.47507786346373
15h	-4.63628156618561	4.93661569597036	13.27990242216442
16h	-1.99559462015186	0.65657052036498	3.48100162687342
17h	-0.90521575844888	2.04515506551254	0.86088922019195
18h	-3.31936024499524	3.29797639943965	2.46853547814916

S_1			
Atom	Cartesian Coordinates		
1 n	-1.62703390826668	2.30946026125948	2.49091992909918
2 c	0.16586782242339	3.90995896776812	4.31990150919996
3 h	1.91713385202865	2.79008114713907	4.38940620654318

	4 h	0.46387420527704	5.68622482902814	3.27973320560207
	5 c	-1.05448324460082	4.24703032055716	6.79788602303394
	6 c	-0.69987793819553	2.41933670031856	8.80550582556063
	7 h	0.65177136658038	0.86889601224348	8.55883360576687
	8 c	-2.69089073461707	6.38745563447334	7.28524684565247
	9 h	-2.87055077923716	7.88895431575181	5.86930462989348
	10c	-2.02714297913603	2.67555535427997	11.17382990888117
	11h	-1.71784990753883	1.25976109543861	12.64678800962880
	12c	-4.00752103084758	6.62246448478057	9.66168532936328
	13h	-5.23040360645960	8.26028412711845	9.96473377724603
	14c	-3.71580706489384	4.75467392945031	11.60831468041835
	15h	-4.73033650422084	4.93039990663816	13.39566497491300
	16h	-1.99885649312505	0.57725819703623	3.29054927762282
	17h	-0.85002324902728	2.02295774780876	0.72592319413534
	18h	-3.32775659930894	3.22563106012808	2.27561437772794

Table SI3 Calculated geometries of phenylethylamineH^+ at the RI-MP2/aug-cc-pVDZ level of theory for the S_0 ground state and at the RI-CC2/aug-cc-pVDZ level for the S_1 excited state.

S_0

Atom		Cartesian Coordinates	
1 n	4.09196154547150	3.30773720170521	2.18624907619821
2 h	5.44797414797081	2.87868056640190	3.50740269152286
3 c	1.78138314564319	4.48849443234733	3.40383724073929
4 h	0.63934043158229	5.24213255947255	1.84292172018172
5 c	0.34977791579022	2.41485268856248	4.84528645375197
6 h	1.43941799993800	1.82330558881111	6.52173265271666
7 h	-1.43347719079805	3.24627744656219	5.52603338253308
8 c	-0.11577241531605	0.19306562132030	3.09886688416186
9 c	-1.98332014614766	0.34600503647422	1.19567356828859
10h	-3.23509069558900	1.99348915376756	1.10644710384136
11c	1.44525834238791	-1.97338573942188	3.22082412143543
12h	2.84208313750314	-2.15213137241153	4.74248380846903
13c	-2.28847172114997	-1.63687853200392	-0.54725103095993
14h	-3.75936300779438	-1.51648996981681	-1.99351761206638
15c	1.14480695807528	-3.95729220741565	1.46885464377528
16h	2.33967177655887	-5.63815134617870	1.59935071782034
17c	-0.71571379982042	-3.78190101938003	-0.42176623086368
18h	-0.96178953291806	-5.32341013219757	-1.77485922418402
19h	2.43881973140846	6.04489393459633	4.61024469738701
20h	4.89981396176496	4.45076130710195	0.84427390856757
21h	3.53784452453049	1.61584614017780	1.36055510957134

S_1

Atom		Cartesian Coordinates	
1 n	4.27290243596910	3.22611794104176	2.41249710375578
2 h	5.56552824571205	3.10220541654986	3.85723229689466
3 c	1.83875751893270	4.46918961413929	3.29620505591790
4 h	0.83567519516260	5.06432880140087	1.57790726455940
5 c	0.28741247040579	2.49711298852180	4.77506352692578
6 h	1.30233395054672	1.95277965198220	6.51830382304229
7 h	-1.49615690939305	3.41783694923153	5.34032638462191
8 c	-0.19117732204173	0.24253631532882	3.11640295498623
9 c	-2.25801336476864	0.27708744413534	1.32415209860747
10h	-3.63953085608036	1.81620526621271	1.40688469929207
11c	1.62666444590297	-1.82103141901748	3.06177832046291
12h	2.96804359135505	-2.04271911209865	4.62790229128788
13c	-2.53226705425733	-1.70774681452201	-0.51850298859040
14h	-4.09456214796071	-1.66307581685565	-1.86681995827400
15c	1.28317371096773	-3.85851847997565	1.27298125499576
16h	2.56681507966227	-5.47735006225252	1.30183306245386
17c	-0.76632986494380	-3.77939495890215	-0.51976567372668
18h	-0.99513735821984	-5.32869119406638	-1.86651089326804
19h	2.35722340520502	6.13366127383248	4.42844396919473
20h	5.11245706195588	4.17624957567726	0.94170260496287
21 h	3.86134287497912	1.36911797811141	1.85562648478516

Table SI4 Calculated geometries of 4-aminophenolH^+ at the RI-MP2/aug-cc-pVDZ level of theory for the S_0 ground state and at the RI-CC2/aug-cc-pVDZ level for the S_1 excited state. The excited state convergence using TD/DFT(B3LYP) cannot be obtained due to a direct H loss from NH_3 in the optimization process.

S_0

Atom		Cartesian Coordinates	
1 c	-1.28889455845802	3.47999447181847	6.91927312158507
2 c	-0.36942814205593	2.96220296280968	9.35584670691975
3 c	1.81558221195882	1.46558649879313	9.66384174511225
4 c	3.08791626408473	0.48191810841660	7.53255634635631
5 c	2.18648005222016	0.98715457037795	5.09607962599144
6 c	0.01147903688562	2.47970284082821	4.84710774417253
7 n	-0.95108946887153	3.01975683206583	2.25866153987762
8 h	-2.98458268077796	4.64161325942661	6.68160312303248
9 o	2.82399004239193	0.87909049751559	11.95037011094661
10h	3.17406354476545	0.22364298682595	3.44636040088161
11h	-1.35834962845831	3.72642237410675	11.00263326614457
12h	4.77588892423840	-0.67179620717469	7.81935414846839
13h	-2.54590323619501	4.12721879913185	2.33817219154150
14h	0.36369763723353	3.97037439668954	1.18602353175433
15h	-1.42328110597856	1.38785173229485	1.31166976442365
16h	1.83913687843673	1.62616278164812	13.30402669729650

S_1

Atom		Cartesian Coordinates	
1 c	-1.37550984432701	3.49343498941248	6.93227794333359
2 c	-0.46135825750700	2.94935674939409	9.42942172073260
3 c	1.82406806053366	1.46515315484984	9.62602424449661
4 c	3.22289820209720	0.50079233885689	7.51796486386121
5 c	2.30712342437957	1.07053451831857	5.00813022271062
6 c	0.04710771525516	2.51026050842976	4.86831576290397
7 n	-0.96641967719129	2.99555606766861	2.29609887045672
8 h	-3.10149781918158	4.58819031763476	6.62428021592733
9 o	2.79485329291435	0.87502167633261	11.91491243039964
10h	3.27355594061485	0.38909789389072	3.31427372514243
11h	-1.44402448258681	3.62840370807528	11.11433851864268
12h	4.92038146911395	-0.62346967262901	7.84768645381514
13h	-2.17193931718484	4.52460941349810	2.29617874525654
14h	0.48838655679552	3.37673334552073	1.05360165502264
15h	-1.93963902701195	1.44967301777040	1.61386361051059
16h	1.73871953470628	1.59354887855066	13.25621108129224

Table SI5 Calculated geometries of 4-hydroxybenzylamineH^+ at the RI-MP2/aug-cc-pVDZ level of theory for the S_0 ground state and at the RI-CC2/aug-cc-pVDZ level for the S_1 excited state.

S_0

Atom		Cartesian Coordinates	
1 c	-3.66798302969689	4.78063613866877	11.49174609639579
2 c	-2.06639307509423	2.68979000966459	11.06354789991947
3 c	-0.80956971233411	2.43455099605624	8.75577873683648
4 c	-1.12848288947733	4.25815008871764	6.83085269959361
5 c	-2.72073989065154	6.34960819196221	7.26839085898549
6 c	-3.98109116845262	6.61417791953956	9.58121214751079
7 c	0.13947328340350	3.92350396126623	4.32764520836040
8 n	-1.56618582658342	2.33390108691482	2.61269673881717
9 h	1.93585461923907	2.88323386888820	4.45097272322101
10h	0.44420614629827	5.71439136892200	3.31622506987901
11h	0.46985297615882	0.82699384482144	8.47643471868178
12h	-2.94931848665648	7.81609890524511	5.82121467717481
13h	-1.81648615845312	1.30840731349095	12.58050521962346
14h	-5.19151915140948	8.26169375262301	9.91125795900516
15o	-4.81042148300443	4.90066143448792	13.77060815349877
16h	-1.92336175345598	0.60845575309463	3.44249881793568
17h	-0.80843807164977	2.01687805702793	0.84510956216888
18h	-3.29143663938457	3.20965870984812	2.39091216528796
19h	-5.81110117002075	6.43391995714332	13.86236981780640

S_1

Atom		Cartesian Coordinates	
1 c	-3.68137586743445	4.73885906282091	11.43481911851374
2 c	-2.21129197732777	2.52319477568144	10.94632093758854
3 c	-0.90215890200408	2.32540995882840	8.54991437719433
4 c	-1.12772952780665	4.39129713179614	6.79196796951171
5 c	-2.64022991847222	6.58656904616234	7.30114846908455
6 c	-3.91800941443674	6.80671073566903	9.67105980848750
7 c	0.07364585577224	4.08223259466927	4.25448577361149
8 n	-1.49512457579941	2.14538774774705	2.77379746236850
9 h	1.98847514752605	3.26973569882822	4.37004718441480
10h	0.10486943318237	5.82227503108369	3.11850048725424
11h	0.48767102094815	0.82053353898574	8.23496152611485
12h	-2.77527972630321	8.09460996683220	5.89004234037520
13h	-2.09477427975316	1.05652727443133	12.39513341070434
14h	-5.06232564618133	8.46756797987216	10.12763037119163
15o	-4.84913803979023	4.80066418874641	13.69850740440585
16h	-1.72997214575806	0.55886406480722	3.89051757413654
17h	-0.69326171137430	1.61681161185226	1.07713020373472
18h	-3.27804422895088	2.84922805233836	2.42384673304535
19h	-5.74908697726142	6.40823289723058	13.85014811896412

Table SI6 Calculated geometries of protonated tyramine at the RI-MP2/aug-cc-pVDZ level of theory for the S_0 ground state and at the RI-CC2/aug-cc-pVDZ level for the S_1 excited state.

S_0

Atom			
1 n	0.01216466828741	0.23474314195663	-0.53914974730923
2 h	-0.38185924910067	0.08418319524903	1.35552682147070
3 c	2.82268451115484	0.00432489901843	-1.04624585895560
4 h	3.01181444466542	-0.24529444504832	-3.09817210419830
5 c	4.10407656996063	2.45818487342773	-0.16785440374750
6 h	4.07410268863763	2.57435090388318	1.91395036277283
7 h	6.10021001030216	2.36308978649519	-0.75159525065216
8 c	2.76401316310590	4.70632190248750	-1.32612487564618
9 c	3.14134503237206	5.34288719816380	-3.89107455117354
10h	4.55426043419343	4.32860262767653	-5.01463556258658
11c	0.96421155305148	6.09710934750123	0.08184723244093
12h	0.70574556626502	5.70395517468635	2.10088261184638
13c	1.77010018836949	7.31477157387805	-5.02047919192399
14h	2.10990125691883	7.80720865861858	-7.00138213348955
15c	-0.42673675308683	8.06686722207221	-1.03090898255904
16h	-1.79059486751350	9.17009017960276	0.05966551845736
17c	-0.02744969575862	8.67394104252608	-3.59264238203403
18o	-1.44003247053953	10.60465856504418	-4.55478019042940
19h	-0.96942547243569	10.92548530895552	-6.29627793260960
20h	3.49945871954216	-1.69538282290070	-0.06463626079240
21h	-1.03576914553281	-1.09790986754925	-1.47969382683512
22h	-0.54406633369035	2.03260282164137	-1.10278635576710

S_1

Atom			
1 n	0.00906448679843	0.18822527508278	-0.17431027015609
2 h	-0.13774069821067	-0.26048028915440	1.71030205675956
3 c	2.72758502166955	0.04090428029438	-1.07803463947828
4 h	2.64429931693832	-0.13727641319063	-3.14554507818095
5 c	4.11515547204739	2.48526615535123	-0.31098857690157
6 h	4.20520657837443	2.63452921878661	1.77050112744307
7 h	6.06423338382723	2.34515455087179	-1.03219743486081
8 c	2.73967998686751	4.70595153590927	-1.43872047710035
9 c	3.36781629450946	5.53264670585965	-3.93287311087235
10h	4.95922741773264	4.63988953594322	-4.90973742700039
11c	0.54991048416270	5.68462712538389	-0.08561372902761
12h	0.45808564686185	5.39855393371771	1.96870830752384
13c	1.92121027887568	7.43440228178440	-5.16819782550932
14h	2.30687896196225	8.03948113142723	-7.10596801711527
15c	-0.64612338074073	7.90040834373807	-1.14833874970930
16h	-2.00758531820586	9.04131687968128	-0.09336774359673
17c	-0.00686232257541	8.64128990849358	-3.66853293125102
18o	-1.32289750380973	10.64113705325885	-4.56901165650275
19h	-0.72689300857098	11.06088635209705	-6.27059266102933
20h	3.59019612831398	-1.66324586368545	-0.25929892583943
21h	-1.17268719658502	-0.99882559632523	-1.15887381449479
22h	-0.61960521107463	2.09994918206078	-0.36587548682146

Notes and references

[a] *PIIM, Aix-Marseille Université, CNRS UMR 7345, Avenue Escadrille Normandie-Niémen, 13397 Marseille Cedex 20, France*
[b] *Institut des Sciences Moléculaires d'Orsay, CNRS UMR 8214, Université Paris Sud 11, 91405 Orsay Cedex, France*
[c] *CLUPS (Centre Laser de l'Université Paris-Sud/LUMAT FR 2764), Bâtiment 106, Université Paris Sud 11, 91405 Orsay Cedex, France*
[d] *Laboratoire de Physique des Lasers, Université Paris 13, Sorbonne Paris Cité, CNRS UMR 7538, 93430 Villetaneuse, France*
* *Corresponding Author: christophe.jouvet@univ-amu.fr*

† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

1. S. Fally, M. Carleer, and A. C. Vandaele, *J. Quant. Spectrosc. Radiat. Transfer*, 2009, **110**, 766–782.
2. H. Mori, H. Kugisaki, Y. Inokuchi, N. Nishi, E. Miyoshi, K. Sakota, K. Ohashi, and H. Sekiya, *Chem. Phys.*, 2002, **277**, 105–115.
3. S. Yamamoto, T. Niwa, and M. Ito, *Laser Chem.*, 1990, **10**, 169–175.
4. J. Yeh, T. Shen, D. G. Nocera, G. E. Leroi, and E. Lansing, *J. Phys. Chem.*, 1996, **100**, 4385–4389.
5. C. M. Western, *PGOPHER, a Program for Simulating Rotational Structure*, University of Bristol; available at http://pgopher.chm.bris.ac.uk.
6. G. Grégoire, C. Jouvet, C. Dedonder, and A. L. Sobolewski, *J. Am. Chem. Soc.*, 2007, **129**, 6223–6231.