The hidden life of cosmic carbon

Infrared fingerprint spectroscopy and fragmentation chemistry of gas-phase polycyclic aromatic hydrocarbons

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Appendix A

Appendices to Chapter 4

A.1 Anthracene

A.1.1 Anthracene cation mass spectrum

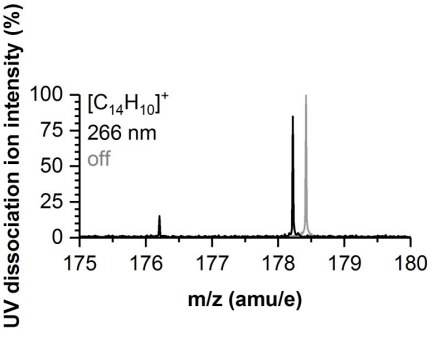

FIGURE A.1: Fragmentation mass spectrum of the anthracene cation $C_{14}H_{10}{}^{+}$. The black trace was recorded after exposure to 1 mJ pulses at 10 Hz of a 266 nm (4th harmonic of a Nd:YAG laser) for 3 s, while the gray trace was recorded with the laser off and was given an offset of 0.2 amu for legibility.

Figure A.1 shows fragmentation mass spectra for the radical cation $C_{14}H_{10}{}^{+}$ at $m/z = 178$ (gray). After UV irradiation (black), the fragmentation mass spectrum shows one fragment at $m/z = 176$, depicting the loss of two H atoms as the only dissociation process from the radical cation, which was also observed by Ekern *et al.* [205].

A quantitative interpretation of mass spectra exhibiting sequential H-loss could be complicated by the presence of naturally abundant ^{13}C isotopologs of the PAH under investigation, amounting to 15.3 % for a molecule with 14 carbons. To ensure the isotopic purity, the mass spectra were made as clean as possible prior to isolation, that is, minimizing the intensity of the cations in the case of protonation, and optimizing deuteronation versus protonation for the deuteronated anthracene. Using unisolated mass spectra, it is possible to make accurate estimates of the isotopic contamination in the precursor peaks

for each spectrum. Knowing that the cation only loses two hydrogen atoms, we can distinguish contributions of the protonated and deuteronated isomers from the contributions of the radical cationic ^{13}C isomers.

A.1.2 Anthracene band positions

Table A.1 lists all of the measured band positions of protonated anthracene featured in Fig. 4.1g–i, and compares them with the theoretical band positions of the three different position isomers as calculated using DFT.

Table A.2 lists those measured and calculated for deuteronated anthracene given in Fig. 4.1j–l. Interestingly, the only band not predicted by the 9-isomer is precisely the experimental band at 1360 cm^{-1}. Suitable modes are predicted at 1355 cm^{-1} for the 1-isomer (k) and at 1363 for the 2-isomer (l). However, the predicted features of the 1- and 2-isomers around 900 cm^{-1} are not present in the experiment. Overall, the features are consistent with the 9-isomer.

Table A.3 lists all measured and calculated for protonated, perdeuterated anthracene given in Fig. 4.1m–o. Only calculated frequencies that exhibit enough intensity to allow for comparison with the experimental features are listed.

A.1.3 Theoretical spectra for additional anthracene isomers

Figure A.2 displays the six different isotopic isomers that can be formed by a $[D-C_{14}H_{10}]^+$ with the aliphatic group at the 9-position. These spectra mostly differ in terms of intensity ratios. The only spectrum showing significant changes in band position, is the one where the D is at the 5 site, opposite the C–HH group, which is the most symmetric configuration. This increased symmetry leads to improved resonant enhancement of the in-plane C–H bending vibrations, which significantly changes the shape of the spectrum. However, this theoretical spectrum is clearly not in agreement with the experimental spectrum.

A.2 Phenanthrene

A.2.1 Band positions for phenanthrene

Table A.4 lists all of the measured bands visible in Fig. 4.4b–f, and compares them with the calculated band positions of the five different position isomers.

TABLE A.1: Band positions in cm^{-1} of the experimental spectrum of protonated anthracene $[H-C_{14}H_{10}]^+$ and the most intense modes of the unconvoluted, theoretical spectra, capped off at 10 km/mol. A scaling factor of 0.9662 has been applied to the calculated spectrum to correct for anharmonicity. The experimental IR intensities are normalized to the highest intensity, while the theoretical IR intensities are the absolute cross sections in km/mol.

$[H-C_{14}H_{10}]^+$							
experiment		9-isomer		1-isomer		2-isomer	
$\bar{\nu}$ (cm^{-1})	I (a.u.)	$\bar{\nu}$ (cm^{-1})	I (km/mol)	$\bar{\nu}$ (cm^{-1})	I (km/mol)	$\bar{\nu}$ (cm^{-1})	I (km/mol)
759	0.11	755	84	743	41	741	38
						873	34
						886	11
						888	16
						900	15
				932	25	911	11
						944	20
		984	10	1047	15	1005	11
1146	0.49	1146	88	1163	25	1155	52
		1166	15				
1185	0.30	1191	63	1177	88	1181	68
				1223	70	1221	28
		1276	20	1257	12	1261	13
						1290	74
1319	0.61	1312	220	1324	139	1309	113
		1337	18				
		1347	14	1335	35	1333	26
		1355	43	1355	128	1364	163
				1376	22	1381	49
		1409	65	1406	13	1419	12
		1438	168	1432	324		
1445	1.00	1441	25			1441	66
		1476	18	1492	404	1466	25
1505	0.84	1501	305			1506	32
		1535	11	1521	85	1523	56
		1539	35	1555	101	1568	99
1581	0.83	1578	429	1590	14	1592	443
		1592	21	1602	228	1611	103

TABLE A.2: Band positions in cm^{-1} of the experimental spectrum of deuteronated anthracene $[D-C_{14}H_{10}]^+$ and the most intense modes of the unconvoluted, theoretical spectra, capped off at 10 km/mol. A scaling factor of 0.9662 has been applied to the calculated spectrum to correct for anharmonicity. The experimental IR intensities are normalized to the highest intensity, while the theoretical IR intensities are the absolute cross sections in km/mol.

$[D-C_{14}H_{10}]^+$							
experiment		9-isomer		1-isomer		2-isomer	
$\tilde{\nu}$ (cm^{-1})	I (a.u.)	$\tilde{\nu}$ (cm^{-1})	I (km/mol)	$\tilde{\nu}$ (cm^{-1})	I (km/mol)	$\tilde{\nu}$ (cm^{-1})	I (km/mol)
758	0.07	755	86	743	44	737	13
						742	26
				811	14	869	29
				828	10	888	20
				896	35	913	28
		984	10	1048	17	950	14
1146	0.42	1150	81	1159	50	1142	33
		1158	12	1177	95	1152	137
		1167	19			1155	46
1191	0.24	1188	66	1183	37	1183	26
		1201	25	1223	54	1220	29
		1276	20	1265	10	1261	12
1315	0.61	1308	178	1319	19	1307	15
		1333	54				
1360	0.27	1337	16	1355	168	1363	194
		1406	55	1374	25	1380	48
				1403	13		
				1424	6		
1439	1.00	1438	180	1432	334	1441	65
		1441	24			1466	27
		1474	25				
1499	0.85	1501	305	1490	434	1505	42
		1534	13	1520	81	1523	61
		1538	35	1554	92	1567	93
1569	1.00	1577	429	1590	10	1592	473
		1592	21	1602	237	1609	95

TABLE A.3: Band positions in cm^{-1} of the experimental spectrum of protonated, perdeuterated anthracene $[H-C_{14}D_{10}]^+$ and the most intense modes of the unconvoluted, theoretical spectra, capped off at 10 km/mol. A scaling factor of 0.9662 has been applied to the calculated spectrum to correct for anharmonicity. The experimental IR intensities are normalized to the highest intensity, while the theoretical IR intensities are the absolute cross sections in km/mol.

$[H-C_{14}D_{10}]^+$							
experiment		9-isomer		1-isomer		2-isomer	
$\bar{\nu}$ (cm^{-1})	I (a.u.)	$\bar{\nu}$ (cm^{-1})	I (km/mol)	$\bar{\nu}$ (cm^{-1})	I (km/mol)	$\bar{\nu}$ (cm^{-1})	I (km/mol)
		938	29	932	11		
		1139	13			1152	134
		1197	13	1179	74		
		1206	31				
				1227	14	1233	14
		1277	67			1289	24
		1311	70				
1321	0.13	1324	13	1327	112	1337	291
		1349	28	1334	39	1349	33
1380	0.21	1371	110	1402	263	1391	9
		1389	19	1403	46	1410	43
1450	1	1451	451	1452	552	1473	16
		1494	73	1486	169	1488	120
		1499	27	1506	74	1532	11
1540	0.79	1540	555			1560	524
		1559	14	1575	273	1577	162

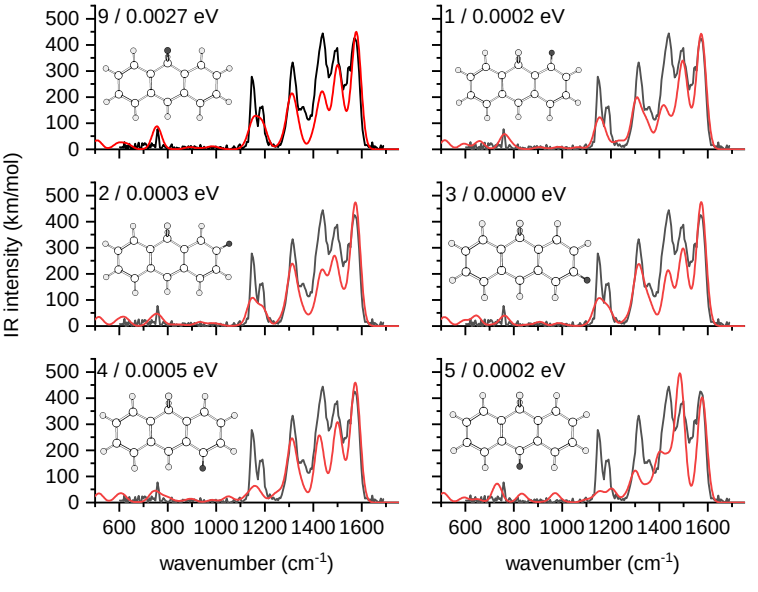

FIGURE A.2: Calculations for the six scrambled isomers of the 9-isomer of deuteronated anthracene (red) compared to the FELIX IRMPD spectrum of $[D-C_{14}H_{10}]^+$ (black). The shifting D atom is marked in black on the molecule, and the label in the upper right corner of each panel indicates its position. The energy of each of these isomers is listed in eV with respect to the global minimum.

TABLE A.4: Band positions in cm^{-1} of the experimental spectrum of protonated, perdeuterated phenanthrene $[H{-}C_{14}D_{10}]^+$ and the most intense modes of the unconvoluted, theoretical spectra, capped off at 10 km/mol. A scaling factor of 0.9662 has been applied to the calculated spectrum to correct for anharmonicity. The experimental IR intensities are normalized to the highest intensity, while the theoretical IR intensities are the absolute cross sections in km/mol.

$H^+C_{14}D_{10}$

experiment		9-isomer		1-isomer		3-isomer		4-isomer		2-isomer	
$\bar{\nu}$ (cm^{-1})	I (a.u.)	$\bar{\nu}$ (cm^{-1})	I (km/mol)	$\bar{\nu}$ (cm^{-1})	I (km/mol)	$\bar{\nu}$ (cm^{-1})	I (km/mol)	$\bar{\nu}$ (cm^{-1})	I (km/mol)	$\bar{\nu}$ (cm^{-1})	I (km/mol)
		1080	24			1108	22				
		1119	15								
		1152	74	1153	81	1145	128	1154	29	1137	120
				1168	23						
		1298	44			1303	60				
				1314	394	1308	103			1314	83
				1317	22			1323	48		
1353	1	1351	284	1332	165	1352	125	1332	187	1345	31
		1367	169			1365	55				
		1387	23					1387	46	1382	182
								1398	262		
						1435	125			1402	39
1463	0.75	1450	99	1456	323	1452	277	1451	284	1465	48
										1496	65
						1520	238	1483	24	1532	232
		1551	44	1510	170	1541	29	1517	29	1558	100
1565	0.59	1560	287	1556	54	1579	115	1566	134	1567	140