

Photofragmentation Mechanisms in Protonated Chiral Cinchona Alkaloids

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Supplementary Information

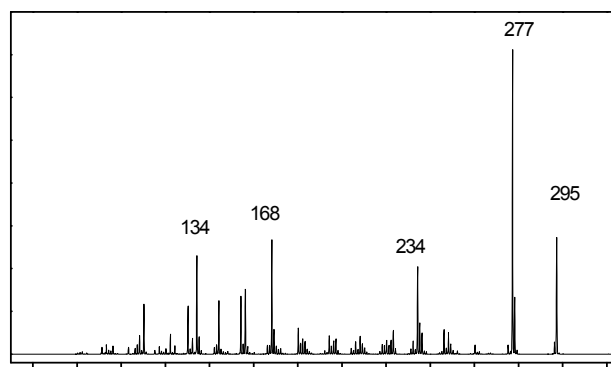


Figure S1: CID-MS² mass spectrum of CdH⁺

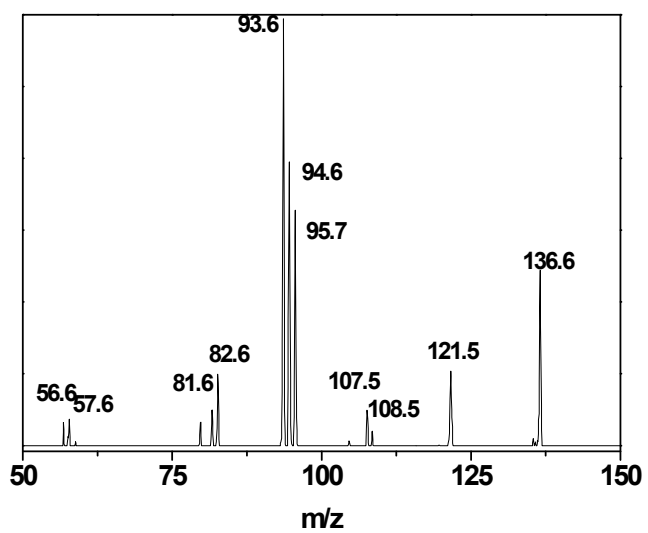
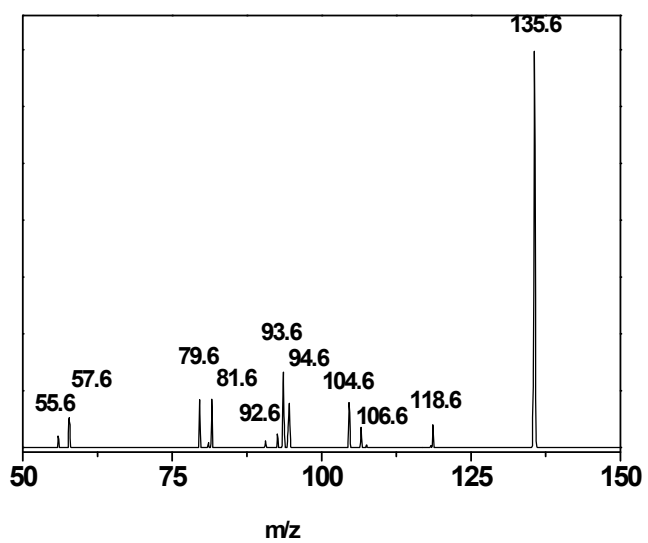


Figure S2: CID-MS³ fragmentation mass spectra of photoproducts at m/z 136 (top) and m/z 137 (bottom). The spectra have been normalized at the most intense peak.

Table S1: Experimental vibrational frequencies for ions at m/z 136 and 137. Unscaled harmonic frequencies of the lowest energy calculated isomers, determined at the b3lyp/6-31++g(d,p) level of theory, and band assignments. The reported calculated intensities given in parentheses are in km/mol.

$(m/z$ 136)			$(m/z$ 137)		
Experimental frequency (cm^{-1})	Calculated frequency (cm^{-1})	Assignment	Experimental frequency (cm^{-1})	Calculated frequency (cm^{-1})	Assignment
-	974 (29) 989 (39)	C=CH ₂ wag	960	996 (56) 1015 (20)	Coupled CH bend, CH ₂ and CH ₃ wag
-	1204	CH and CH ₂ bend	1215	1194 (32) 1204 (35)	Coupled CH and CH ₂ bend
-	1352 (15) 1391 (18)	Coupled CH ₂ scissoring and CH bend	1315	1285 (15)	Coupled CH ₂ scissoring and CH bend
-	1470 (28)	CH ₂ scissoring	1395	1415 (26)	CH ₂ bend
1440	1522 (22) 1492 (15) 1470 (29) 1425 (35) 1412 (26)	NH bend CH ₂ scissoring	1440	1475 (10) 1482 (10) 1493 (19) 1496 (20) 1415 (25)	CH and CH ₂ scissoring
1630	1714 (89)	Ring deformation	1690	1731 (5)	C=C stretch

Table S2 Structural parameters and relative energies of the most stable isomers of CdH⁺ at the ri-cc2/aug-ccpVDZ level.

CdH ⁺	τ_1	τ_2	τ_3	T3	$\Delta E_0(\text{kcal/mol})$
γ -open(10)	97	-80	48	171	0.0
γ -open(3)	98	168	-63	-176	1.0
γ -closed(1)	-111	48	175	177	1.1
γ -closed(2)	68	49	173	178	1.5