Electronic supplementary information for

Photofragmentation of Corannulene ($C_{20}H_{10}$) and Sumanene ($C_{21}H_{12}$) cations in gas phase and its Astrophysical implications †

Pavithraa Sundararajan,*[a,b] Alessandra Candian,[c] Jerry Kamer, [a,b] Harold Linnartz,[a,b] and Alexander G.G.M. Tielens[b,d]

[a] Laboratory for Astrophysics, Leiden University, PO Box 9513, NL-2300, RA Leiden, the Netherlands.; E-mail: sundararajan@strw.leidenuniv.nl

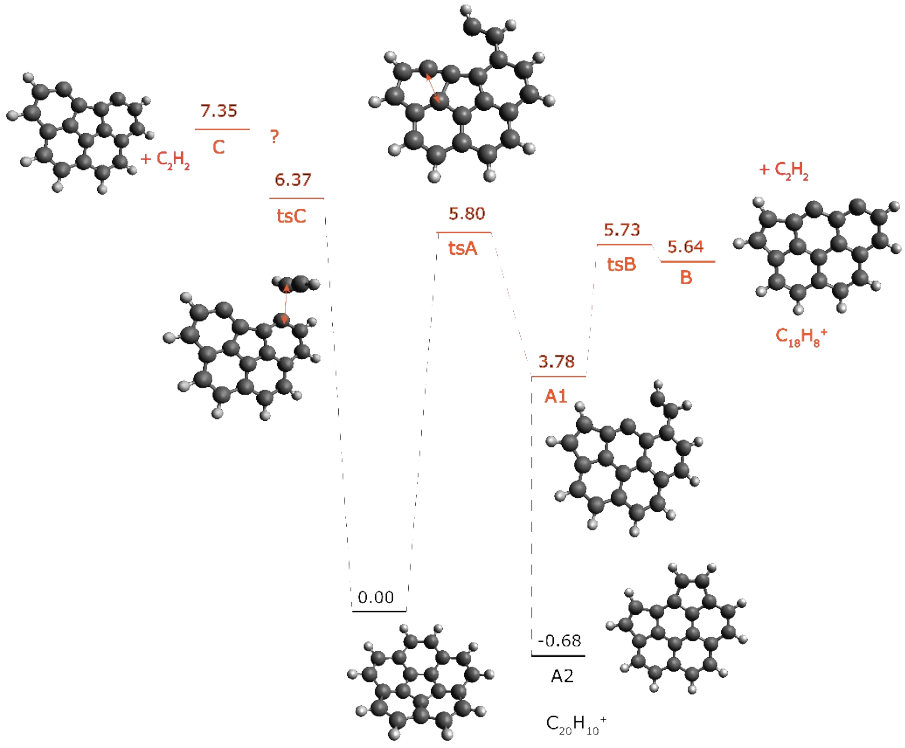
[b] Leiden Observatory, Leiden University, 2300 RA Leiden, The Netherlands.

[c] Anton Pannekoek Institute, University of Amsterdam, Science Park 904, 1098XH Amsterdam, The Netherlands.

[d] Astronomy Department, University of Maryland, College Park, MD 20742, USA.

Searching for C_2H_2 dissociation paths in Corannulene:

Starting from Corannulene cation, we looked for a direct path toward C_2H_2 loss via the breaking down of 2 C-C bonds (left side of Figure S1). A transition state (ts C) was found at 6.37 eV, however the products of the unimolecular dissociation process (C) lie higher at 7.35 eV. An IRC calculation was unsuccessful in establishing if the products and reactants were connected. We the try to break down a C-C bond at the time (right side of the figure). A transition state (ts A) at 5.80 eV was found where there is a rearrangement involving the breaking of a C-C bond and the formation of a new one (orange arrow), leading to intermediate A1 in the quadruplet PES with a CH-CH chain. From A1, a C_2H_2 unit can be removed with additional 5.73 eV (ts B). However when the structure A1 is optimised as a doublet, we obtain intermediate A2, a



more stable and flat isomer of corannulene, which is likely the end product of the process.

Figure S1: Schematics of two different routes explored to find a path toward C_2H_2 (instead of CCH_2) loss starting from Corannulene. Energies are in eV and in respect to corannulene cation.

The orange colour highlights the quadruplet PES, while in black we have point on a doublet PES.

Table S1: Cartesian coordinates of the molecular structure of the cationic corannulene ($C_{20}H_{10}^{+}$).

Atom	x	y	z
C	-1.157260000	-0.367194000	0.645107000
C	-0.000071000	-1.196916000	0.626884000
C	1.157212000	-0.367319000	0.645098000
C	0.719919000	0.947711000	0.603141000
C	-0.719815000	0.947792000	0.603143000
C	-2.372326000	-0.754942000	0.113689000
C	-2.436748000	-2.135935000	-0.260019000
C	-1.310478000	-2.940968000	-0.279938000
C	-0.000141000	-2.447814000	0.067481000
C	1.310140000	-2.941107000	-0.279942000
C	2.436505000	-2.136197000	-0.260028000
C	2.372241000	-0.755204000	0.113683000
C	3.267785000	0.331686000	-0.217342000
C	2.847363000	1.637900000	-0.232312000
C	1.478786000	1.988492000	0.082192000
C	0.715160000	3.114571000	-0.283488000
C	-0.714800000	3.114650000	-0.283489000
C	-1.478559000	1.988653000	0.082188000
C	-2.847171000	1.638216000	-0.232323000
C	-3.267742000	0.332047000	-0.217348000
H	-3.365839000	-2.544414000	-0.634164000
H	-1.411400000	-3.950319000	-0.657153000
H	1.410952000	-3.950468000	-0.657161000
H	3.365546000	-2.544781000	-0.634183000
H	4.270383000	0.104690000	-0.553664000
H	3.528090000	2.406340000	-0.571948000
H	1.205721000	3.989091000	-0.692173000
H	-1.205263000	3.989227000	-0.692171000
H	-3.527810000	2.406730000	-0.571970000
H	-4.270364000	0.105166000	-0.553678000

Table S2: Cartesian coordinates of the molecular structure of the cationic sumanene ($C_{21}H_{12}^{+}$).

Atom	x	y	z
C	2.282432000	-2.463010000	0.458117000
C	1.029744000	-3.171888000	0.459770000
C	-0.139795000	-2.614905000	-0.053310000
C	2.375548000	-1.195184000	-0.064334000
C	3.327515000	0.000059000	0.131375000
C	-3.315264000	0.701615000	0.432451000
C	-2.220492000	1.427949000	-0.076975000
C	-1.642192000	2.819734000	0.215663000
C	-3.315238000	-0.701732000	0.432451000
C	-2.220439000	-1.428028000	-0.076975000
C	-1.242441000	-0.690793000	-0.727554000
C	-1.242466000	0.690748000	-0.727554000
C	-0.004072000	1.393902000	-0.690022000
C	-0.139891000	2.614901000	-0.053309000
C	1.029627000	3.171924000	0.459771000
C	2.282342000	2.463090000	0.458117000
C	2.375505000	1.195269000	-0.064333000
C	1.206366000	0.696177000	-0.684363000
C	1.206391000	-0.696136000	-0.684365000
C	-0.004021000	-1.393904000	-0.690025000
C	-1.642089000	-2.819791000	0.215667000
C	-4.120910000	-1.209752000	0.944840000
C	-4.120954000	1.209606000	0.944840000
C	-1.833228000	-3.127053000	1.242873000
C	0.999411000	-4.112817000	0.993975000
C	3.108095000	-2.913150000	0.991589000
C	4.127437000	0.000074000	-0.611186000
C	3.107988000	2.913261000	0.991590000
C	0.999262000	4.112852000	0.993976000
C	-1.833345000	3.126992000	1.242868000
C	3.788524000	0.000067000	1.116353000
C	-2.072284000	-3.584031000	-0.436645000
C	-2.072414000	3.583956000	-0.436652000