Electronic Supplementary Information (ESI) for

The Structure of Coronene Cluster Ions Inferred from H_2 Uptake in the Gas Phase

Marcelo Goulart,[1] Martin Kuhn,[1] Bilal Rasul,[1,2] Johannes Postler,[1] Michael Gatchell,[1,3] Henning Zettergren,[3] Paul Scheier,[1] Olof Echt[1,4]

[1] Institut für Ionenphysik und Angewandte Physik, Universität Innsbruck, Technikerstr. 25, A-6020 Innsbruck, Austria
[2] Department of Physics, University of Sargodha, 40100 Sargodha, Pakistan
[3] Department of Physics, Stockholm University, S-10691 Stockholm, Sweden
[4] Physics Department, University of New Hampshire, Durham NH 03824, USA

* Corresponding authors: Paul Scheier <paul.scheier@uibk.ac.at>, Olof Echt <olof.echt@unh.edu>

The mass resolution of our time-of-flight mass spectrometer is $m/\Delta m$ = 3000 (Δm = full-width-at-half-maximum); this is not sufficient to resolve all ions of interest. Ions of the composition H_xCor^+ (with Cor = coronene = $C_{24}H_{12}$) will, for a given value of x, contribute to several mass peaks because of the ^{13}C isotope (natural abundance 1.07 % of ^{12}C). Relative to isotopically pure coronene ($^{12}C_{24}H_{12}$), 26.1 % will contain one ^{13}C, 3.3 % will contain two ^{13}C, and 0.26 % will contain three ^{13}C (for, say, the coronene trimer ion the corresponding values are 77.9 %, 29.9 %, and 7.5 %). These ions have the same nominal mass as ions that contain isotopically pure coronene but 1, 2, or 3 additional hydrogen atoms. Contributions from deuterium, natural abundance 0.015 %, may be neglected in the present discussion.

The mass difference between ^{13}C and $H^{12}C$ is only 0.0045 u, much less than the peak width Δm = 0.1 u of our instrument at 300 u. Mass peaks due to H_xCor^+ containing one or more ^{13}C essentially coincide with those of isotopically pure ions containing one or more additional hydrogen atoms. Thus, the measured ion yield (e.g., the amplitude of mass peaks) does not directly reflect the abundance of ions with a specific composition.

The problem and possible solutions are illustrated in Fig. S1. Panel a displays a section of a mass spectrum in the vicinity of Cor^+ (note the semilogarithmic y-scale). The prominent mass peak at a (nominal) mass of 300 u is mostly due to isotopically pure coronene because any spill-over of isotopologues from the much weaker mass peaks at and below 299 u will be small. But what fraction of the mass peak at 301 u is due to Cor^+ containing 1 ^{13}C, and what fraction is due to isotopically pure $HCor^+$?

For a spectrum as clean as the one in Fig. S1a, the answer can be obtained by the following, rather pedestrian but instructive approach: 1) Start at the far left of the spectrum, preferably with a weak mass peak, e.g. at 294 u, that is not preceded by an intense peak. Assume that only isotopically pure $H_xC_y^+$ ions contribute to this peak. For the peak at 294 u we assume y = 24 which may be off by a few units, but any error will have negligible impact on the results for peaks at and beyond 300 u (the peaks at 298 and 299 u are certainly due to $H_{10}C_{24}^+$ and $H_{11}C_{24}^+$). 2) Compute the expected abundances of heavier isotopologues of $H_6C_{24}^+$ and subtract them from the measured ion yields at $m \geq 295$ u. The difference obtained for the peak at 295 u equals the abundance of isotopically pure $H_7C_{24}^+$. 3) Repeat the procedure for subsequently higher masses to cover the complete mass range of interest.

The histogram in Fig. S1b shows the result of this analysis. The top section of each bar indicates the abundance of the isotopically pure H_xCor^+ ion at the given mass. The next section of the bar shows the contribution from $H_{x-1}Cor^+$ that contains one ^{13}C, the following section that of $H_{x-2}Cor^+$ containing two ^{13}C, etc.. Overall, each bar exactly matches the corresponding peak height because the number of unknowns (ion abundances) equals the number of knowns (peak heights).

The full dots connected by a line in Fig. S1c represent the abundances of isotopically pure H_xCor^+ (i.e. the top section of each bar in Fig. S1b), now plotted with a linear *y*-scale. The mass spectrum is superimposed. The anomaly identified in the abundance distribution of $(H_2)_nHCor^+$ at $n = 6$ (see Fig. 3 in the main manuscript) corresponds to the anomaly at $x = 13$ in Fig. S1c.

The procedure described above is conceptually simple but mass spectra are rarely as clean as the one in Fig. S1a. Other ions may contribute, often with a small but discernible shift with respect to the ions of interest. Fig. S1d shows a mass spectrum covering the range where the solvation shell of $(H_2)_nHCor^+$ closes. Here one also observes He_n^+, marked by asterisks. Furthermore, barely resolved satellite peaks appear to the left of the H_xCor^+ ion peaks.

We have developed a powerful software package that fits a mass spectrum with user-defined contributions from specific ions (e.g. $OHCor^+$, H_2OCor^+, H_3OCor^+) and cluster ion series (H_x^+, H_xCor^+, $H_2OH_xCor^+$, He_n^+, He_nCor^+) including contributions from their isotopologues. The software corrects for experimental artifacts such as gradually changing background levels, non-Gaussian peak shapes and mass drift over time. A detailed description of the algorithm has been published in ref. 1.

Abundance distributions shown in the main article were deduced using this software. The abundance of H_xCor^+ is displayed in Fig. S1d (solid dots connected by a line; error bars are smaller than the dots). Note that the ion yield of weak peaks (e.g. at $x = 78$) has significant contributions from preceding, strong peaks (at $x = 77$, the "magic" $(H_2)_{38}HCor^+$). In other words, anomalies in abundance distributions are more pronounced than in the ion yield.

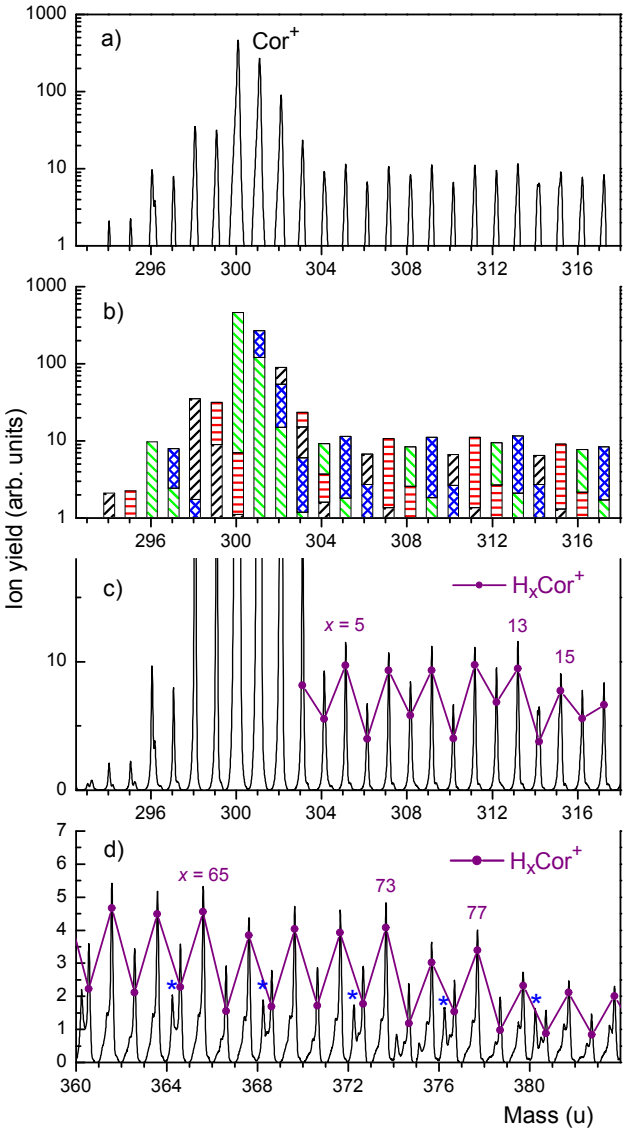

Fig. S1. Mass spectrum of helium droplets doped with coronene and hydrogen (panel a), and the ion abundance of H_xCor^+ ions extracted from the spectrum.

1. S. Ralser, J. Postler, M. Harnisch, A. M. Ellis and P. Scheier, *Int. J. Mass Spectrom.*, 2015, **379**, 194-199.

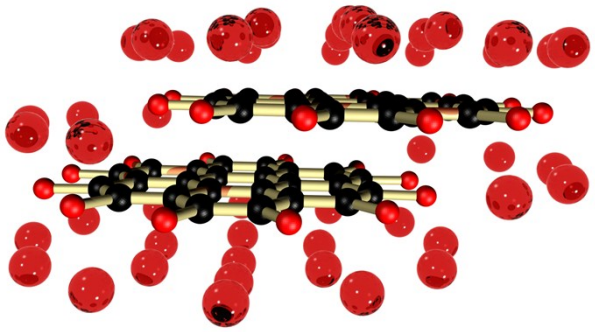

Fig. S2. Artist's view of the parallel-displaced coronene dimer with 19 H_2 molecules (red spheres) adsorbed above the upper coronene, 19 H_2 below the lower coronene, and several additional H_2 on the two terraces.