Supporting Information:

IR Spectroscopic Characterization of $\text{H}_2$

Adsorption on Cationic $\text{Cu}_n^+$ ($n = 4 - 7$) Clusters

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1 Mass spectra

Figure S1: Experimental mass spectrum of the products formed upon reacting Cu\textsuperscript{n+} (n=4-7) with H\textsubscript{2}. The enlargements show the region for Cu\textsubscript{5+} without IR radiation (black) and with IR radiation at 1340 cm\textsuperscript{-1} (red).
2 Energetics of 2H- vs H-loss

We calculate the energy differences for the reactions

\[ [n \text{Cu}, 2\text{H}]^+ \rightarrow [n \text{Cu}]^+ + \text{H}_2 \quad (2\text{H-loss}) \]
\[ [n \text{Cu}, 2\text{H}]^+ \rightarrow [n \text{Cu}, \text{H}]^+ + \text{H} \quad (\text{H-loss}) \]

according to \( \Delta E_{2\text{H-loss}} = E([n \text{Cu}]^+) + E(\text{H}_2) - E([n \text{Cu}, 2\text{H}]^+) \) and \( \Delta E_{\text{H-loss}} = E([n \text{Cu}, \text{H}]^+) + E(\text{H}) - E([n \text{Cu}, 2\text{H}]^+) \), respectively. \( E \) denotes the DFT total energy obtained with the setup described in the computational method section of our manuscript. A positive (negative) sign for \( \Delta E \) characterizes an endothermic (exothermic) reaction. Since the ionization potential of a hydrogen atom is much larger than that of the neutral \([n \text{Cu}, \text{H}]\) cluster, \( \text{H}^+\)-loss is always significantly less energetically favorable compared to H-loss and is not further discussed here.

Tables S1 and S2 compile the results for all structures of \([4\text{Cu}, 2\text{H}]^+\) and \([5\text{Cu}, 2\text{H}]^+\), respectively, that are discussed in this work. These tables illustrate in detail that, without any exception, H-loss is much more endothermic than 2H-loss. More precisely, for all \([4\text{Cu}, 2\text{H}]^+\) (\([5\text{Cu}, 2\text{H}]^+\)) structures, the differences \( \Delta E_{\text{H-loss}} - \Delta E_{2\text{H-loss}} \) amounts to about 1.6 eV (2.1 eV).

We have calculated \( \Delta E_{\text{H-loss}} \) separately for both H-atoms individually in order to account for potentially different bonding as listed in the third column of Tables S1 and S2. This changes \( \Delta E_{\text{H-loss}} \) at most by 92 meV for structures 4D and 4J (341 meV for structure 5F) and thus does not change the energetic favorability of 2H-loss over H-loss in any single case – completely in line with the experimental observations. Substituting hydrogen by deuterium yields identical results.
Table S1: Total energy differences corresponding to the 2H-loss and H-loss reactions for all \([4\text{Cu}, 2\text{H}/2\text{D}]^+\) structures. For all structures, \(\Delta E_{\text{H-loss}}\) has been calculated for both H-atoms separately. If different results are obtained, both are given in descending order (of endothermicity). Otherwise, the results are identical (within 1 meV) for both H atoms.

| Structure | \(\Delta E_{2\text{H-loss}}\) (eV) | \(\Delta E_{\text{H-loss}}\) (eV) |
|-----------|-------------------------------|-------------------------------|
| 4A        | 0.871                         | 2.485                         |
| 4B        | 0.844                         | 2.458                         |
| 4C        | 0.649                         | 2.263                         |
| 4D        | 0.589                         | 2.203, 2.111                  |
| 4E        | 0.482                         | 2.096                         |
| 4F        | 0.456                         | 2.070, 2.000                  |
| 4G        | 0.440                         | 2.054                         |
| 4H        | 0.366                         | 1.888                         |
| 4I        | 0.215                         | 1.737                         |
| 4J        | 0.114                         | 1.728, 1.636                  |

Table S2: Same as Table S1 but for \([5\text{Cu}, 2\text{H}/2\text{D}]^+\).

| Structure | \(\Delta E_{2\text{H-loss}}\) (eV) | \(\Delta E_{\text{H-loss}}\) (eV) |
|-----------|-------------------------------|-------------------------------|
| 5A        | 1.219                         | 3.324                         |
| 5B        | 1.160                         | 3.163                         |
| 5C        | 1.066                         | 3.272, 3.068                  |
| 5D        | 0.973                         | 2.996                         |
| 5E        | 0.973                         | 3.078, 2.978                  |
| 5F        | 0.950                         | 3.296, 2.955                  |
| 5G        | 0.897                         | 2.920, 2.902                  |
| 5J        | 0.826                         | 2.828                         |
| 5I        | 0.784                         | 3.080, 2.806                  |
| 5H        | 0.783                         | 3.080, 2.805                  |
| 5K        | 0.746                         | 3.041, 2.768                  |
| 5L        | 0.703                         | 2.808, 2.726                  |
| 5M        | 0.672                         | 2.694                         |
3 IR spectra for $[5\text{Cu, 2H/2D}]^+$: $^{63}\text{Cu}$ vs $^{65}\text{Cu}$

Figure S2: Comparison of the calculated IR spectra for the global minimum structure of $[5\text{Cu, 2H}]^+$ (top) and $[5\text{Cu, 2D}]^+$ (bottom) using the copper isotopes $^{63}\text{Cu}$ (red) and $^{65}\text{Cu}$ (blue).
4 IR spectra for [4Cu, 2H]⁺ and [4Cu, 2D]⁺

Figure S3: Experimental and calculated IR spectra for [4Cu, 2H]⁺ (left column) and [4Cu, 2D]⁺ (right column). Theoretical spectra are calculated employing the PBE functional.
5 IR spectra for $[5\text{Cu, }2\text{H}]^+$ and $[5\text{Cu, }2\text{D}]^+$

Figure S4: Experimental and calculated IR spectra for $[5\text{Cu, }2\text{H}]^+$ employing the PBE (left column) and PBE0 (right column) functionals.
Figure S5: Experimental and calculated IR spectra for $[5\text{Cu,2D}]^+$ employing the PBE (left column) and PBE0 (right column) functionals.
6 IR spectra for $[\text{6Cu, 2H}]^+$ and $[\text{6Cu, 2D}]^+$

Figure S6: Same as Fig. 4, but for $[\text{6Cu, 2H}]^+$ and $[\text{6Cu, 2D}]^+$, respectively.
7 IR spectra for [\textit{7}Cu, 2H\textsuperscript{+}] and [\textit{7}Cu, 2D\textsuperscript{+}]

Figure S7: Same as Fig. 4 but for [\textit{7}Cu, 2H\textsuperscript{+}] and [\textit{7}Cu, 2D\textsuperscript{+}], respectively.
8 H- and Cu-projected IR spectra

Figure S8: Same as Fig. 3(a) in the article, but for all [4Cu, 2H]+ structures from Fig. S3.
Figure S9: Same as Fig. 3(a) in the article, but for all [5Cu, 2H]^+ structures from Fig. S4.
Figure S10: Same as Fig. 3(a) in the article, but for all [6Cu, 2H]^+ structures from Fig. S6.
Figure S11: Same as Fig. 3(a) in the article, but for all [7Cu,2H]^+ structures from Fig. S7.
9 Similarity of vibrational modes

Figure S12: Same as Fig. 3(b) in the article, but for all [4Cu, 2H/2D]+ structures in Fig. S3
Figure S13: Same as Fig. 3(b) in the article, but for all [5Cu,2H/2D]^+ structures shown in Figs. S4 and S5.
Figure S14: Same as Fig. 3(b) in the article, but for all [6Cu, 2H/2D]⁺ structures in Fig. S6.
Figure S15: Same as Fig. 3b) in the article, but for all \([\text{Cu}_2\text{H}_2]^+\) structures in Fig. S19.
10 Nudged-elastic band calculations

Figure S16: The reaction paths for H$_2$ dissociation over Cu$_4^+$. The reactant, the product and the transition state structures together with their binding energy values without (with) ZPE correction are shown in each panel.
Figure S17: Same as Fig. S16 but the reaction paths for $\text{H}_2$ dissociation over $\text{Cu}_5^+$. 

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11 Adsorption of multiple H$_2$

In the current experiments, reaction products with more than one adsorbed H$_2$ are also formed. Figure S18 shows the IRMPD spectra of [nCu, 4H]$^+$ and [nCu, 4D]$^+$ for $n = 4 - 7$ in direct comparison to their counterparts for [nCu, 2H]$^+$ and [nCu, 2D]$^+$, respectively. The spectra for the clusters with two H$_2$ adsorbed are in general similar in signal-to-noise ratio. On the one hand, one would expect a degradation for the large species, due to their lower numbers present in the cluster distribution. On the other, one can expect that the binding energy of the second hydrogen is reduced, as was also seen for Ar atoms binding to Cu$_n^+$ clusters. Furthermore, it is interesting to note that the spectra for two H$_2$ are on the whole quite similar to those of single adsorbed H$_2$. With our assignment of the spectra of one H$_2$ to a combination of different isomers this is probably not unexpected; the second hydrogen will likely adsorb on an unoccupied, but energetically favorable site. Most likely, a different isomer assigned to the experimental [4Cu, 2H]$^+$ spectrum already has this site occupied, resulting in limited changes to the spectrum observed for [4Cu, 4H]$^+$.

The exception to this is given by Cu$_5^+$: here, one readily recognized the bands also visible for the single adsorbed hydrogen, but pronounced, intense bands have appeared predominantly at lower frequencies. On closer inspection, it appears that the 'new' bands coincide with relative weak bands already in the spectrum of the first hydrogen, and on the whole, all bands also appear broader. This observation, mirrored in the spectra for D$_2$, leads us to speculate that the second hydrogen is bound significantly more weakly, thus more acting as a spectator. Bands directly attributable for the second hydrogen are not easily recognized in the broad absorption bands observed.
Figure S18: Experimental IRMPD spectra for \([n\text{Cu}, 2\text{H}]^+\) and \([n\text{Cu}, 4\text{H}]^+\) (left column) and for \([n\text{Cu}, 2\text{D}]^+\) and \([n\text{Cu}, 4\text{D}]^+\) (right column) with \(n=4-7\).
References

(S1) Jamshidi, Z.; Lushchikova, O. V.; Bakker, J. M.; Visscher, L. Not Completely Innocent: How Argon Binding Perturbs Cationic Copper Clusters. *J. Phys. Chem. A* **2020**, *124*, 9004–9010, DOI: 10.1021/acs.jpca.0c07771.