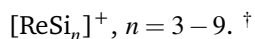


Supporting Information

Pathways of Cluster Growth: Infra-Red Multi-Photon Dissociation Spectroscopy of a Series of Rhenium-Silicon Clusters,



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1 IR-MPD Spectroscopy of $[\text{ReSi}_4]^+$

The IR-MPD spectra for $[\text{ReSi}_3]^+$ and $[\text{ReSi}_4]^+$ are shown in Figure S1, where the peaks for both $[\text{ReSi}_n]^+ \cdot \text{Xe}$ and $[\text{ReSi}_n]^+ \cdot \text{Xe}_2$ are shown in blue and red, respectively. The $[\text{ReSi}_3]^+$ spectrum shows a depletion at $\sim 380 \text{ cm}^{-1}$ for both adducts but $[\text{ReSi}_4]^+$ shows an amplification (negative values) when the $[\text{ReSi}_4]^+ \cdot \text{Xe}$ peak is used. This is attributed to the decomposition of $[\text{ReSi}_4]^+ \cdot \text{Xe}_2$ at the same frequencies, which serves to increase the intensity of $[\text{ReSi}_4]^+ \cdot \text{Xe}$. The $[\text{ReSi}_4]^+ \cdot \text{Xe}_2$ peak shows the normal depletion, and it is this spectrum that is reported in the main text.

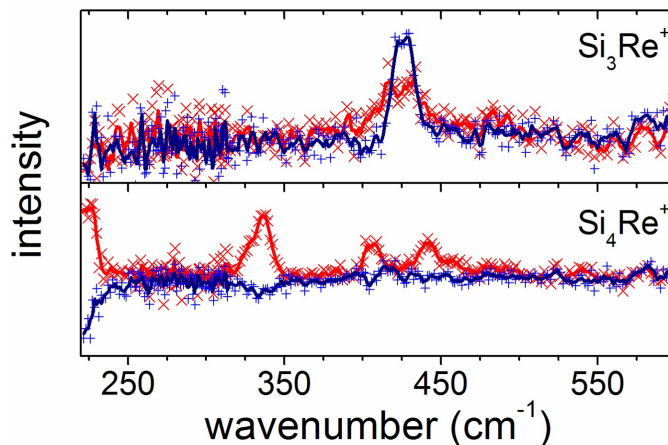


Figure S1 Comparison between the IR spectra for $[\text{ReSi}_3]^+$ and $[\text{ReSi}_4]^+$ with one (blue) and two (red) xenon atoms attached.

2 Cosine similarity values

The cosine similarity value is a way of making a quantitative comparison between computed and experimental spectra. The computed values for low-lying isomers reported in the text is shown in Table S1. The cosine similarity is of most value when the spectrum is complex, with multiple peaks to fit. The very similar values for isomers a and b for $[\text{ReSi}_6]^+$ and for isomers b and c for $[\text{ReSi}_9]^+$, for example, reflects the challenges in distinguishing isomers based on their vibrational spectra when the structures are qualitatively similar.

Table S1 The cosine similarity values for all the isomers. For ReSi_6^+ only the $300\text{-}600 \text{ cm}^{-1}$ region of the spectrum is used to avoid artifacts from fitting to noisy low-frequency region.

Cluster	isomer a	isomer b	isomer c
ReSi_3^+	0.77	-	-
ReSi_4^+	0.69	-	-
ReSi_5^+	0.60	0.49	-
ReSi_6^+	0.70	0.67	0.17
ReSi_7^+	0.55	0.41	0.40
ReSi_8^+	0.71	0.55	0.62
ReSi_9^+	0.54	0.89	0.78

3 Influence of the Xe tag on the computed spectra

In the spectra reported in the manuscript, we have not included the Xe tag in the computational model: the justification for this is that the noble gas element is typically bound weakly via Van der Waals' forces, and so is typically a weak perturbation to the structure and therefore to the vibrational manifold. However, the presence of low-frequency peaks in the computed spectra that appear to have no counterpart in the experiment has encouraged us to explore the impact on including a single Xe atom in the model. Geometries are optimised as described in the computational section. Computed spectra with and without a bound Xe atom are compared in Figure S2.

The reduction in computed intensity for the lowest frequency peak in $[\text{ReSi}_5]^+$ is striking: this mode corresponds to the Re–Si₅ stretching mode. Similar features emerge in the spectra of $[\text{ReSi}_6]^+$ and $[\text{ReSi}_7]^+$, where low-frequency modes lose intensity when the Xe tag is included in the model.

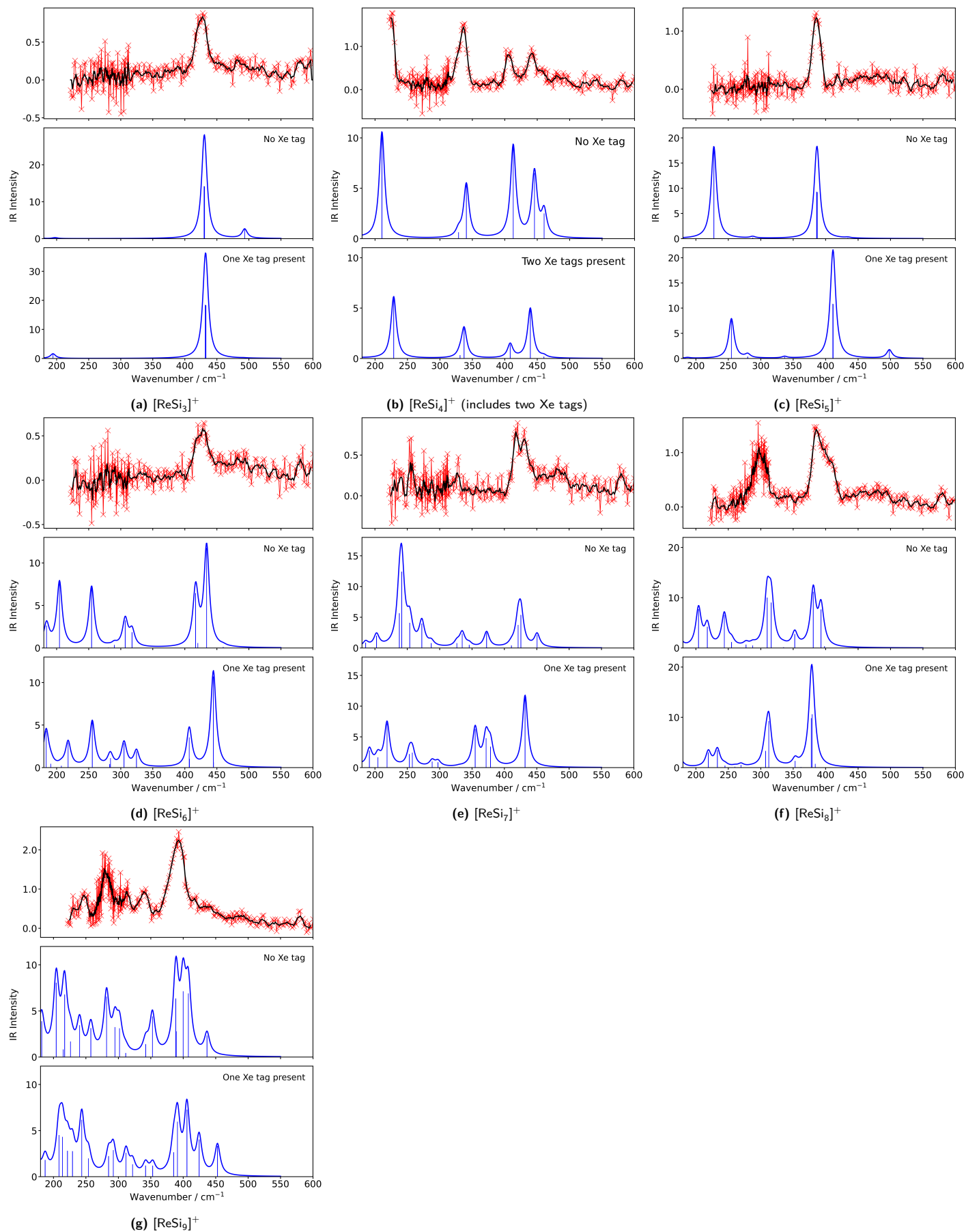


Figure S2 Comparison of spectra of $[\text{ReSi}_x]^+$ with and without explicit inclusion of Xe tags in the computational model

4 Final metal encapsulated structures

In Figure 6 of the main text we have proposed that the growth pattern of the $[\text{ReSi}_n]^+$ clusters can be viewed as steps towards a limiting Frank-Kasper-type ReSi_{16} architecture. It is equally possible, however, to view the growth pattern in terms of other approximately spherical limits, such as the icosahedron shown in Figure S3. The point that we wish to emphasise is that the Si_n network is growing around the central Re ion, as opposed to alongside it, as we see in the early stages of growth of the $[\text{MnSi}_n]^+$ family.

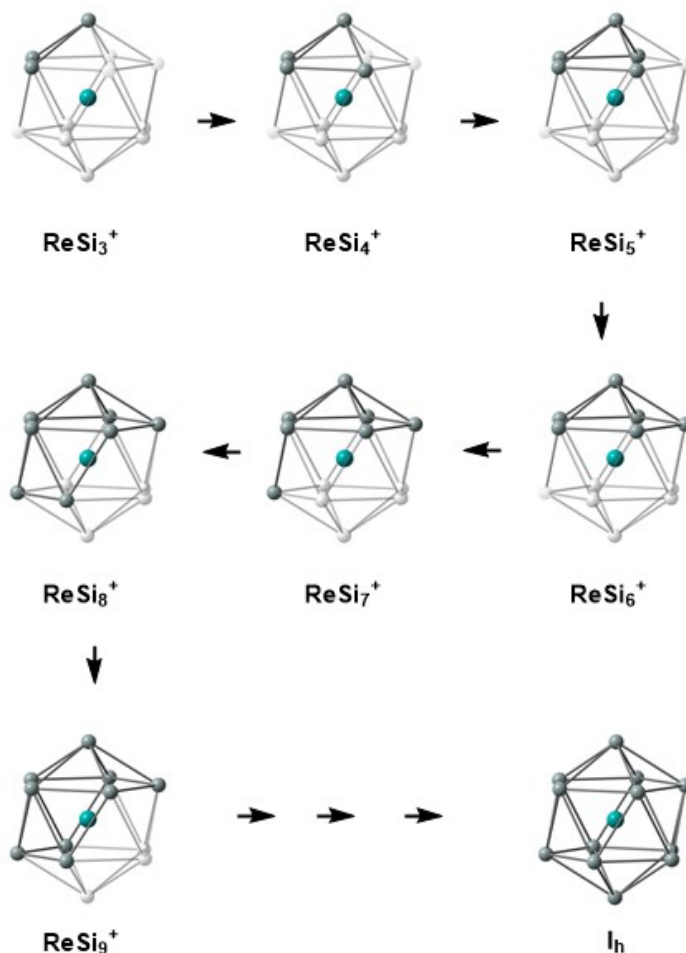


Figure S3 Growth pattern based on an icosahedral limit.

5 Cartesian coordinates of optimised geometries

All cartesian coordinates can be found in .xyz format in the .zip file Optimized_Coordinates.zip included in the supporting information. Files are arranged in subfolders identified as ReSi_n^+ .

6 Vibrational modes

Animated gifs for all vibrational modes discussed in this paper are collected in the .zip file gifs.zip. Files are arranged in subfolders identified as ReSi_n^+ , and within each folder, animated gifs are identified by the frequency shown in the relevant spectrum.

7 Sample ADF input file

A sample ADF input file (for $[\text{ReSi}_3]^+$) is shown below.

```
System
ATOMS
  Re  0.0  0.0      0.0
  Si  0.0 -0.52468604 1.94084777
  Si  0.0 -1.62872474 0.00000000
  Si  0.0 -0.52468604 -1.94084777
END
charge      1
symmetrize  True
end
symmetry
  symmetrizetolerance  0.001
end
Task      GeometryOptimization
Properties
  NormalModes      True
End
NormalModes
  Hessian      Analytical
end

Engine      ADF
  Unrestricted      False
  XC
    GGA      PBE
  end
  basis
    type      TZ2P
    core      small
    createoutput  no
  end
  analyticalfreq
    max_cpks_iterations  100
  end
  relativity
  level      scalar
  formalism  zora
  end
endengine
```