Supplementary Information

Vibrational Solvatochromism and Electrochromism of Cyanide, Thiocyanate, and Azide Anions in Water†

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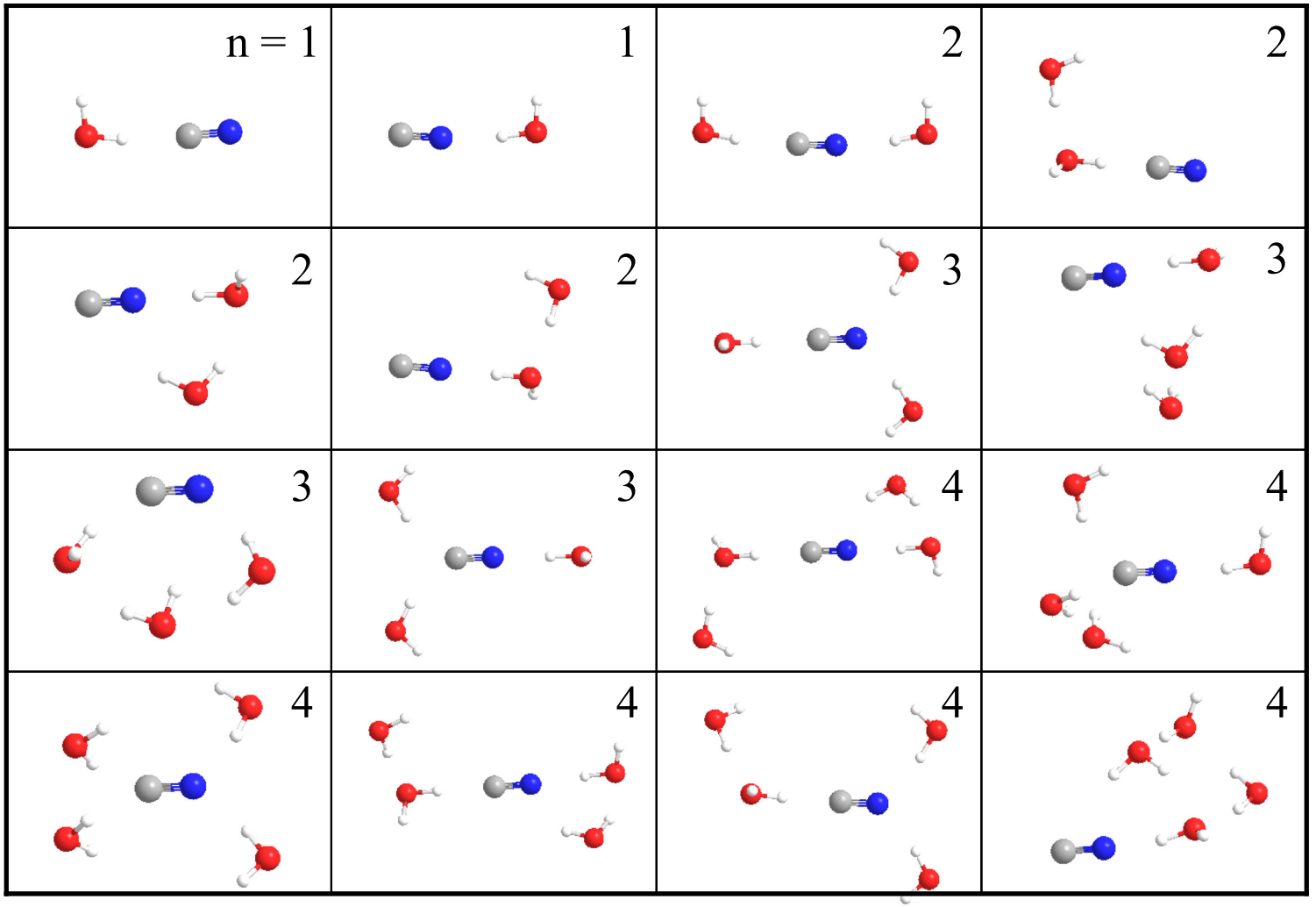
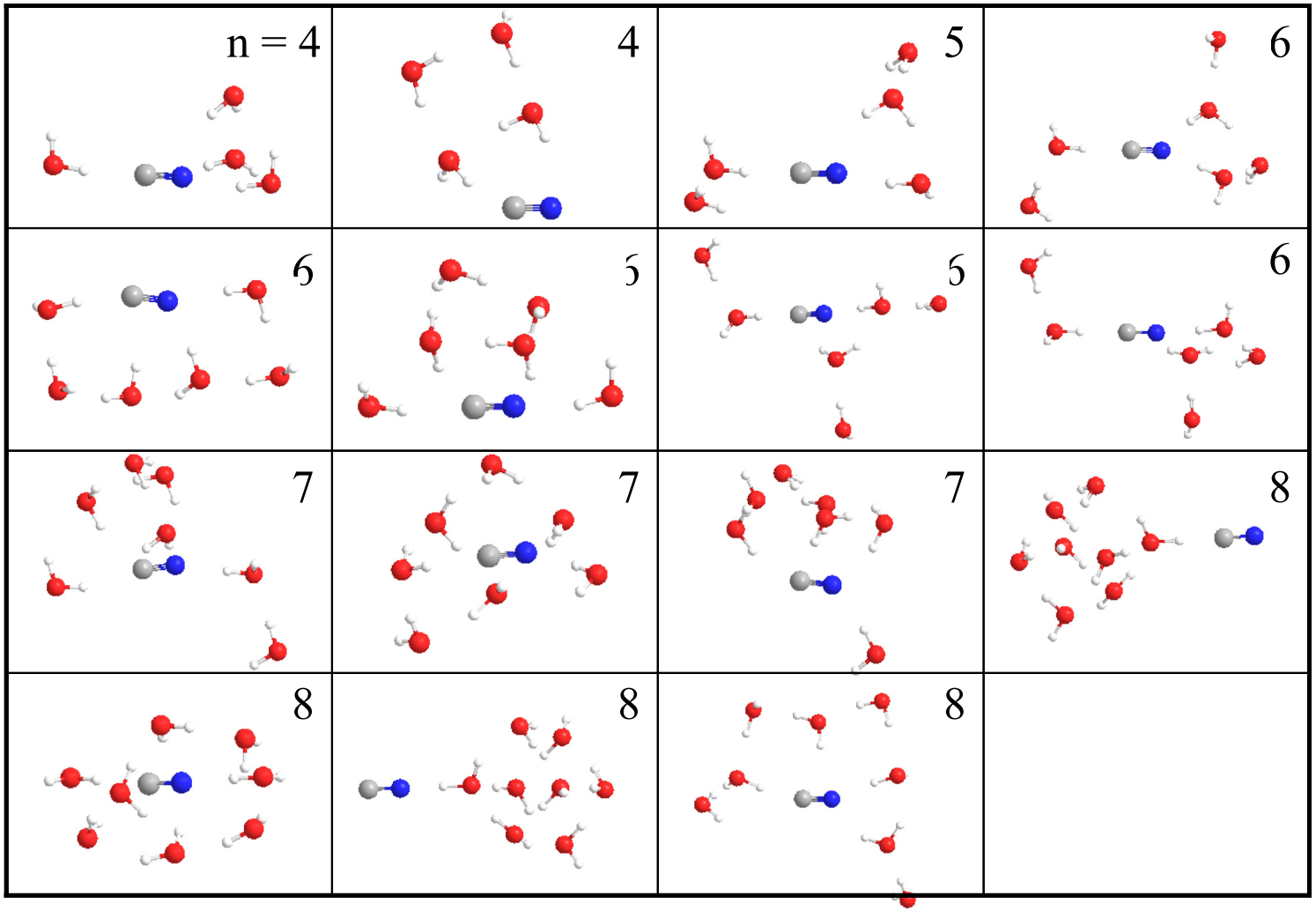
In this supplementary information, the density functional theory (DFT) geometry-optimized structures of 49 cyanide-water clusters, 29 thiocyanate-water clusters, and 39 azide-water clusters are shown. In addition, the correlations between the electric field vector component projected onto the chemical bond and the DFT calculated frequency shift are examined by choosing different locations to calculate the electric field due to local environment.

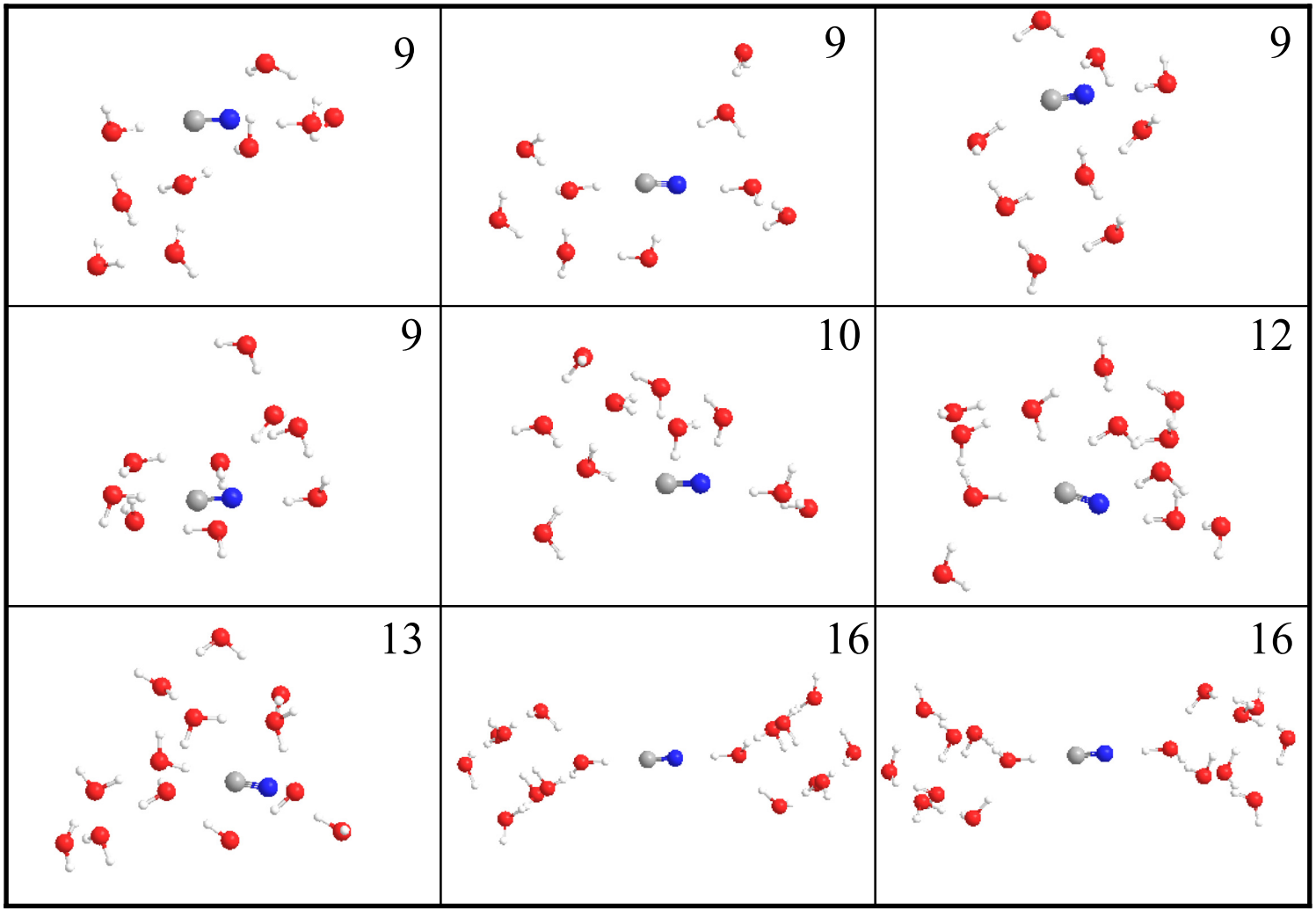
Cyanide-$(H_2O)_n$ clusters



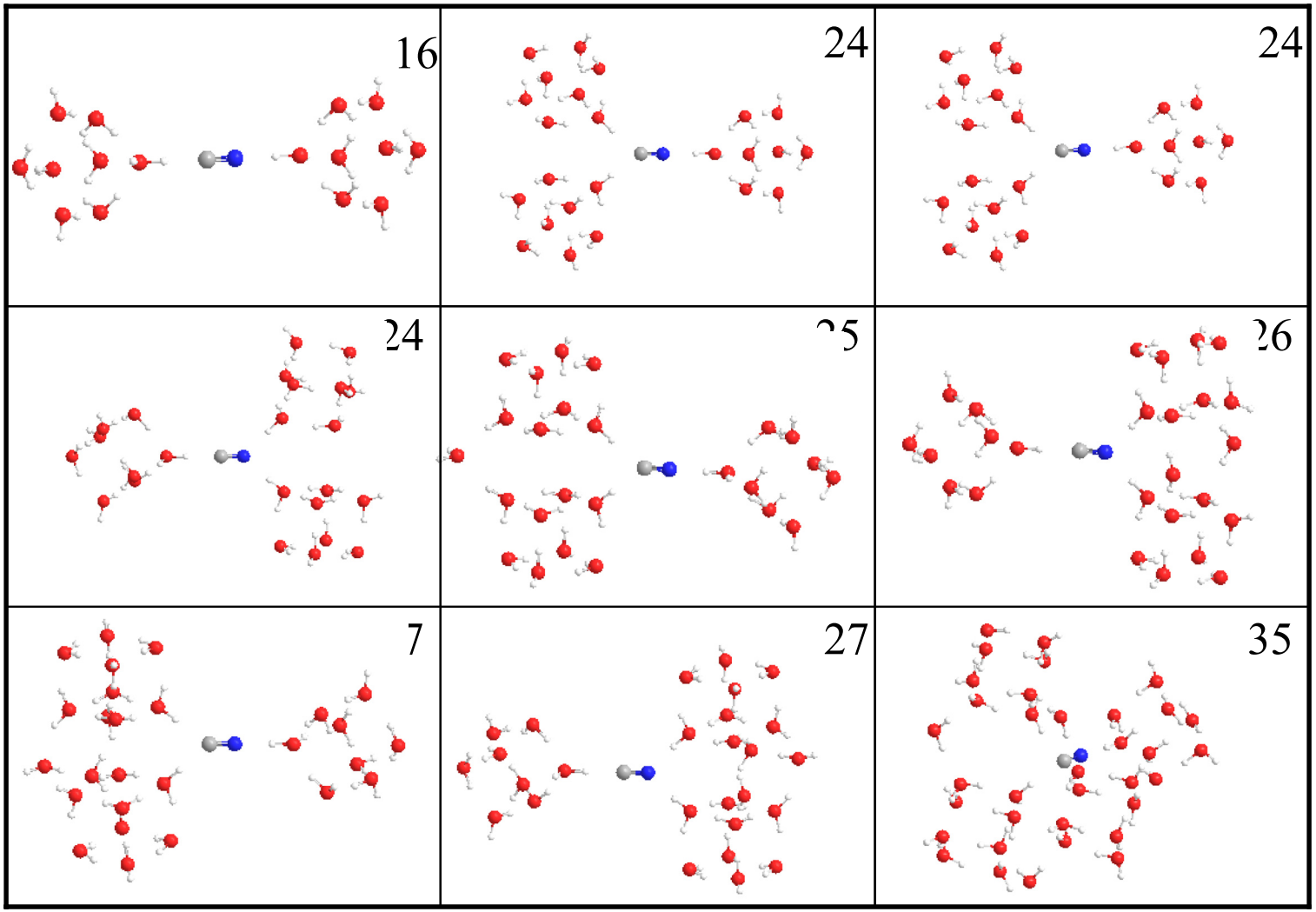
Cyanide-$(H_2O)_n$ clusters



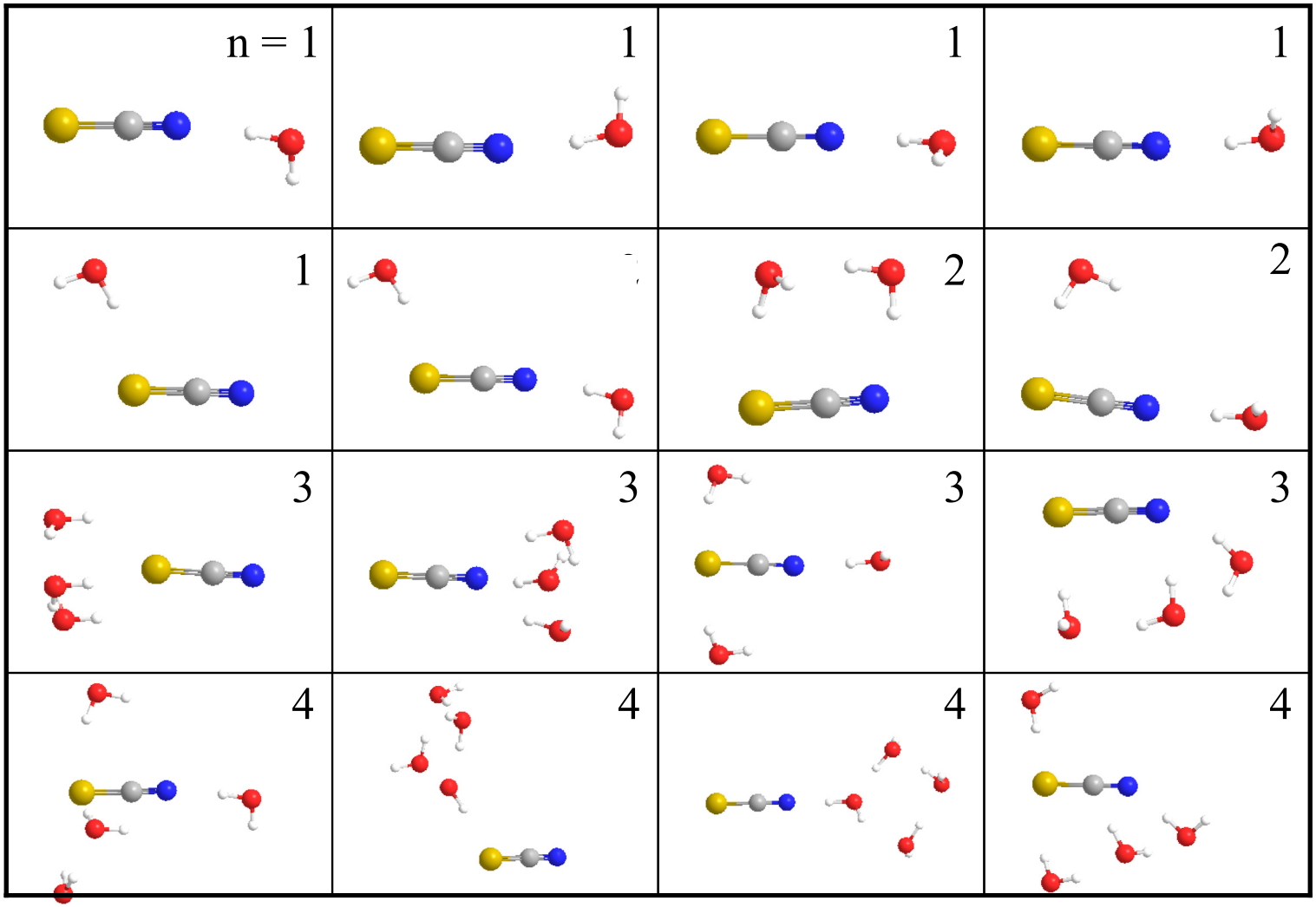
Cyanide-$(H_2O)_n$ clusters



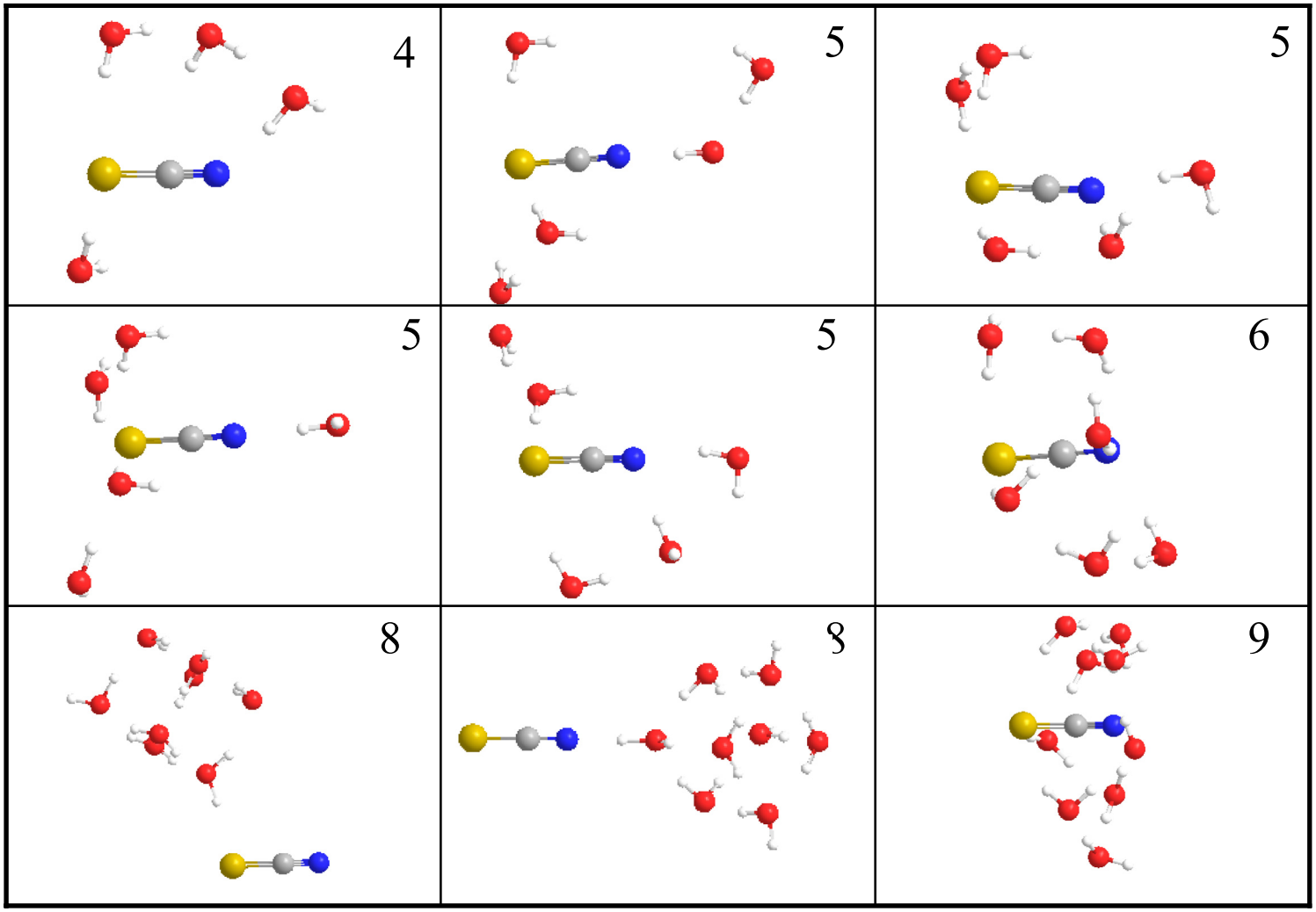
Cyanide-$(H_2O)_n$ clusters



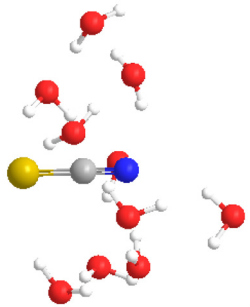
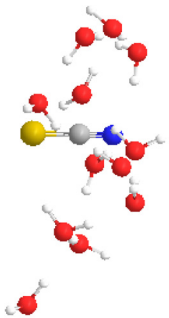
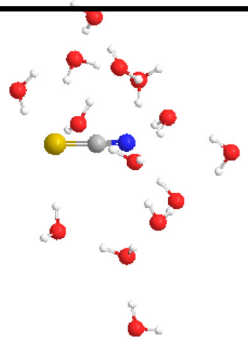
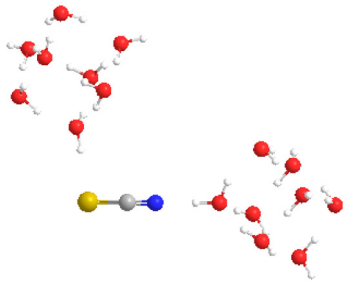
Thiocyanate-$(H_2O)_n$ clusters



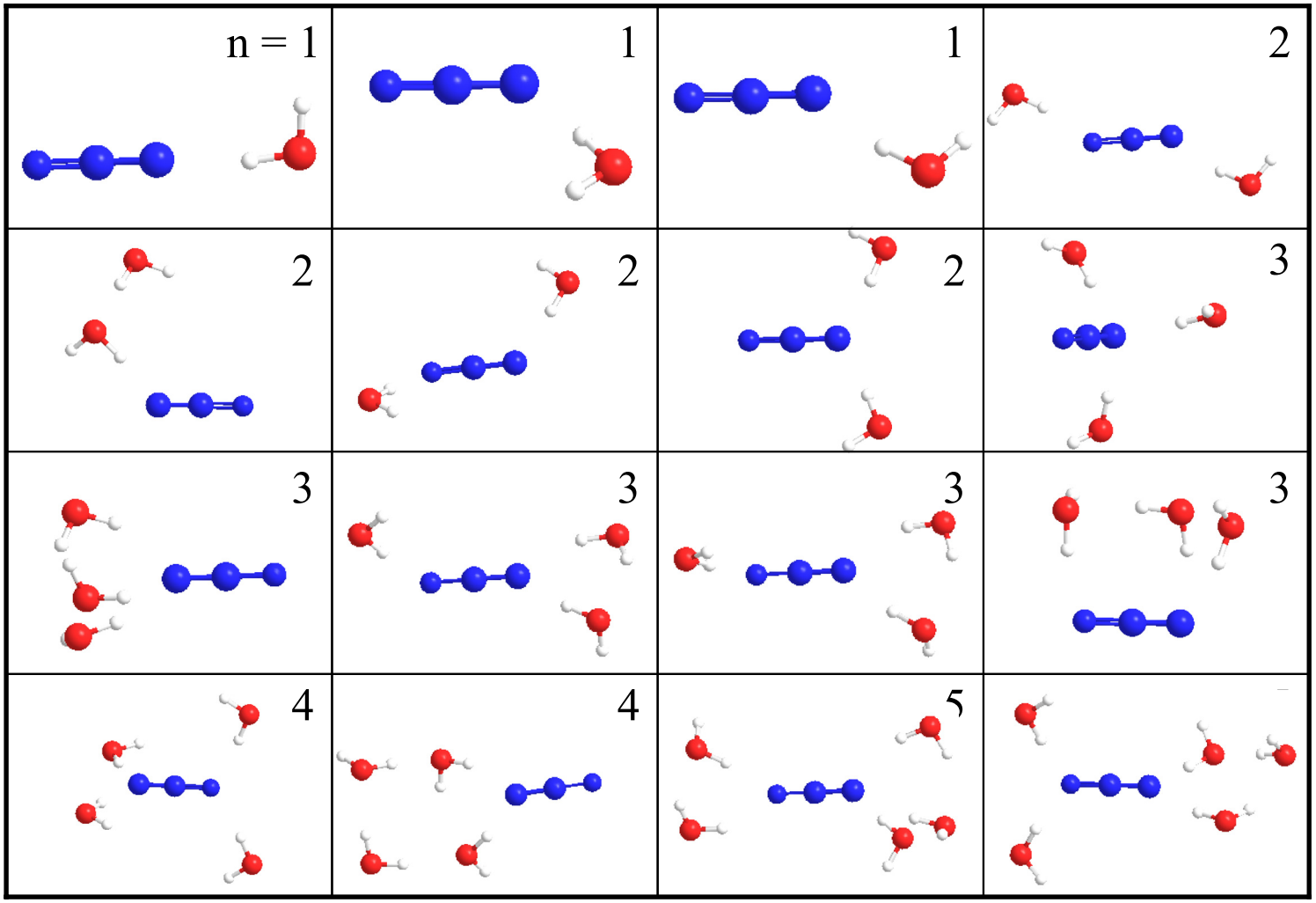
Thiocyanate-$(H_2O)_n$ clusters



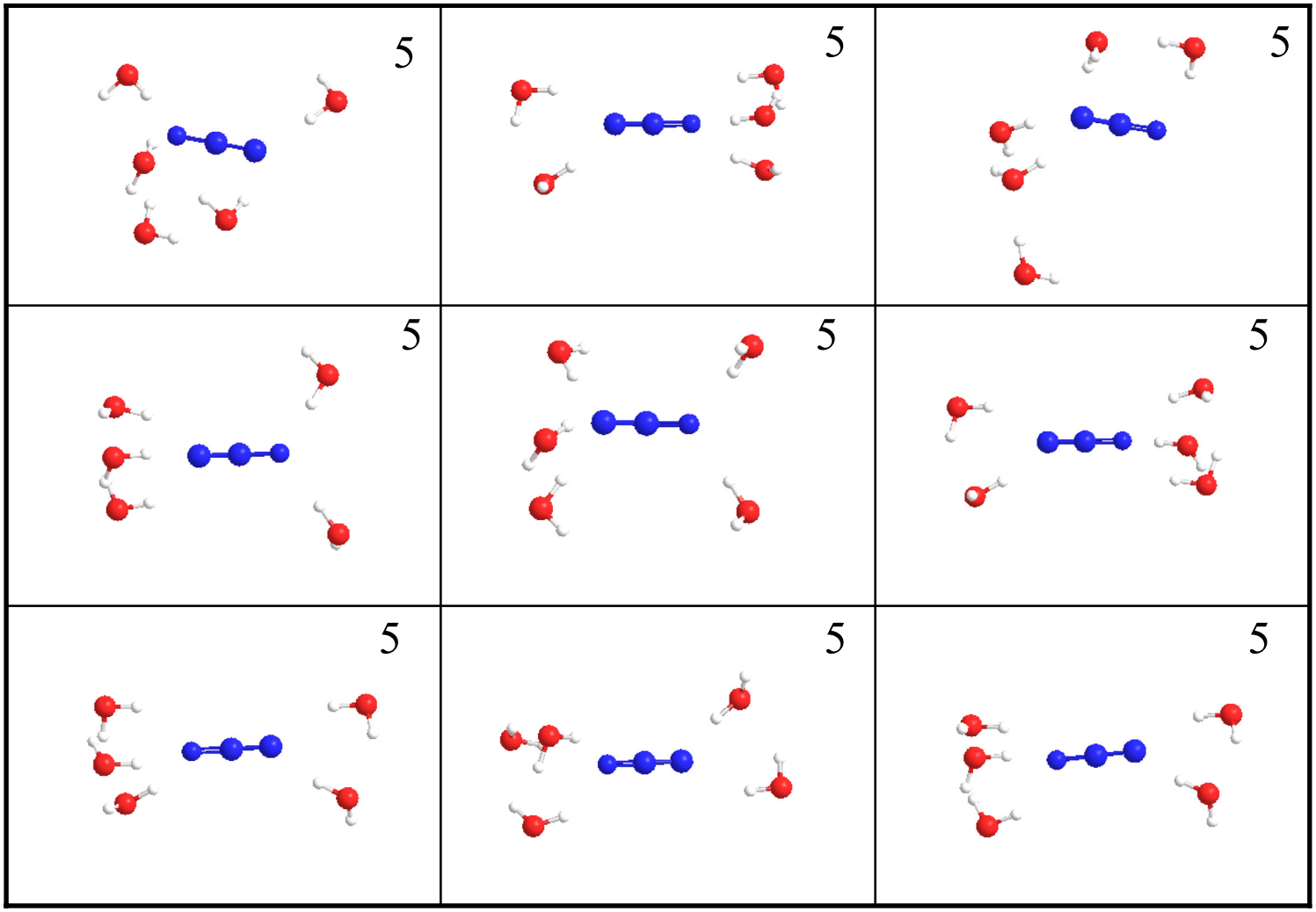
Thiocyanate-$(H_2O)_n$ clusters

10 	12 	14 
16 		

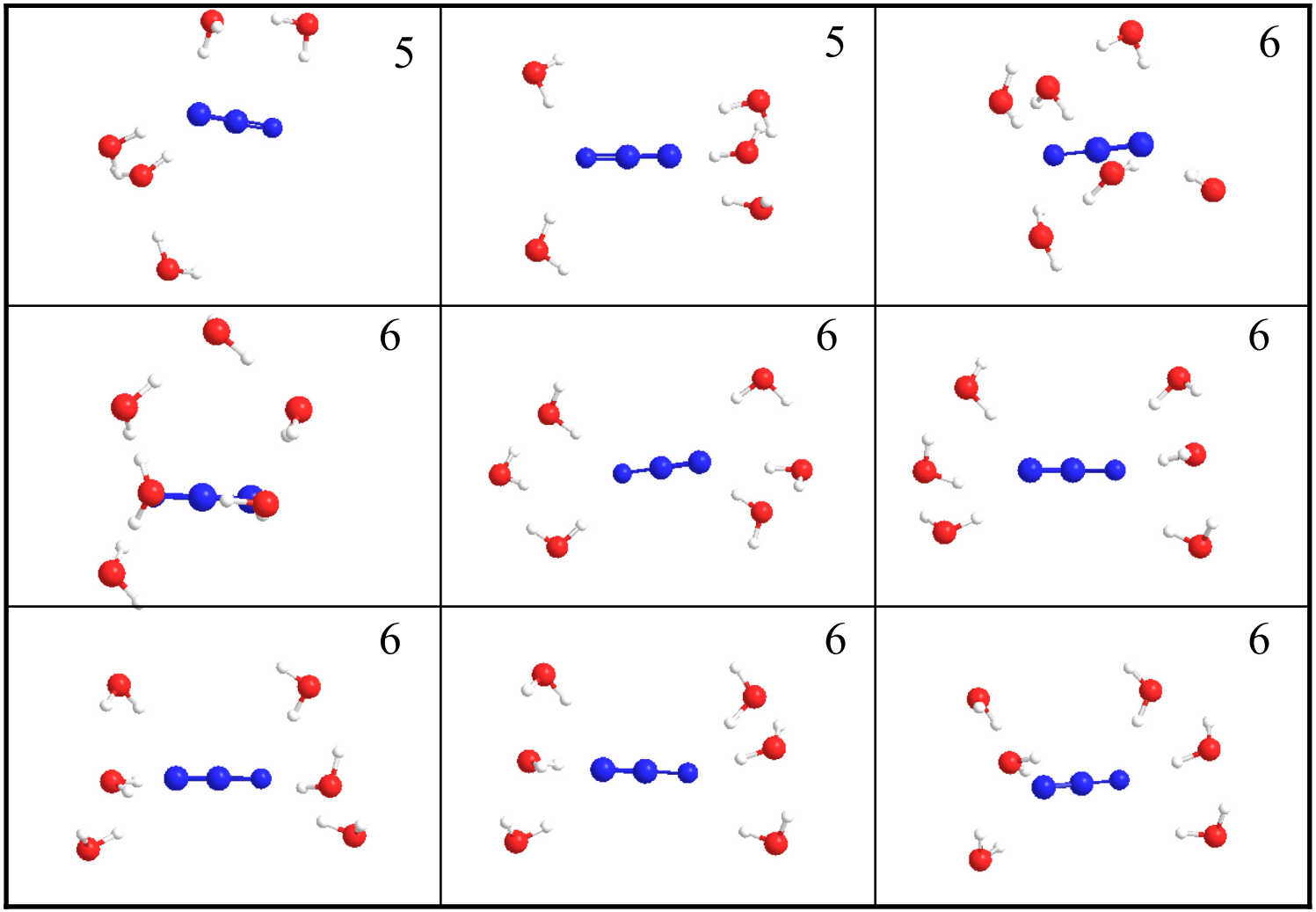
Azide-$(H_2O)_n$ clusters



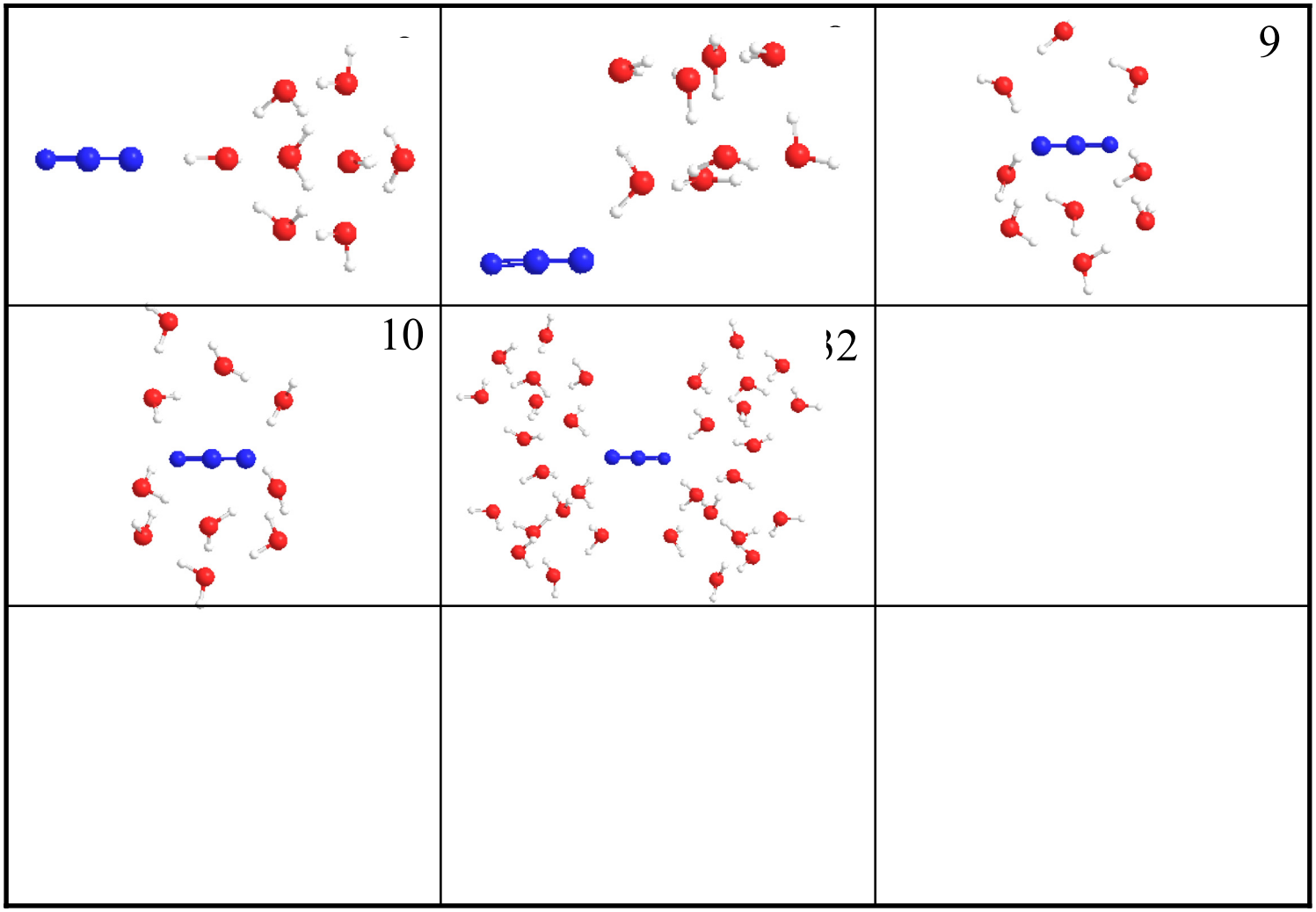
Azide-$(H_2O)_n$ clusters



Azide-$(H_2O)_n$ clusters



Azide-$(H_2O)_n$ clusters



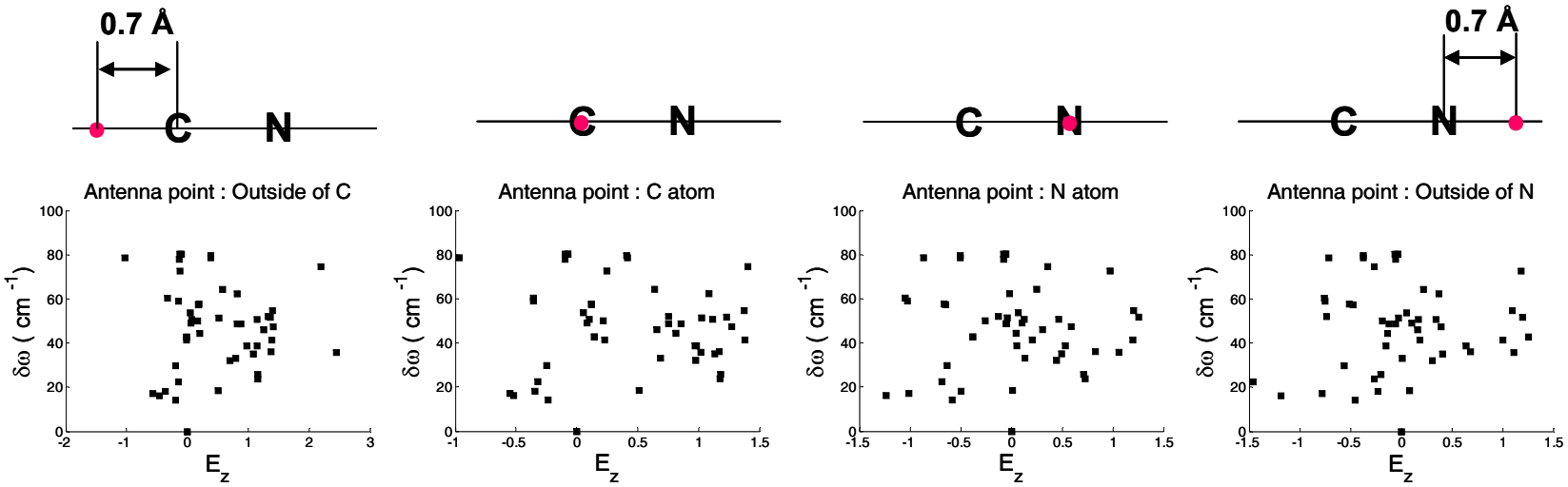


Figure S1. Plots of vibrational frequency shift δω versus E_z (in atomic unit) for cyanide, where the location to calculate electric field varies. Here, E_z is the projection of the electric field vector, produced by the distributed charges of surrounding water molecules. From left to right, the location is at (i) 0.7 Å away from the C-atom, (ii) C-atom, (iii) N-atom, and (iv) 0.7 Å away from the N-atom.

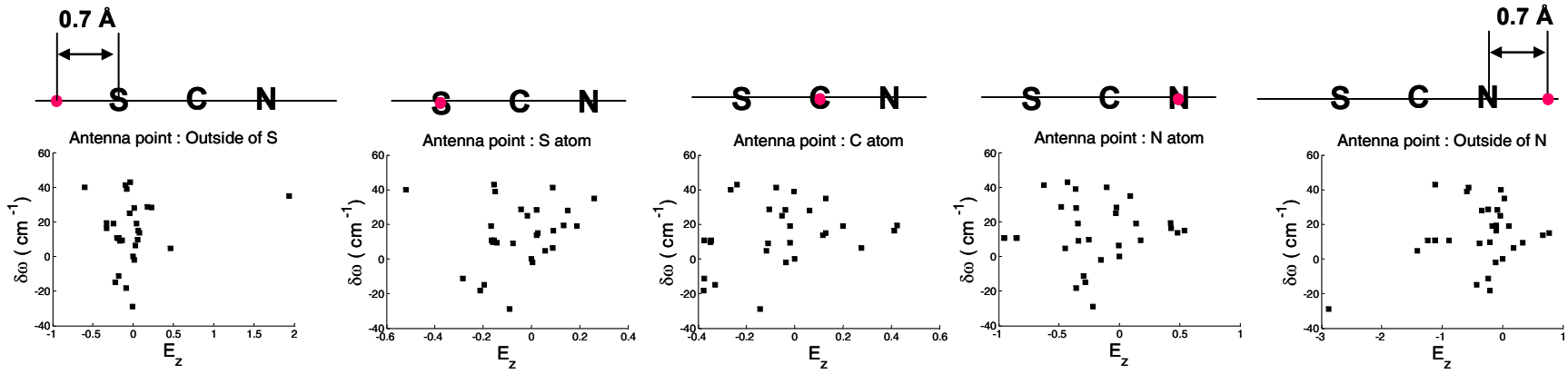


Figure S2. Plots of vibrational frequency shift δω versus E_z (in atomic unit) for thiocyanate, where the location to calculate electric field varies. From left to right, the location is at (i) 0.7 Å away from the S-atom, (ii) S-atom, (iii) C-atom, (iii) N-atom, and (iv) 0.7 Å away from the N-atom.

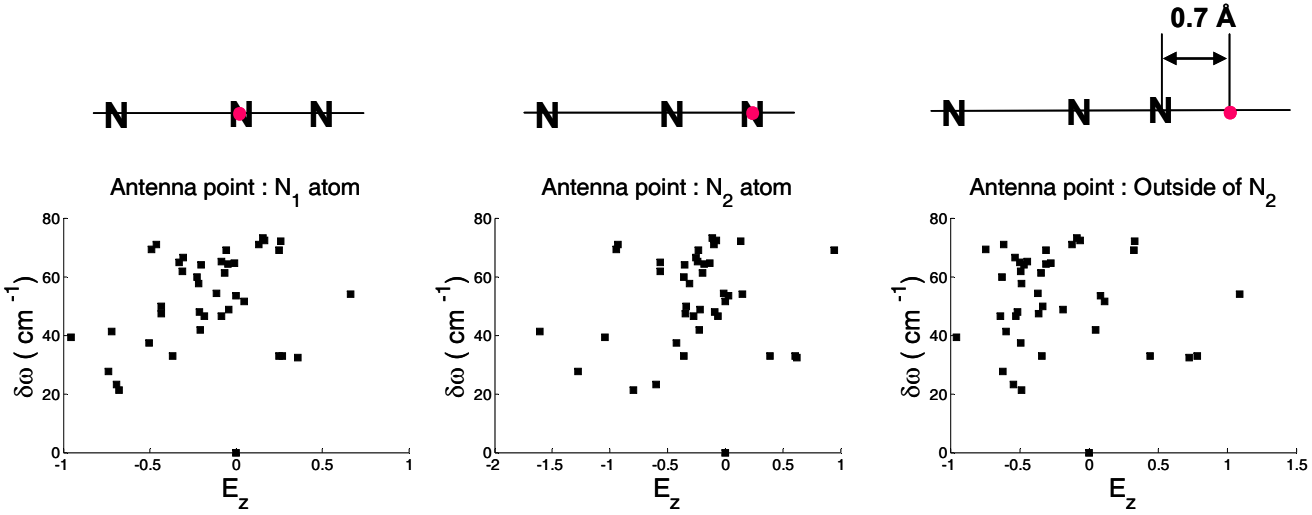


Figure S3. Plots of vibrational frequency shift δω versus E_z (in atomic unit) for azide, where the location to calculate electric field varies. From left to right, the location is at (i) the middle N-atom, (ii) terminal N-atom, and (iii) 0.7 Å away from the terminal N-atom.