Supporting information

Spectroscopic evidence of a Xe-Xe bond in the linear Xe$_2$Au$^+$Xe ion

Piero Ferrari[1,2,*], Joost M. Bakker[2] and Ewald Janssens[1]

[1]Quantum Solid-State Physics, Department of Physics and Astronomy, KU Leuven, Celestijnenlaan 200d, 3001 Leuven, Belgium
[2]Institute for Molecules and Materials, FELIX Laboratory, Radboud University, 6525 ED Nijmegen, Netherlands

Content

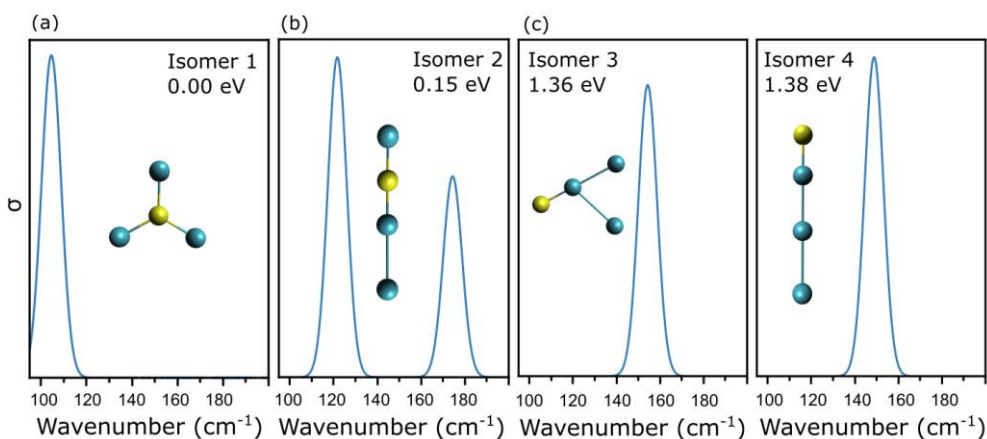## i)   Infrared spectra of additional isomers

Figure S1. Vibrational spectra of four isomers of AuXe$_3^+$. Isomers 1 and 2 are discussed in the main article. The relative energy, with respect to isomer 1, is calculated with DFT using the PBE functional and the Def2-TZVPP basis set plus the D3 dispersion correction.

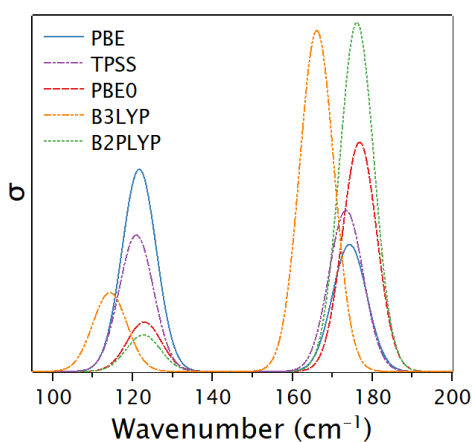## ii)   Comparison of the infrared spectra calculated with different functionals

Figure S2. Comparison of the infrared spectrum of isomer 2 calculated using different exchange-correlation functionals. The plots are constructed by Gaussian functions centred around each vibrational mode, with an artificial width of 10 cm^{-1}.

iii) Extracting Xe binding energy from temperature-dependent mass spectra

In this procedure, it is assumed that the intensities in mass spectra recorded at a certain temperature T reflect the relative amount of each complex in equilibrium conditions. Under this assumption, the equilibrium constant K^0 at a standard pressure p^0 is given by Eq. (S1) [1].

$$K^0 = \frac{I\left(AuXe_3{}^+, T\right)}{I\left(AuXe_2{}^+, T\right) \cdot p(Xe)/p^0} \tag{S1}$$

Here, $I(X, T)$ is the intensity of the complex X in a mass spectrum recorded at temperature T, and $p(Xe)$ the partial pressure of Xe in the formation chamber of the source. The ratio $p(Xe)/p^0$ cannot be measured and its precise value is therefore unknown. The equilibrium constant K^0 can be related to the standard enthalpy change ΔH^0 and the standard entropy change ΔS^0, via Eq. (S2):

$$\ln(K^0) = \frac{-\Delta H^0}{R}\frac{1}{T} + \frac{\Delta S^0}{R} \tag{S2}$$

Given the uncertainty in $p(Xe)/p^0$, determination of ΔS^0 is not possible. However, from the slope of a plot of $\ln(K^0)$ versus $1/T$ (Figure 2a in main article), ΔH^0 can be determined. This quantity equals the Xe binding energy in $AuXe_2{}^+$-Xe.

[1]   E. Janssens, P. Gruene, G. Meijer, L. Wöste, P. Lievens, and A. Fielicke, Phys. Rev. Lett. 99, 063401, 2007.

iv)   Energy decomposition analysis

Table S1. Absolute values of the different components of the binding energy (in eV) of $AuXe_2{}^+$-Xe and Xe-Xe, obtained via the energy decomposition analysis (EDA).

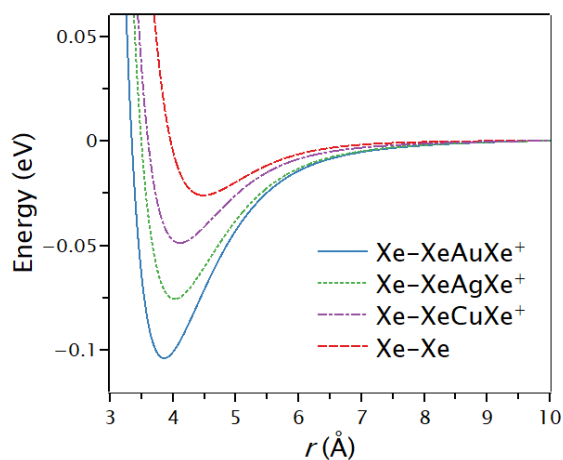| Energy component	Au$^+$Xe$_2$-Xe	Xe-Xe
E_{orb}	0.060	0.003
E_{pauli}	-0.041	-0.005
E_{elec}	0.017	0.004
E_{dis}	0.014	0.008

v)   Potential energy surfaces

Figure S3. DFT calculated (PBE/Def2-TZVPP+D3) potential energy surface of Xe-XeAuXe$^+$ (blue), Xe-XeAgXe$^+$ (green), Xe-XeCuXe$^+$ (purple) and Xe-Xe (red), with r the Xe-Xe distance.

3

vi) **Comparison of properties of Xe$_2^+$, Xe$_2$Au$^+$Xe, FXe$_2$H and Xe$_2$**

Table S2. Values of Xe-Xe bond lengths, Xe-Xe binding energies, Xe-Xe Wiberg bond indexes, partial charge on the Xe atom pair and ELF values at the critical points for Xe$_2^+$, Xe$_2$Au$^+$Xe, FXe$_2$H and Xe$_2$. Calculations performed at the CCSD(T)/Def2-TZVPP level.

	Xe-Xe bond length	E_b	Wiberg bond index	Partial charge Xe pair	ELF
Xe$_2^+$	3.114 Å	1.136 eV	0.5	+0.500/0.500 e	0.20
Xe$_2$Au$^+$Xe	4.097 Å	0.057 eV	0.1	+0.339/0.036 e	0.04
FXe$_2$H	3.224 Å	1.232 eV	0.6	+0.312/0.381e	0.32
Xe$_2$	4.742 Å	0.009 eV	0.0	0.000/0.000 e	0.01

vii) **XYZ coordinates**

Isomer 1
Au   -2.1583604602   0.4065837772   -0.0000097685
Xe   -2.1555404196   3.1845736111   -0.0000885175
Xe   0.3473386036   -0.7885678529   -0.0004539190
Xe   -4.4832877238   -1.0667255355   0.0005522050

Isomer 2
Au   -4.2509785212   0.8675128972   -0.0000006156
Xe   -6.8719901753   0.8785433548   0.0000012350
Xe   -1.6366395371   0.8539510521   -0.0000024675
Xe   2.3084781748   0.7857875519   0.0000018480

Isomer 3
Au   -2.3165677407   0.1817121162   -0.0002431799
Xe   -0.4636253345   2.0196335251   0.0003000728
Xe   3.3048157629   0.1567951660   -0.0008318439
Xe   2.0910060446   4.5611039544   0.0007749509

Isomer 4
Au   -1.9028113062   0.0000000265   -0.0000000082
Xe   0.7063703226   -0.0000000207   0.0000000141
Xe   4.4371049033   -0.0000000491   -0.0000000145
Xe   8.7593360804   0.0000000432   0.0000000086