Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Various Bond Interactions between NO and Anionic Gold Clusters: A Theoretical Calculation

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Fig. S1 The reported structures of Au_n^- (*n* = 2-20), which were further optimized at the B3LYP level with the basis set of def2-SVP for Au. For their names, the *n* and *n'* stand for the lowest-lying structure and another major isomer of each Au_n^-, respectively. If a structure is not the lowest-lying one, there is a bracketed number showing its relative energy in eV.

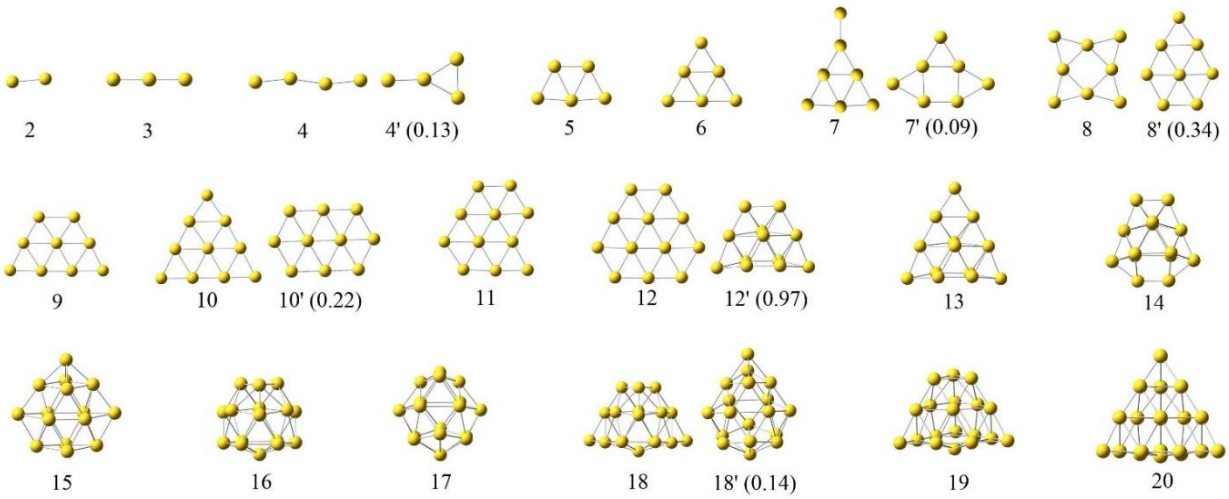

Fig. S2 The low-lying structures of Au_nNO^- (n = 1-10) calculated at the B3LYP level with the basis sets of lanl2dz for Au and 6-31G(d) for N and O. The numeral "n" in the structure name denotes the number of the gold atoms; the apostrophe (if there is) means that the metal geometry in this Au_nNO^- corresponds to a major isomer rather than the lowest-lying structure of Au_n^-; the capital letters "S/D/T/Q" denote various electronic states of singlet/doublet/triplet/quartet; the lower-case letters "a/b/c…" distinguish different structures of Au_nNO^- containing the same gold geometry and on the same electronic state, while with NO on various adsorption sites. If a structure is not the lowest-lying one, there is a bracketed number showing its relative energy in eV.

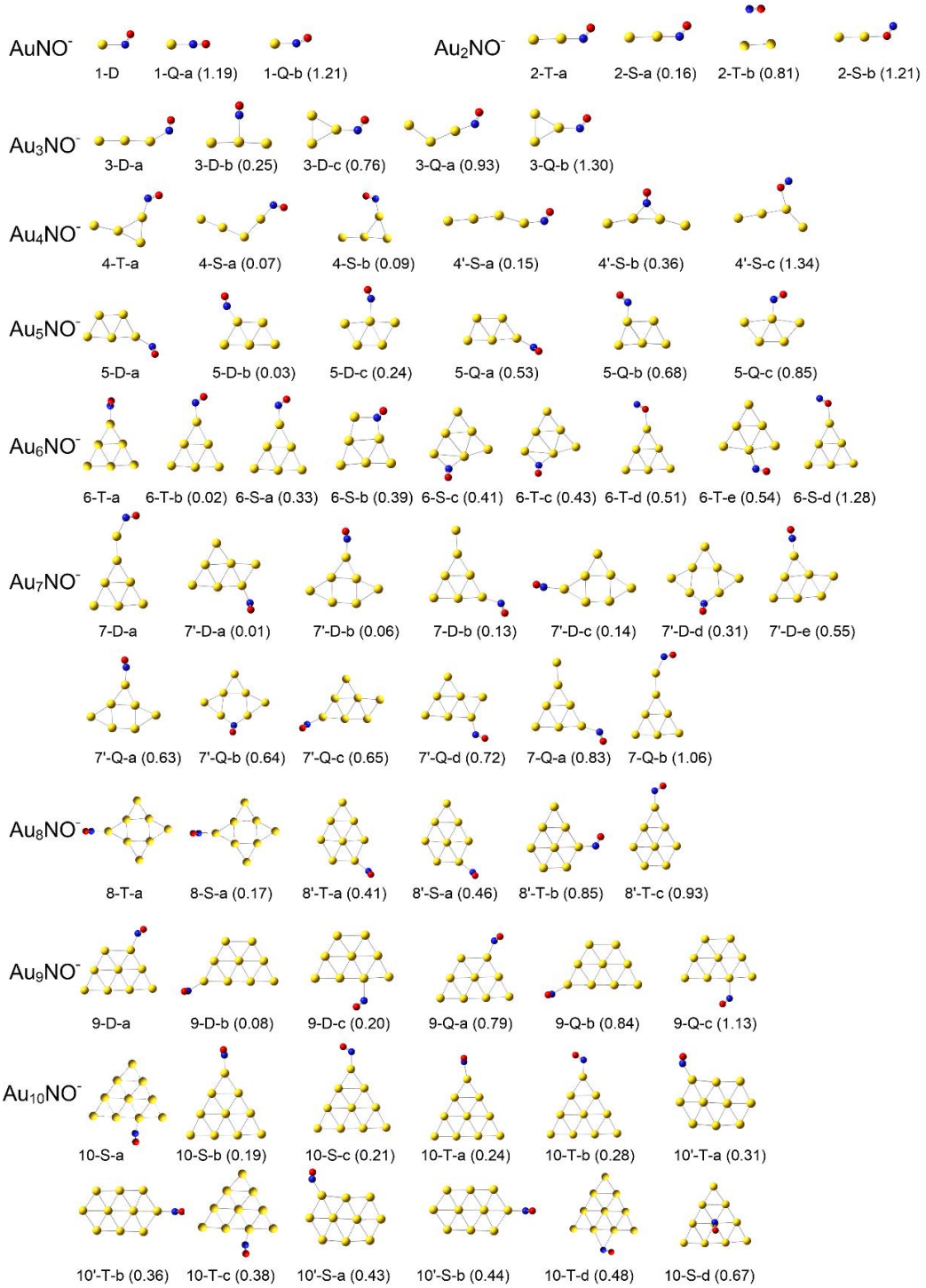

Fig. S3 Same as Fig. S2, but for Au_nNO^- (n = 11-20).

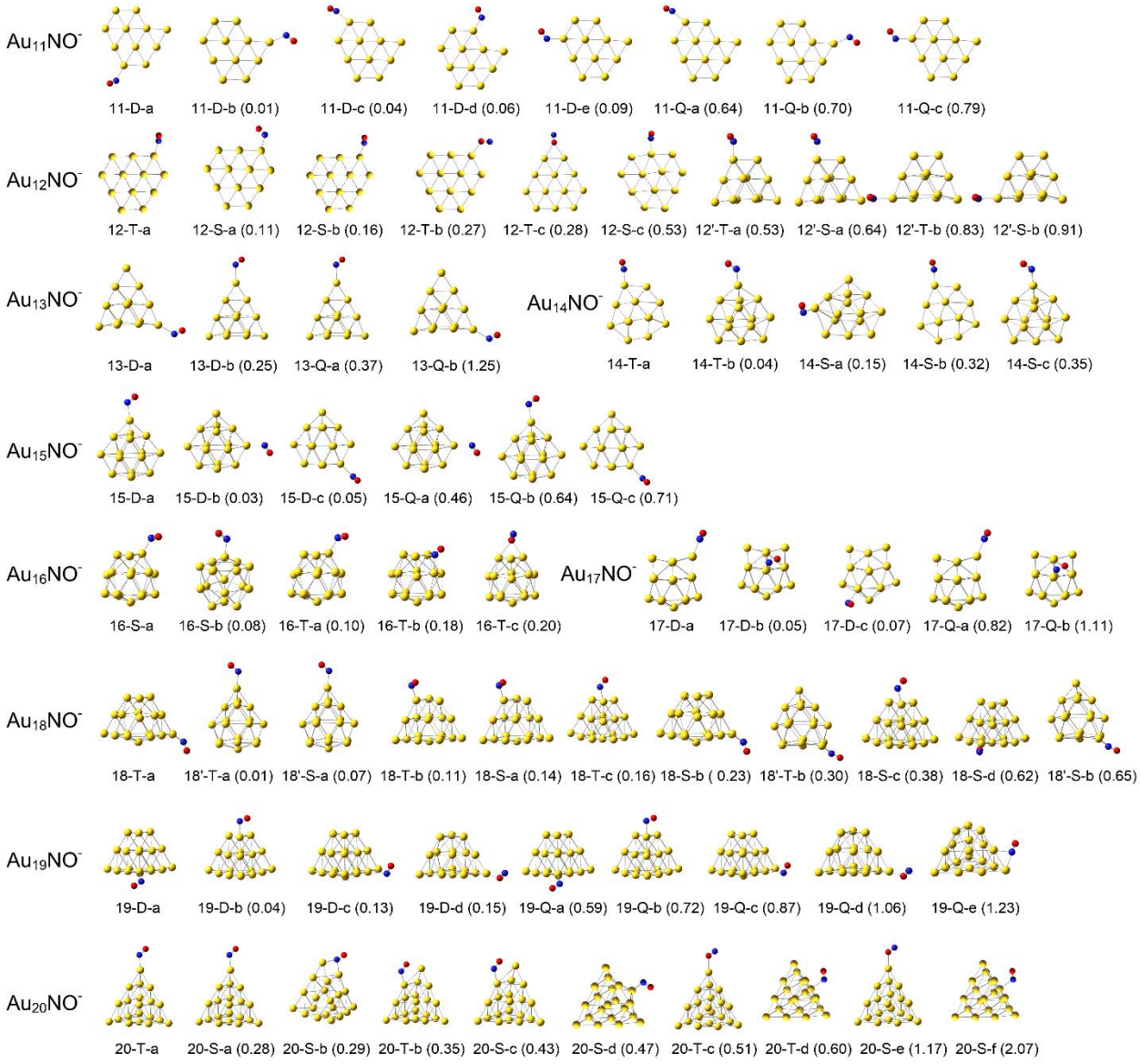

Fig. S4 The DOS and PDOS (NO) figures of (a) Au_5^-, (b) Au_5NO^- (5-D), (c) Au_6^-, (d) Au_6NO^- (6-T), (e) Au_{19}^-, (f) $Au_{19}NO^-$ (19-D), (g) Au_{20}^-, and (h) $Au_{20}NO^-$ (20-T). In each panel, the DOS and PDOS (NO) figures are plotted in black and in red, respectively; the HOMO position is indicated by a dotted line. The figures of some crucial orbitals (the 5σ and 1π orbitals of NO and the crucial ones around the HOMO position) are shown to illustrate the bond interaction between Au_n^- and NO. The orbital components of gold are named after the electron shells, $1S^21P^42S^21D^4$… and $1S^21P^62S^21D^{10}1F^{14}$…, which form in the flat triangle and the tetrahedron structures, respectively. The results were obtained according to the calculations at the B3LYP level with the basis sets of def2-SVP for Au, and def2-TZVP for N and O.

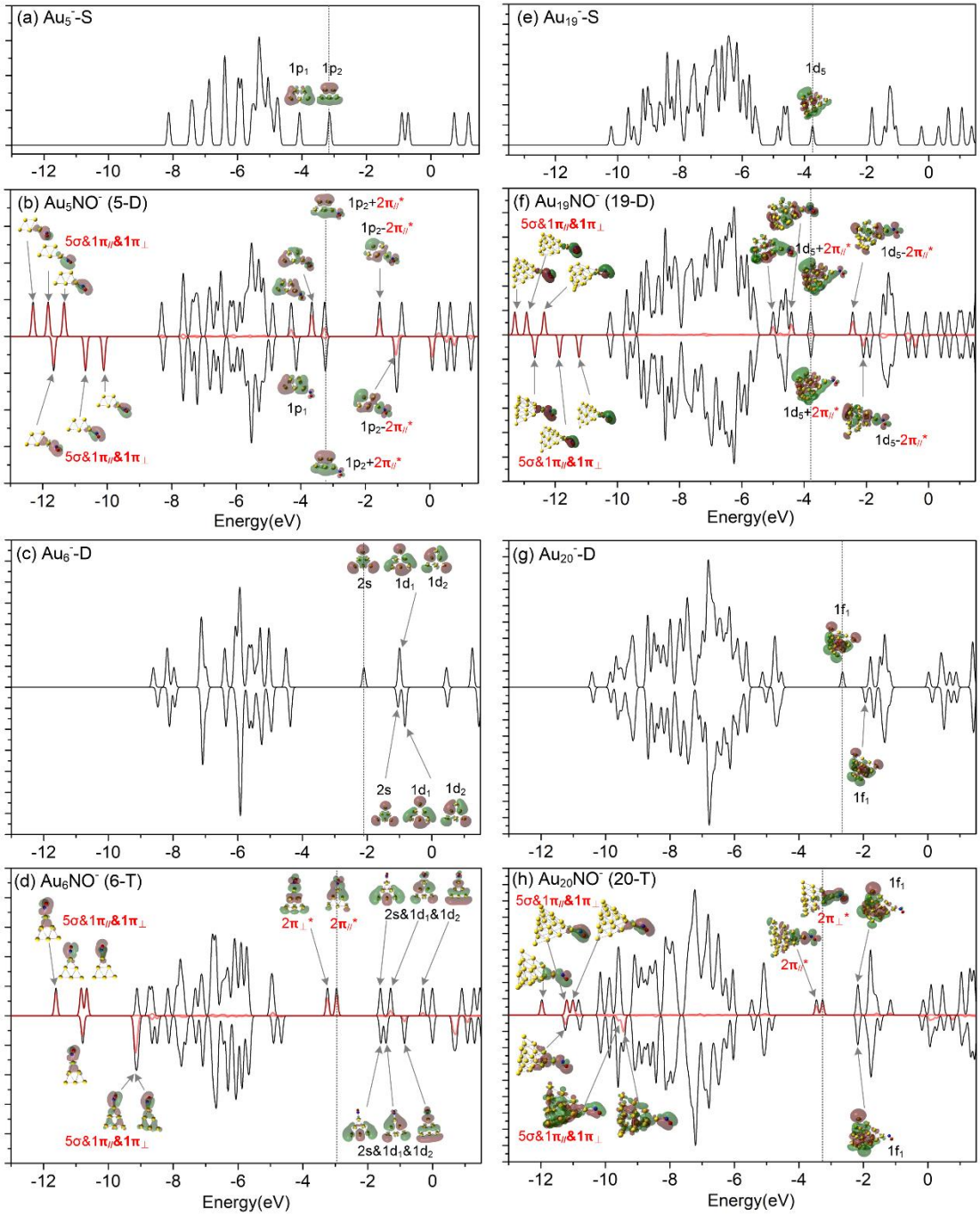

Fig. S5 The DOS and PDOS (O_2) figures of (a) $Au_{10}O_2^-$ (Doublet) and (b) $Au_{16}O_2^-$ (Doublet). The details are the same as those in Fig. S4, except that the shown orbitals in these clusters are named after the electron shells, $1S^21P^42S^21D^4$… and $1S^21P^61D^{10}$…, which form in the flat triangle and the cage structures, respectively.