Supplementary Information for:
A flat-lying dimer as a key intermediate in NO reduction on Cu(100)

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I. SUPPLEMENTARY TEXT

A. Decomposition of adsorption energy

The adsorption energy of the $(\mathrm{NO})_2$ per NO molecule is defined by

$$E_{\mathrm{ads}} = \frac{1}{2}\left(E_{\mathrm{tot}}^{(\mathrm{NO})_2/\mathrm{Cu}(100)} - E_{\mathrm{tot}}^{\mathrm{Cu}(100)} - 2E_{\mathrm{tot}}^{\mathrm{NO}}\right), \tag{1}$$

where $E_{\mathrm{tot}}^{(\mathrm{NO})_2/\mathrm{Cu}(100)}$, $E_{\mathrm{tot}}^{\mathrm{Cu}(100)}$, and $E_{\mathrm{tot}}^{\mathrm{NO}}$ are the total energies of $(\mathrm{NO})_2/\mathrm{Cu}(100)$, clean Cu(100), and gas-phase NO, respectively. The adsorption energy can be decomposed into the contribution from the interaction between $(\mathrm{NO})_2$ and surface and that from the interaction between NO molecules in $(\mathrm{NO})_2$ in the adsorbed geometry as follows: The interaction energy between$(\mathrm{NO})_2$ and Cu(100) is defined by

$$E_{\mathrm{int}}^{(\mathrm{NO})_2-\mathrm{Cu}(100)} = \frac{1}{2}\left(E_{\mathrm{tot}}^{(\mathrm{NO})_2/\mathrm{Cu}(100)} - E_{\mathrm{tot}}^{\mathrm{Cu}(100)} - E_{\mathrm{tot}}^{(\mathrm{NO})_2^*}\right) \tag{2}$$

where $E_{\mathrm{tot}}^{(\mathrm{NO})_2^*}$ is the total energy of $(\mathrm{NO})_2$ in the adsorbed geometry. The positive (negative) value means that the interaction of the NO *dimer* with the surface is attractive (repulsive). The interaction energy between NO molecules in $(\mathrm{NO})_2$ in the adsorbed geometry is defined by

$$E_{\mathrm{int}}^{\mathrm{NO-NO}} = \frac{1}{2}\left(E_{\mathrm{tot}}^{(\mathrm{NO})_2^*} - 2E_{\mathrm{tot}}^{\mathrm{NO}}\right) \tag{3}$$

The negative (positive) value indicates the attractive (repulsive) interactions between NO molecules.

TABLE S1. Adsorption energy (E_{ads}), interaction energies (E_{int}'s), N–O bond length ($d_{\mathrm{N-O}}$), N–N bond length ($d_{\mathrm{N-N}}$), O–O bond length ($d_{\mathrm{O-O}}$) and tilting angles of NO from the surface normal ($\angle_{\mathrm{NO}}/^\circ$) of a_0-$(\mathrm{NO})_2$, upright ONNO, and flat-lying ONNO.

Dimer species	E_{ads}/eV	$E_{\mathrm{int}}^{(\mathrm{NO})_2-\mathrm{Cu}(100)}$/eV	$E_{\mathrm{int}}^{\mathrm{NO-NO}}$/eV	$d_{\mathrm{N-O}}$/Å	$d_{\mathrm{N-N}}$/Å	$d_{\mathrm{O-O}}$/Å	$\angle_{\mathrm{NO}}/^\circ$
a_0-$(\mathrm{NO})_2$	−1.54	−1.75	0.21	1.24	2.83	2.61	5
Upright ONNO	−1.52	−1.62	0.10	1.24	1.56	2.67	27
Flat-lying ONNO	−1.70	−2.41	0.71	1.33	1.33	2.55	27

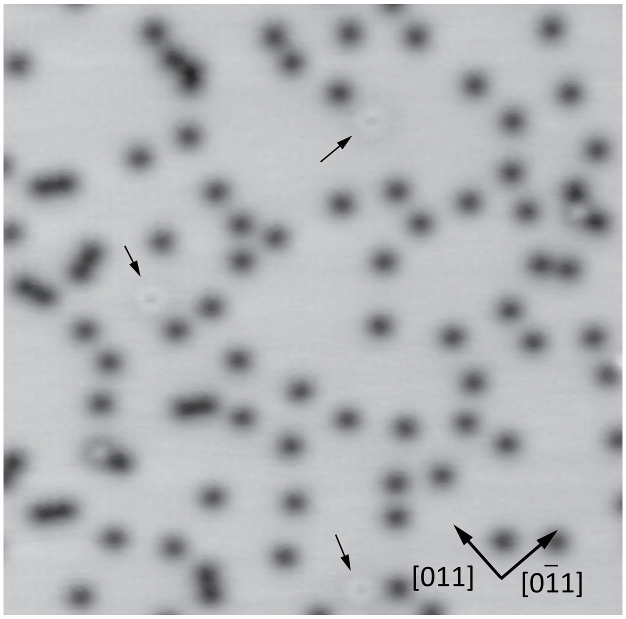

FIG. S1. Typical STM image of Cu(100) after exposed to NO at 64 K (molecular adsorption) and then heated to 85 K (for the reaction). The image was obtained at 64 K. The unreacted NO molecules (bright rings) are indicated by the arrows. The image size is 150×140 Å. V_s=0.1 V and I=2 nA.

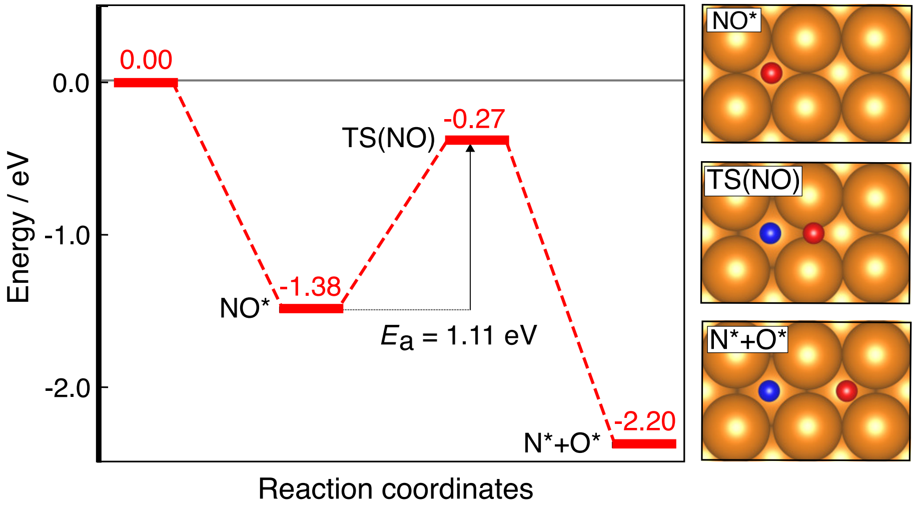

FIG. S2. Energy diagram of NO direct dissociation on Cu(100). The energy is referenced to the sum of the total energies of the clean surface and gas-phase NO.

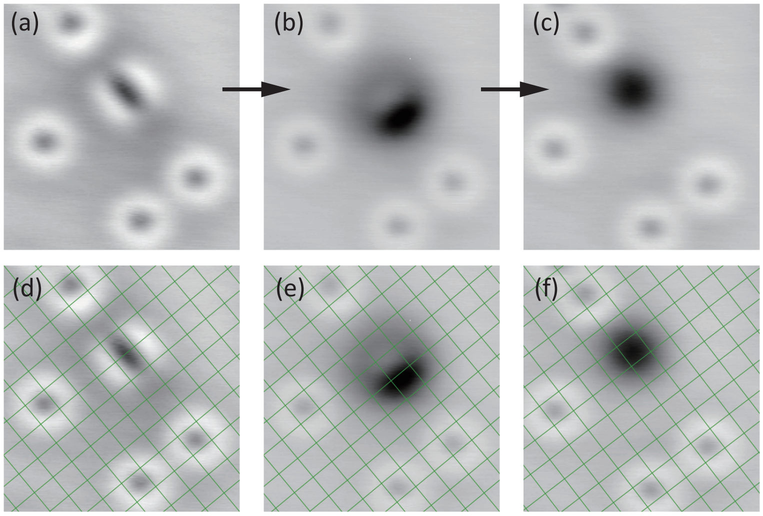

FIG. S3. (a)-(c) Sequential STM images of NO molecules induced to react by voltage pulses at 6 K. A a_0-dimer in (a) imaged as twin elongated protrusions was first converted to a flat-lying ONNO (semicircle depression) and then to an oxygen atom (round depression). (d)-(f) The same images as (a)-(c) with the lattice of Cu(100) superimposed, clearly showing the registries of the molecules with the surface.

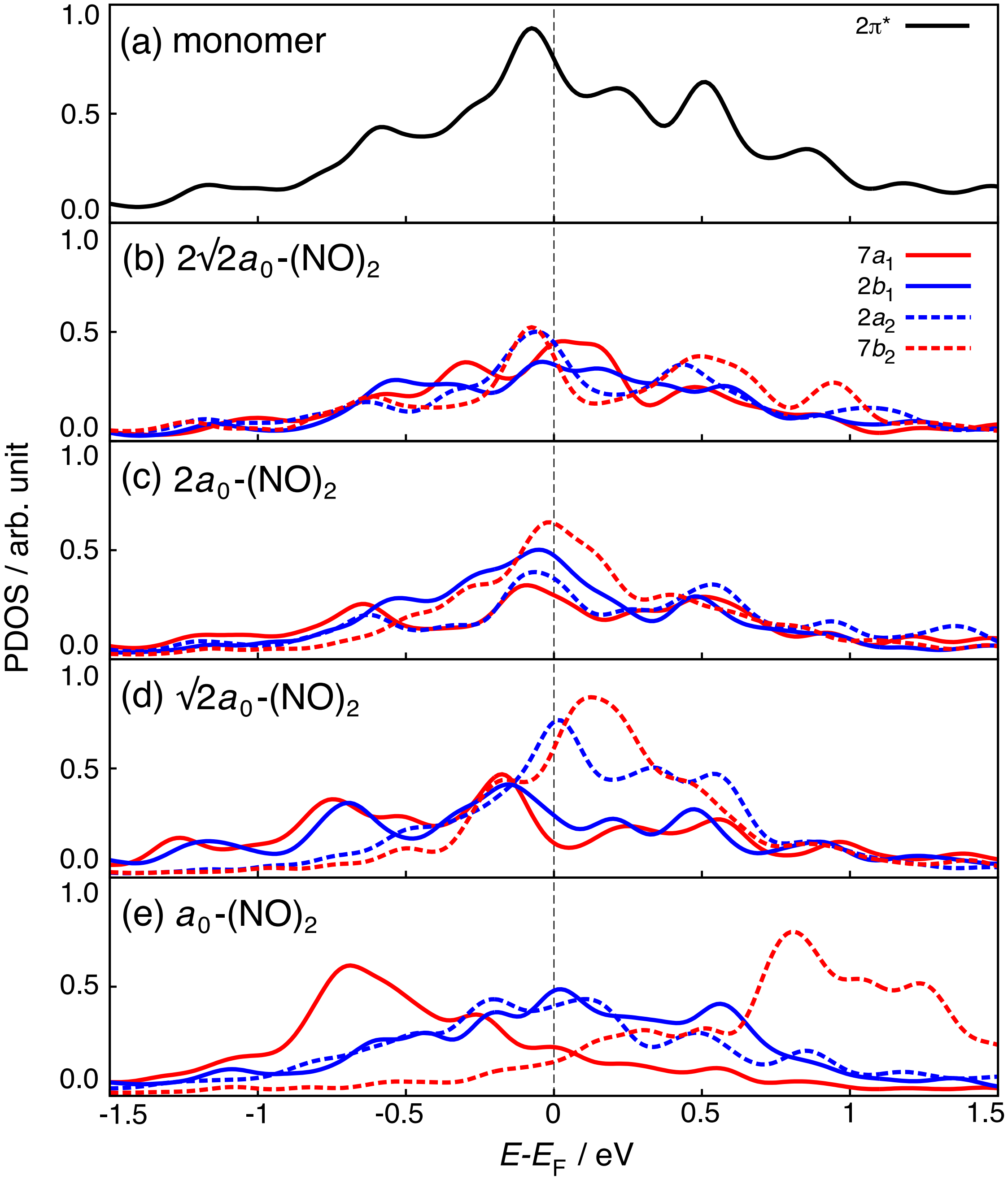

FIG. S4. Projected densities of states (PDOS) onto (a) the $2\pi^*$ orbital of NO monomer on Cu(100), PDOSs onto the molecular orbitals consisting of $2\pi^*$ orbitals ($7a_1$, $2b_1$, $2a_2$, and $7b_2$) for dimer at the distance of (b) $2\sqrt{2}a_0$, (c) $2a_0$, (d) $\sqrt{2}a_0$, and (e) a_0.

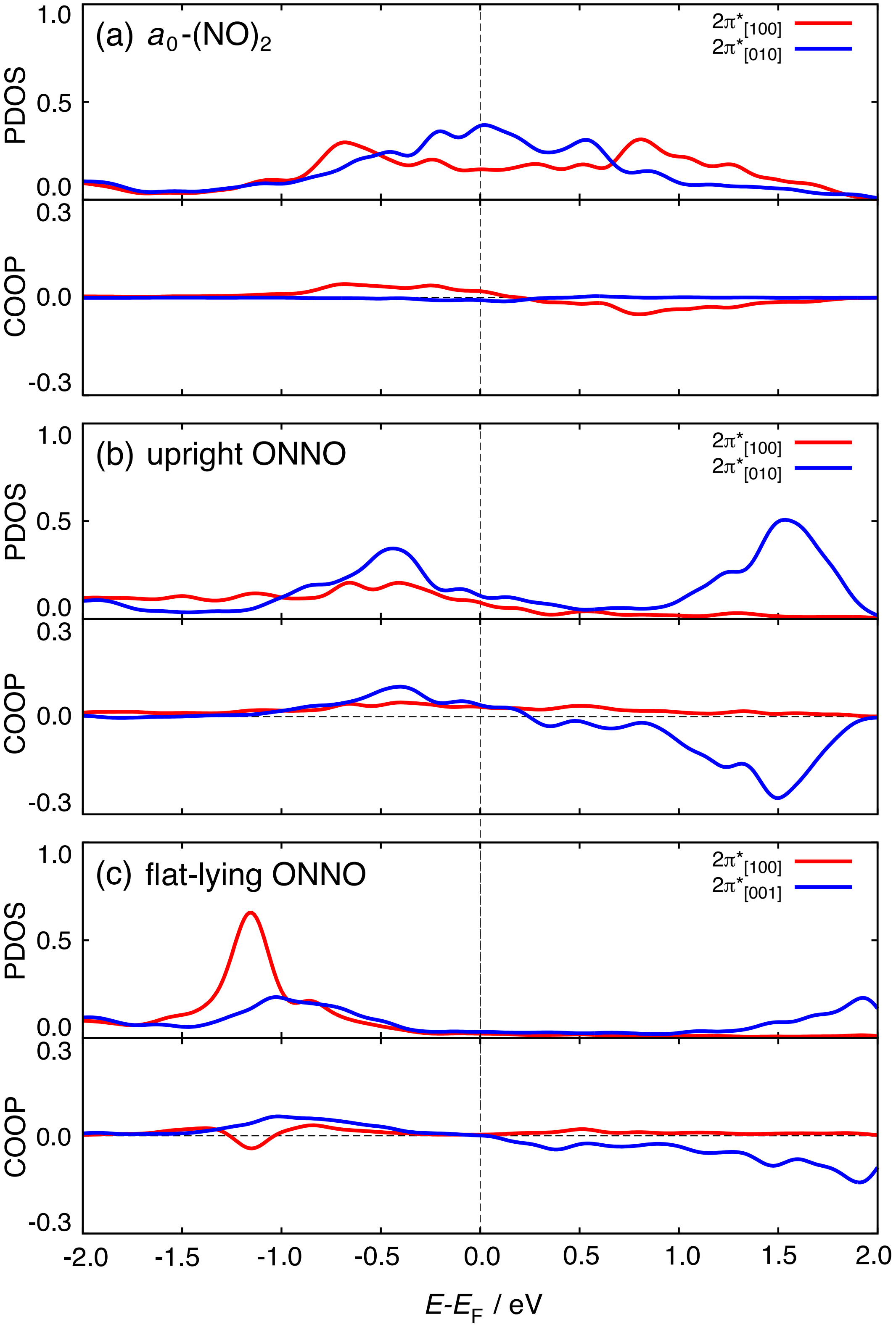

FIG. S5. Projected densities of states (PDOS) and crystal orbital overlap population (COOP) between the $2\pi^*$ orbitals of NO monomers in (a) a_0-(NO)$_2$, (b) upright ONNO, and (c) flat-lying ONNO.