Supporting Information

Photoelectron spectroscopy of cryogenically cooled NiO$_2$‾ *via* slow photoelectron velocity-map imaging

Mark C. Babin,[†,a)] Martin DeWitt,[†] Jascha A. Lau,[†] Marissa L. Weichman,[†,b)] Jongjin B. Kim,[†,c)] Lan Cheng,[∇,*] Daniel M. Neumark [†,⊥,*]

[†] Department of Chemistry, University of California, Berkeley, CA 94720, USA.

[∇] Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, USA.

[⊥] Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.

[a)] Current address: Department of Chemistry and Chemical Biology, Harvard University, 12 Oxford St, Cambridge, MA 02138, USA.

[b)] Current address: Department of Chemistry, Princeton University, Princeton, New Jersey 08544, USA

[c)] Current address: KLA Corporation, 1 Technology Dr, Milpitas, CA 95035

Corresponding Authors

* lcheng24@jhu.edu, dneumark@berkeley.edu

Computational Methods

In a CCSD or CCSDT calculation of the $\tilde{X}^1 \Sigma_g^+$ state of NiO_2, the cluster amplitudes for the double excitations into the $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(1\delta_g)^4(3\sigma_g^+)^2(2\sigma_u^+)^2(1\pi_u)^4(1\pi_g)^2(2\pi_g)^2$, $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(1\delta_g)^4(3\sigma_g^+)^2(2\sigma_u^+)^2(1\pi_u)^2(1\pi_g)^4(2\pi_g)^2$, and $(1\sigma_g^+)^2(1\sigma_u^+)^2(2\sigma_g^+)^2(1\delta_g)^4(3\sigma_g^+)^2(2\sigma_u^+)^0(1\pi_u)^4(1\pi_g)^4(2\pi_g)^2$ configurations are greater than 0.1. This leads to a relatively slow convergence of CC results with respect to the increase of the excitation rank. As shown in Table S1, the differences between CCSDTQ and CCSDT results are around half of those between CCSDT and CCSD results while using a double-zeta basis. On the other hand, the CC series still offers a monotonic convergence for the molecular parameters studied here. The CC results presented here are sufficiently converged to establish the linearity of the equilibrium structure for the ground electronic state of NiO_2.

Interestingly, the CCSD(T) results for these parameters appear to be reasonably accurate. By inspecting the trend of convergence in CCSD, CCSDT, and CCSDTQ series, one sees that CCSD(T) perhaps slightly overestimates the vibrational frequency of the bending mode ω_2 and underestimates those of the antisymmetric stretching and symmetric stretching modes (ω_3 and ω_1). Although the accuracy of CCSD(T) for this challenging system is somewhat fortuitous, CCSD(T) calculations can provide equilibrium structure parameters and harmonic vibrational frequencies for the $\tilde{X}^1 \Sigma_g^+$ state of NiO_2 that are sufficiently accurate to enable a Franck-Condon simulation of the vibrational structures in the present photoelectron spectrum.

The corresponding CCSD wave function for the $\tilde{X}^2 \Pi_g$ state of NiO_2^- has only one double excitation amplitude around 0.1. The relatively small variation between CCSD and CCSD(T) results shown in Table S1 also indicates that the CCSD(T) results are reasonably accurate.

The EOM-CCSDT values in Table S2 have been obtained by augmenting EOM-CCSD/aug-cc-pVQZ results with the triples corrections calculated as the differences between EOM-CCSDT/cc-pVDZ and EOM-CCSD/cc-pVDZ results. The computed excitation energies for the $(3\sigma_g^+)^1(2\sigma_u^+)^2(1\pi_u)^4(2\pi_g)^1$ and $(3\sigma_g^+)^1(2\sigma_u^+)^1(1\pi_u)^4(2\pi_g)^1$ states are relatively insensitive to

triples contributions, e.g., the EOM-CCSD excitation energy of the $^3\Pi_g$ is 0.57 eV, only 0.1 eV lower than the corresponding EOM-CCSDT value of 0.67 eV. In contrast, triples contributions amount to more than 0.5 eV of the excitation energies for the $(3\sigma_g^+)^1(2\sigma_u^+)^2(1\pi_u)^3(2\pi_g)^1$ states.

Computational Tables

	R(Ni-O)	$\omega_1(\sigma_g)$	$\omega_2(\pi_u)$	$\omega_3(\sigma_u)$
NiO_2				
CCSD	1.567	928	81i	1175
CCSDT	1.598	838	90	1055
CCSDTQ	1.616	782	110	998
CCSD(T)	1.619	744	140	955
NiO_2^-				
CCSD	1.628	810	31	996
CCSD(T)	1.650	763	101	896

Table S1: Computed bond length (Angstrom) and harmonic vibrational frequencies (cm^{-1}) for the $\tilde{X}^1\Sigma_g^+$ state of NiO_2 and the $\tilde{X}^2\Pi_g$ state of NiO_2^-. Scalar-relativistic effects have been taken into account using the SFX2C-1e scheme. The cc-pVDZ basis sets and aug-cc-pVDZ basis sets recontracted for the SFX2C-1e scheme have been used for NiO_2 and NiO_2^-, respectively.

	Nominal excitation from ground state	EOM-CCSD	EOM-CCSDT
$^3\Pi_g$	$3\sigma_g \rightarrow 2\pi_g$	0.46	0.56
$^1\Pi_g$	$3\sigma_g \rightarrow 2\pi_g$	0.86	0.88
$^3\Sigma_u$	$1\pi_u \rightarrow 2\pi_g$	0.42	1.08
$^3\Delta_u$	$1\pi_u \rightarrow 2\pi_g$	0.83	1.43
$^3\Sigma_u$	$1\pi_u \rightarrow 2\pi_g$	1.08	1.62
$^1\Sigma_u$	$1\pi_u \rightarrow 2\pi_g$	1.11	1.62
$^1\Delta_u$	$1\pi_u \rightarrow 2\pi_g$	1.14	1.67
$^3\Pi_u$	$2\sigma_u \rightarrow 2\pi_g$	1.94	1.93
$^1\Pi_u$	$2\sigma_u \rightarrow 2\pi_g$	2.37	2.24

Table S2. Excitation energies of NiO_2 computed in the equilibrium structure of the $\tilde{X}^2\Pi_g$ state of NiO_2^-. EOM-CCSD values have been obtained using the aug-cc-pVQZ basis sets, while the EOM-CCSDT values have been obtained by augmenting the EOM-CCSD results with triples corrections obtained using cc-pVDZ basis sets.