Supporting Information

Photoelectron Spectrum of NO$_2^-$: SAC-CI Gradient Study of Vibrational-Rotational Structures

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Basis set dependence for the photoelectron spectra of NO$_2^-$

We showed the photoelectron spectra of NO$_2^-$ using the cc-pVTZ(-f) basis sets in Figures S1 to S4. The photoelectron spectra with the cc-pVTZ(-f) basis set are almost the same as those with the aug-cc-pVTZ basis set. Thus, the basis set dependence is small for the photoelectron spectra of NO$_2^-$. 
Figure S1. Experimental and SAC-CI photoelectron spectra of NO$_2^-$ at 350K. The SAC-CI theoretical spectrum (Total) with the cc-pVTZ(-f) basis set is the sum of the contributions from the vibrational ground state (1$_0^2S^+_0$ (a)) and from the vibrational excited states (1$_0^2S^+_1$ (b), 1$_0^2S^+_1$ (c) and 1$_2^2S^+_0$ (d)). The inset of the experimental spectrum shows the enlarged view of the range 1.2-1.5 eV in the electron kinetic energy. The inset of the SAC-CI spectrum (Total) shows the schematic diagram of the vibrational excitations accompanying to the ionization from NO$_2^-$ to NO$_2$. Horizontal axis represents the vibrational coordinate.
Figure S2. Experimental and SAC-CI photoelectron spectra of NO$_2^-$ at 700K. The SAC-CI theoretical spectrum (Total) with the cc-pVTZ(-f) basis set is the sum of the contributions from the vibrational ground state ($1_a^2$) and from the vibrational excited states ($1_b^2$, $1_c^2$, $1_d^2$, $1_e^2$, $1_f^2$, $1_g^2$). The inset of the SAC-CI spectrum (Total) shows the schematic diagram of the vibrational excitations accompanying to the ionization from NO$_2^-$ to NO$_2$. Horizontal axis represents the vibrational coordinate.
Figure S3. Experimental and SAC-CI photoelectron spectra at 350K including rotational effects of NO$_2$\textsuperscript{−}. The SAC-CI theoretical spectrum (Total) with the cc-pVTZ(−f) basis set is the sum of the contributions from the vibrational ground state ($1^0_0^0 2^0_0 3^0_0$ (a)) and from the vibrational excited states ($1^0_0^0 2^0_0 3^0_1$ (b), $1^0_0^0 2^0_0 3^1_0$ (c) and $1^0_0^0 2^0_0 3^1_1$ (d)). The inset of the experimental spectrum shows the enlarged view of the range 1.2-1.5 eV in the electron kinetic energy. The inset of the SAC-CI spectrum (Total) shows the schematic diagram of the vibrational excitations accompanying to the ionization from NO$_2$\textsuperscript{−} to NO$_2$. Horizontal axis represents the vibrational coordinate.
Figure S4. Experimental and SAC-CI photoelectron spectra at 700K including rotational effects of NO$_2^-$. The SAC-CI theoretical spectrum (Total) with the cc-pVTZ-(f) basis set is the sum of the contributions from the vibrational ground state (1$^0_0$2$^-_0$3$^-_0$(a)) and from the vibrational excited states (1$^0_0$2$^-_0$3$^-_1$(b), 1$^0_0$2$^-_0$3$^-_1$(c), 1$^0_0$2$^-_0$3$^-_0$(d), 1$^0_0$2$^-_2$3$^-_0$(e), 1$^0_0$2$^-_2$3$^-_1$(f) and 1$^0_0$2$^-_3$3$^-_0$(g)). The inset of the SAC-CI spectrum (Total) shows the schematic diagram of the vibrational excitations accompanying to the ionization from NO$_2^-$ to NO$_2$. Horizontal axis represents the vibrational coordinate.