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^-.

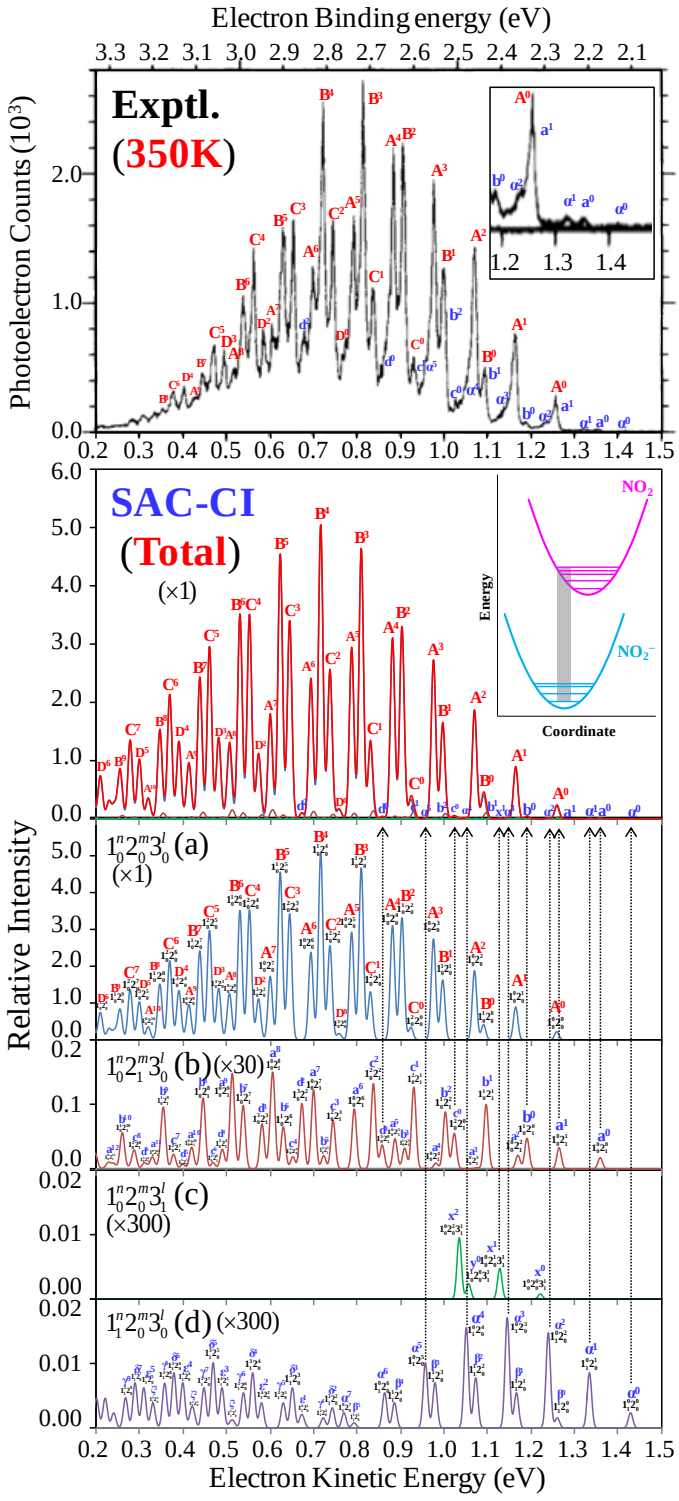

Figure S1. Experimental and SAC-CI photoelectron spectra of NO_2^- at 350K. The SAC-CI theoretical spectrum (Total) with the cc-pVTZ(-f) basis set is the sum of the contributions from the vibrational ground state ($1_0 2_0 3_0$ (a)) and from the vibrational excited states ($1_0 2_1 3_0$ (b), $1_0 2_0 3_1$ (c) and $1_1 2_0 3_0$ (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.

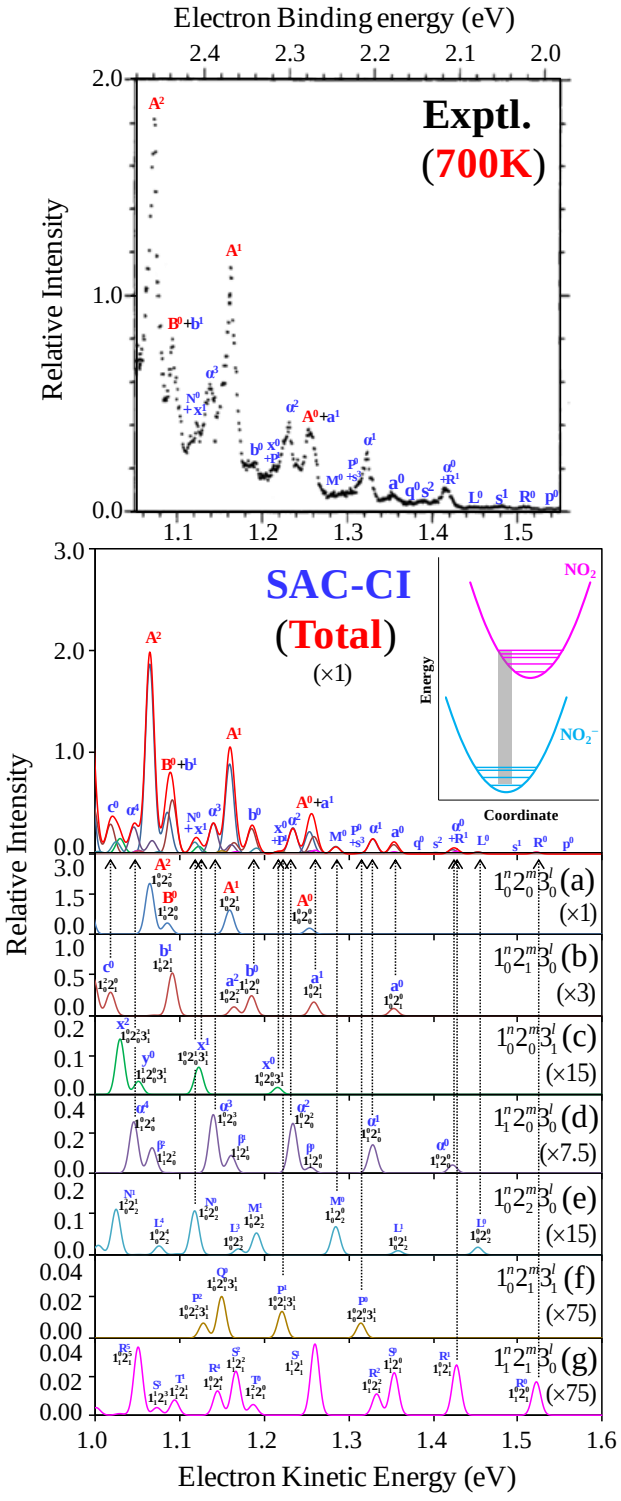

Figure S2. Experimental and SAC-CI photoelectron spectra of NO_2^- at 700K. The SAC-CI theoretical spectrum (Total) with the cc-pVTZ(-f) basis set is the sum of the contributions from the vibrational ground state ($1_0 2_0 3_0$ (a)) and from the vibrational excited states ($1_0 2_1 3_0$ (b), $1_0 2_0 3_1$ (c), $1_1 2_0 3_0$ (d), $1_0 2_2 3_0$ (e), $1_0 2_1 3_1$ (f) and $1_1 2_1 3_0$ (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.

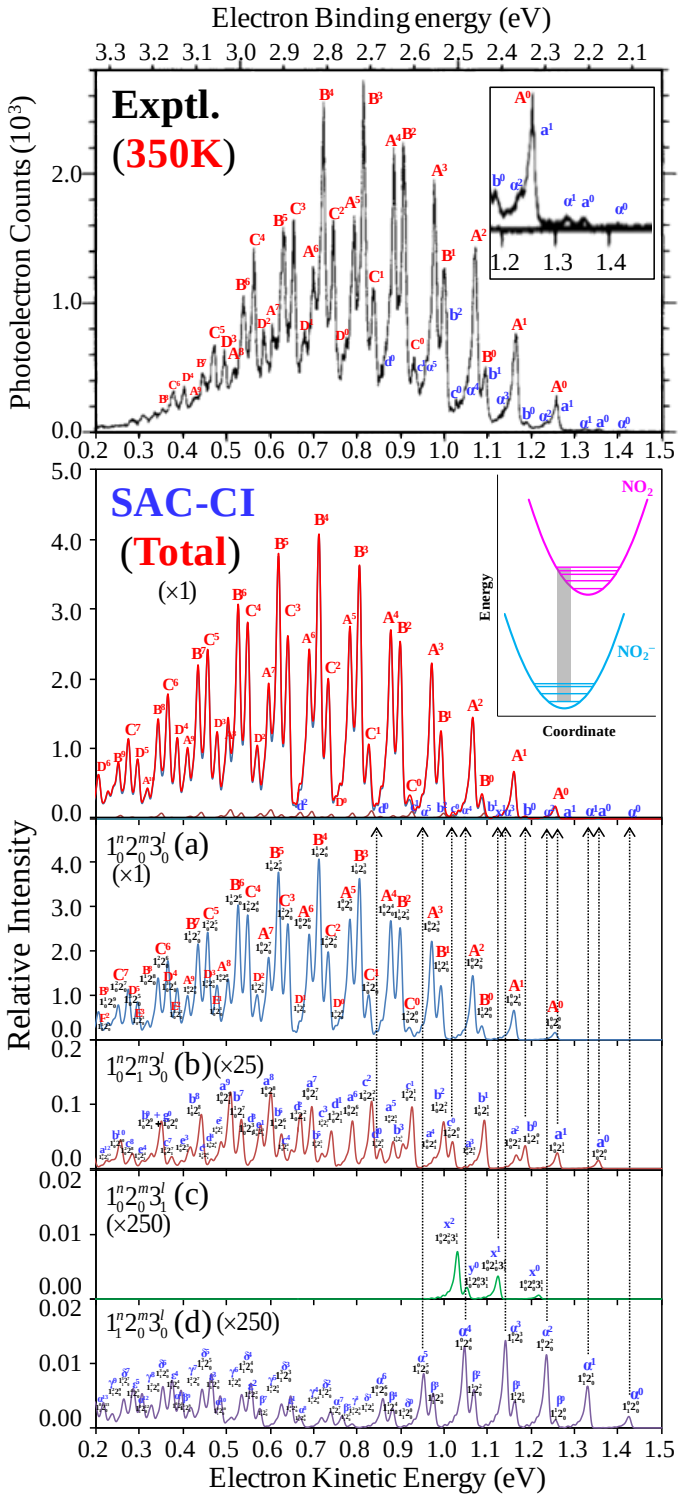

Figure S3. Experimental and SAC-CI photoelectron spectra at 350K including rotational effects of NO_2^-. The SAC-CI theoretical spectrum (Total) with the cc-pVTZ(-f) basis set is the sum of the contributions from the vibrational ground state ($1_0 2_0 3_0$ (a)) and from the vibrational excited states ($1_0 2_1 3_0$ (b), $1_0 2_0 3_1$ (c) and $1_1 2_0 3_0$ (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.

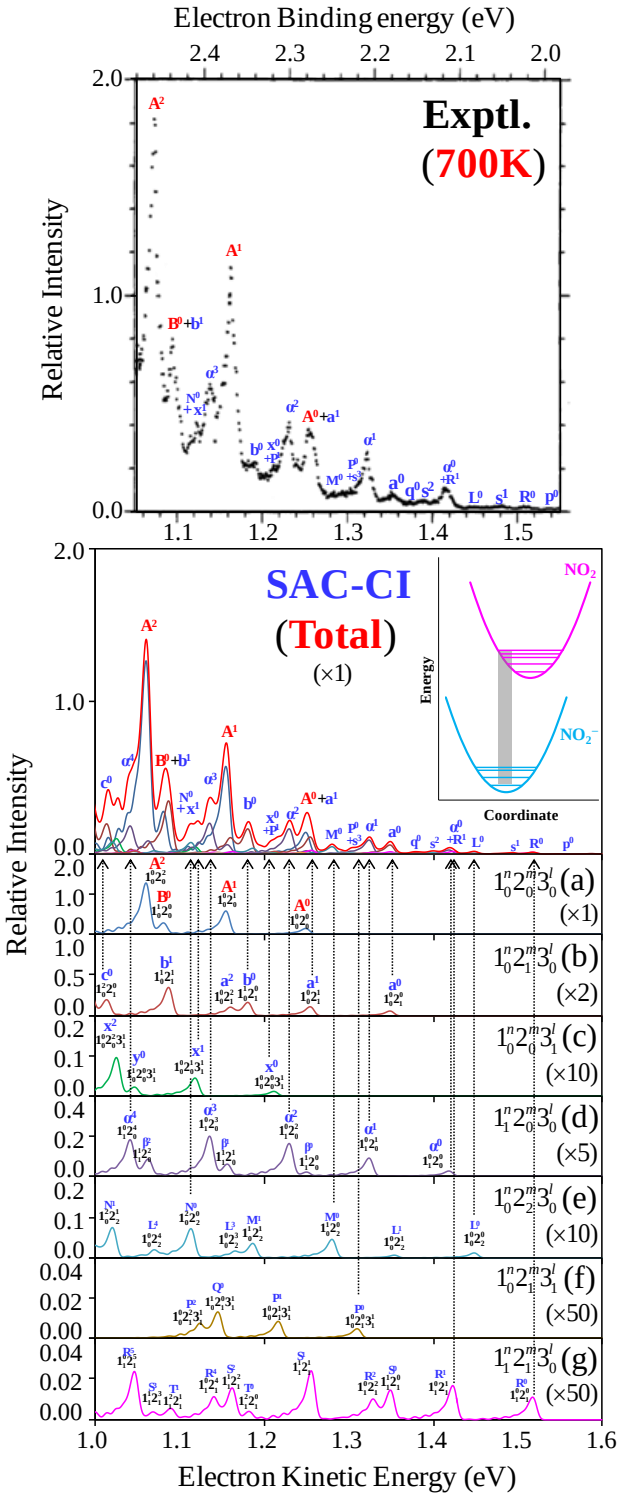

Figure S4. Experimental and SAC-CI photoelectron spectra at 700K including rotational effects of NO_2^-. The SAC-CI theoretical spectrum (Total) with the cc-pVTZ(-f) basis set is the sum of the contributions from the vibrational ground state ($1_0^n2_0^m3_0^l$(a)) and from the vibrational excited states ($1_0^n2_1^m3_0^l$(b), $1_0^n2_0^m3_1^l$(c), $1_1^n2_0^m3_0^l$(d), $1_0^n2_2^m3_0^l$(e), $1_0^n2_1^m3_1^l$(f) and $1_1^n2_1^m3_0^l$(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.