## Supporting Information

## Unravelling the Electronic State of NO<sub>2</sub> Product in Ultrafast Photodissociation of Nitromethane

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Time profiles of photoelectron intensity for the lower eBE region: Figure S1 shows time profiles of photoelectron intensity observed at eBE = 5.4, 6.5, and 8.1 eV. From calculated vertical excitation energies<sup>1</sup> for  $S_3 \leftarrow S_0$ ,  $S_2 \leftarrow S_0$ , and  $S_1 \leftarrow S_0$ , the signal at eBE = 5.4 eV is assigned to be the S<sub>3</sub> state, while the other two are attributed to the S<sub>2</sub> and/or S<sub>1</sub> states.



Figure S1. Time profiles of photoelectron intensity at eBE = 5.4, 6.5, and 8.1 eV.

<sup>1</sup> M. Isegawa, F. Liu, S. Maeda, and K. Morokuma, J. Chem. Phys. 140, 244310 (2014).

**Pump-probe photoelectron spectra for negative and positive delays:** Figure S2 shows pumpprobe photoelectron spectra in the higher eBE region averaged for negative ( $-1400 \sim -400$  fs, black) and positive (+1000 fs, red) time delays. These two represent a photoelectron spectrum before and after the dissociation, respectively, and dissociation probability is evaluated to be 1.0% from them.



**Figure S2.** Photoelectron spectra averaged for negative  $(-1400 \sim -400 \text{ fs}, \text{ black})$  and positive (+1000 fs, red) time delays.

**Reproduced spectra by simpler models:** The experimental spectrum was reproduced using the full (NM, CH<sub>3</sub>, NO<sub>2</sub>(X), and NO<sub>2</sub>(A)) and two simpler (NM, CH<sub>3</sub>, and NO<sub>2</sub>(X); NM, CH<sub>3</sub>, and NO<sub>2</sub>(A)) models in Fig. S3. It was found that the full model fits the experimental spectrum much better ( $R^2 = 0.97$ ) than the simpler models assuming three species ( $R^2 = 0.84$  for NM, CH<sub>3</sub>, and NO<sub>2</sub>(X);  $R^2 = 0.93$  for NM, CH<sub>3</sub>, and NO<sub>2</sub>(A)).



Figure S3. Reproduced spectra by full and simpler models.

**Goodness of the fit:** In Fig. S4, the goodness of the fit was evaluated by the root mean square (RMS) error, as fixed the dissociation time constant  $\tau_{diss}$  to various values. The RMS error increases monotonically for  $\tau_{diss} > 50$  fs, and therefore  $\tau_{diss}$  is reasonably considered to be  $\leq 50$  fs.



Figure S4. Goodness of the fit.