



Supplement of

Heterogeneous nitrosation reactions of amines driven by dinitrogen tetroxide: a missing source of particulate nitrosamines

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Supplementary Methods

Section S1. Unbiased BOMD simulations.

The unbiased BOMD simulations were performed to demonstrate that the N-nitrosation reactions of MA/DMA with N_2O_4 and the hydrolysis of *t*-ONONO₂ mediated by MA and DMA can occur rapidly. The simulation system was fully relaxed to reach statistical equilibrium (Fig. S2). Subsequent simulations confirmed that the above reactions proceed rapidly and spontaneously under equilibrium conditions.

Section S2. Well-tempered metadynamics simulations.

To probe the reaction barriers between HONO and DMA at the air–water interface, metadynamics (MetaD) simulations were carried out. The collective variable (CV), a key parameter for enhanced sampling, was defined to clearly distinguish between reactant, transition, and product states (Fig. S12). The upper and lower bounds of the CV were determined based on the interfacial behavior observed in unbiased BOMD simulations. Gaussian hills with adaptive heights and width parameter σ of 0.3 Å were deposited every 30 steps to efficiently explore the free energy landscape and accelerate convergence (Fig. S13).

Section S3. Wave function analysis.

Wave function analyses were performed to characterize the bonding features of *t*-ONONO₂ and the intermolecular interactions involved in the interfacial reaction processes observed in the BOMD simulations. For the *t*-ONONO₂ molecule, geometry optimization was performed using the B3LYP-D3 functional (Becke, 1993; Lee et al., 1988) with the 6-311++G(3df,2p) basis set as implemented in the Gaussian 16 program (Frisch et al., 2016). This level of theory has been demonstrated to provide reliable descriptions of atmospheric reaction systems in previous studies (Chacón et al., 2020; Li et al., 2018; Wang and Agmon, 2017). The optimized wave function was subsequently analyzed using Multiwfn 3.8 for Mayer bond order (MBO) and interaction region indicator (IRI) analyses.

For representative interfacial products extracted from the BOMD trajectories, single-point electronic structure calculations were performed using CP2K. The resulting molden files were analyzed using Multiwfn 3.8 to perform IRI and ELF analyses. The corresponding interaction isosurfaces were subsequently visualized using VMD 1.9.3.

S3.1 Structural and MBO analysis of *t*-ONONO₂.

The optimized structure of *t*-ONONO₂ (Fig. S7) contains five N–O covalent bonds, among which the N2–O3 bond is the longest (1.623 Å). The MBO values were calculated for all N–O covalent bonds to evaluate their relative bond strengths (Mayer, 1983). The reliability of MBO has been well-established in various studies (Mayer, 1983; Ning et al., 2024). Generally, larger MBO values correspond to stronger covalent interactions. The calculated MBO value of the N2–O3 bond is 0.641, which is the lowest among all N–O bonds in *t*-ONONO₂, indicating its relatively weak covalent character. Together with its elongated bond length, this result indicates that the N2–O3 bond is relatively weaker than the other N–O bonds in *t*-ONONO₂, potentially contributing to its preferential cleavage during the interfacial transformation.

S3.2 IRI analysis.

The IRI analysis was employed to characterize the nature and strength of localized interactions (Lu and Chen, 2021). The IRI isosurfaces were mapped according to the $\text{sign}(\lambda_2)\rho$ function, where $\text{sign}(\lambda_2)$ represents the second-largest eigenvalue of the electron-density Hessian matrix. Negative $\text{sign}(\lambda_2)$ values correspond to attractive interactions, whereas positive values indicate repulsive interactions. As shown in Fig. S8, the N2–O3 bond in *t*-ONONO₂ exhibits a characteristic $\text{sign}(\lambda_2)\rho$ value of approximately -0.190 a.u., corresponding to the weakest attractive interaction among the N–O covalent bonds. Combined with the MBO analysis, these results indicate that the N2–O3 bond possesses the weakest interaction strength within *t*-ONONO₂, providing a structural basis for its spontaneous heterolytic cleavage into the (NO₃[−])(NO⁺) ion pair during equilibration at the air–water interface.

To further characterize the intermolecular interactions involved in the interfacial reaction products, IRI analyses were performed for representative configurations extracted from the BOMD trajectories. The corresponding results are presented in Fig. S11. In the IRI plots, blue regions represent strong attractive interactions, including ionic interactions, hydrogen bonds (HBs), and covalent bonds. Green regions correspond to weak van der Waals interactions, and red regions indicate steric repulsion.

As shown in Fig. S11, distinct green regions are observed between HONO and neighboring species, including NO₃[−], H₂O, MAH⁺, and DMAH⁺, indicating weak van der Waals interactions accompanied by HB interactions.

Section S4. Interfacial reaction rate constant between DMA and HONO.

In this study, the rate constant (k) was calculated using transition state theory (TST) (Truhlar et al., 1996), as given by the following expression:

$$k^{\text{TST}} = \sigma \frac{k_B T}{h} e^{-\Delta G^{0,\ddagger} / (RT)}$$

where σ is the reaction path degeneracy, which was set to 1 in the present calculation, k_B is the Boltzmann constant, T is the absolute temperature (300 K), h is the Planck's constant, R is the molar gas constant, and $\Delta G^{0,\ddagger}$ denotes the Gibbs free energy barrier (the change in Gibbs free energy from reactants to the transition state). The calculated k^{TST} for the interfacial reaction between DMA and HONO is approximately $1.67 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$.

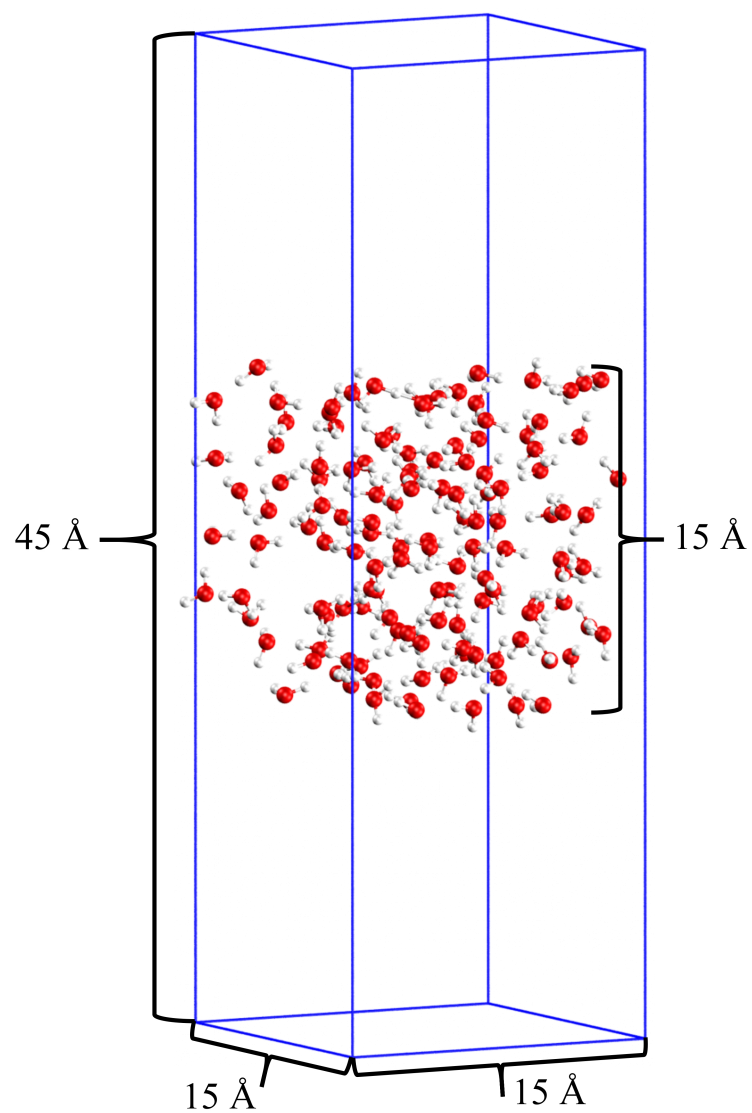


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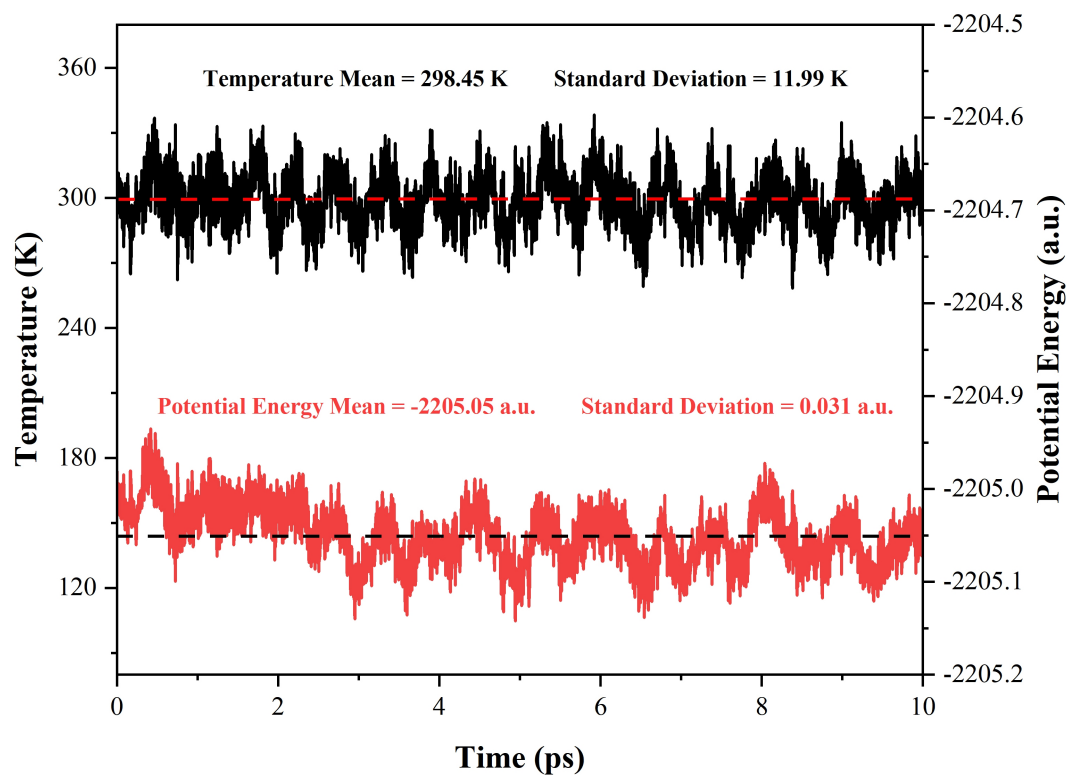


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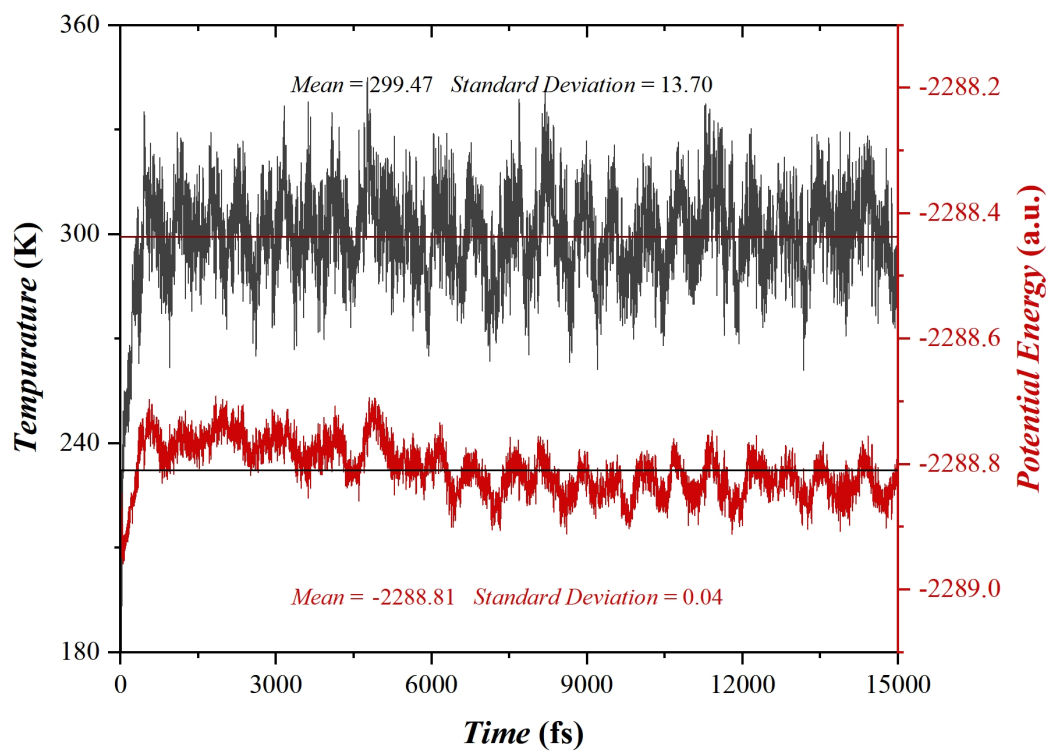


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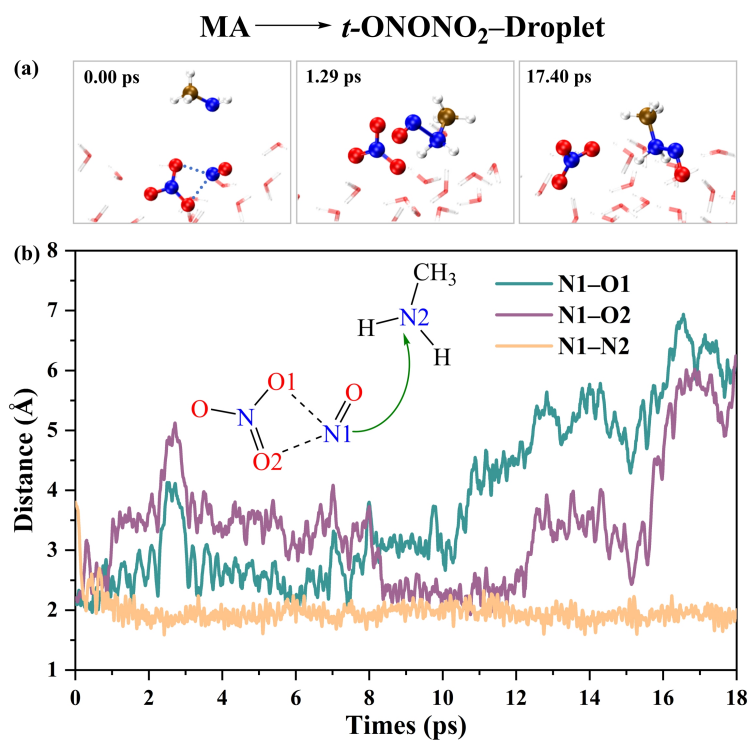


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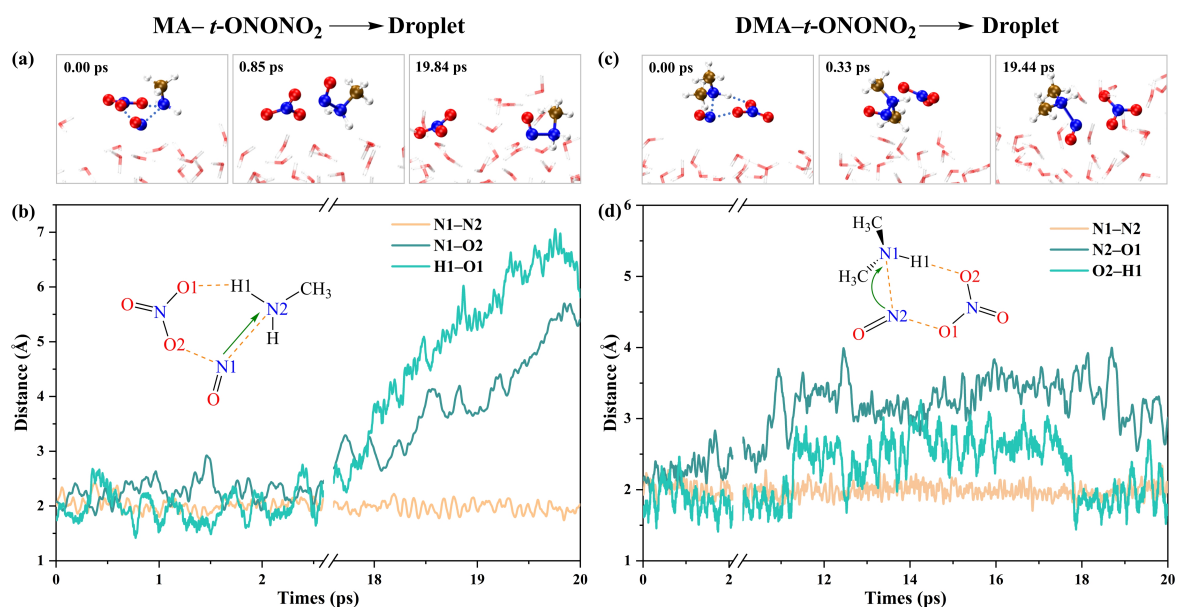


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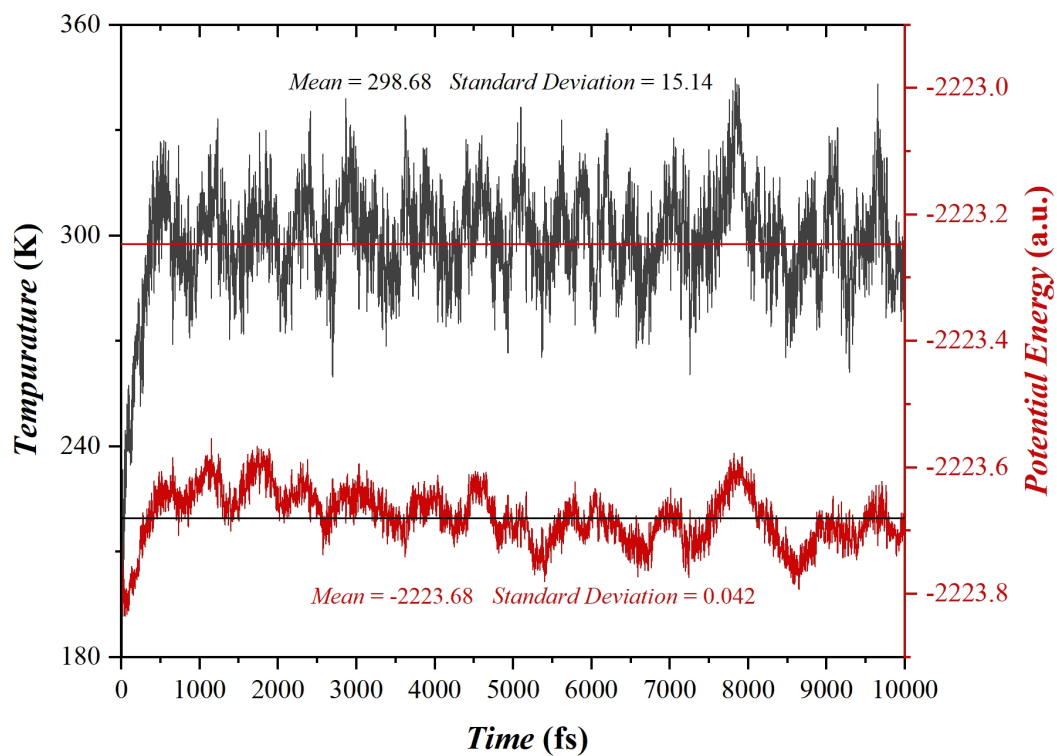


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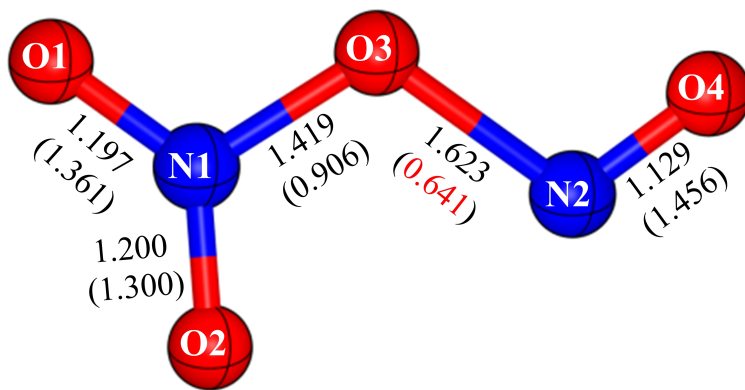


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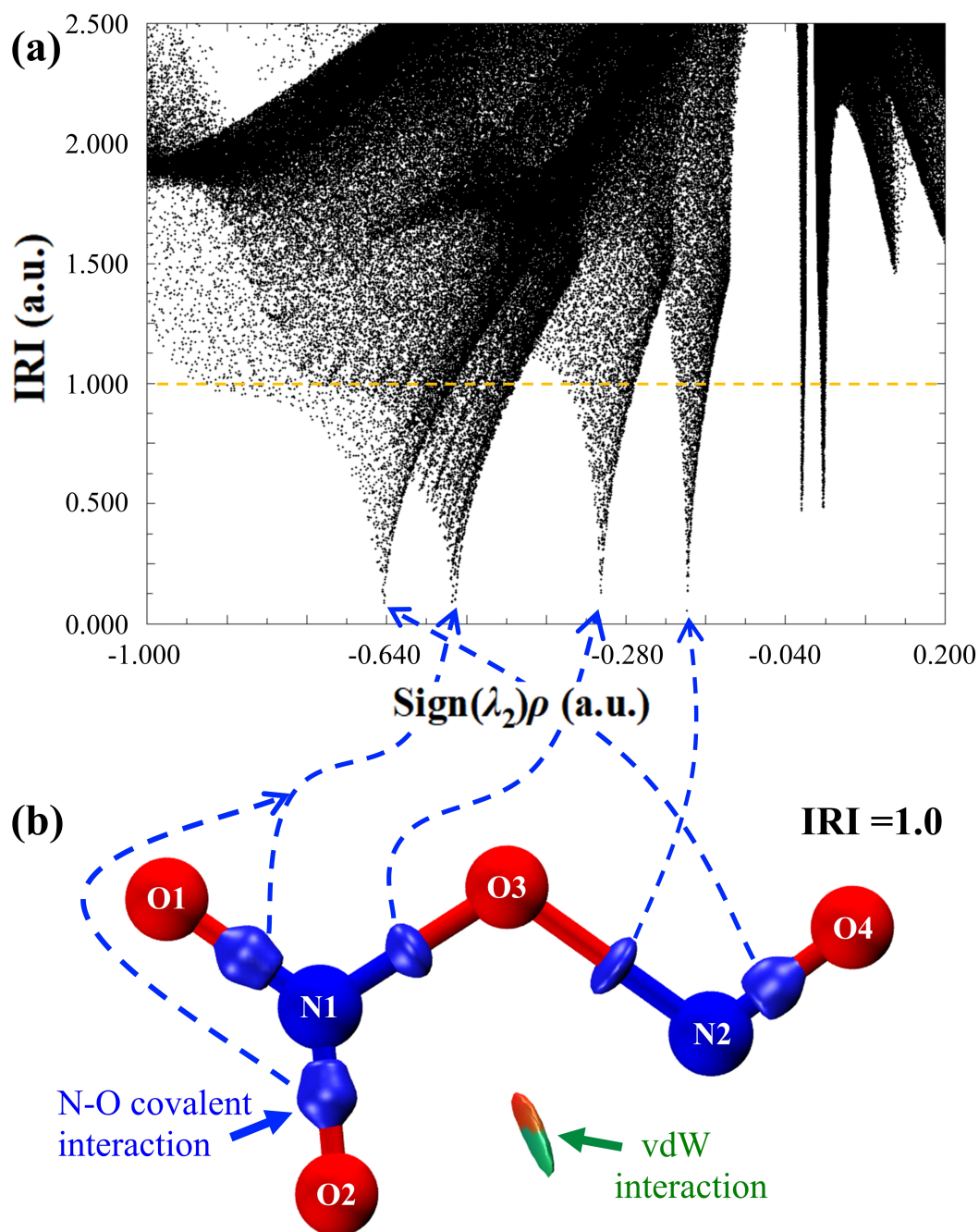


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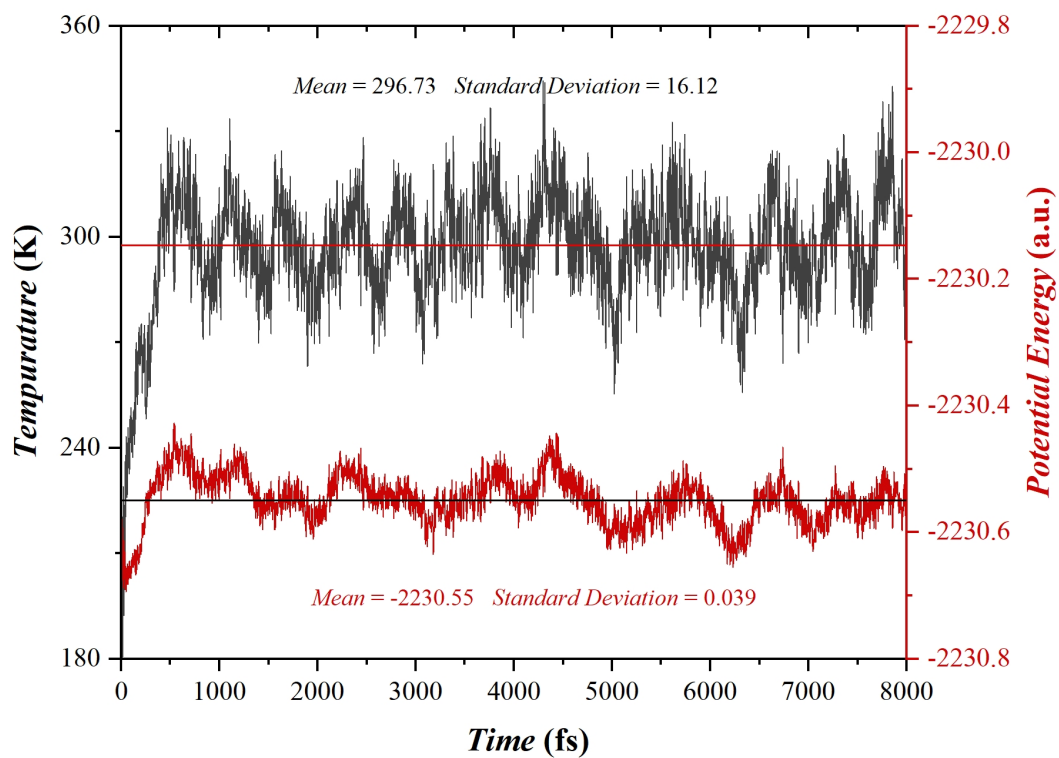


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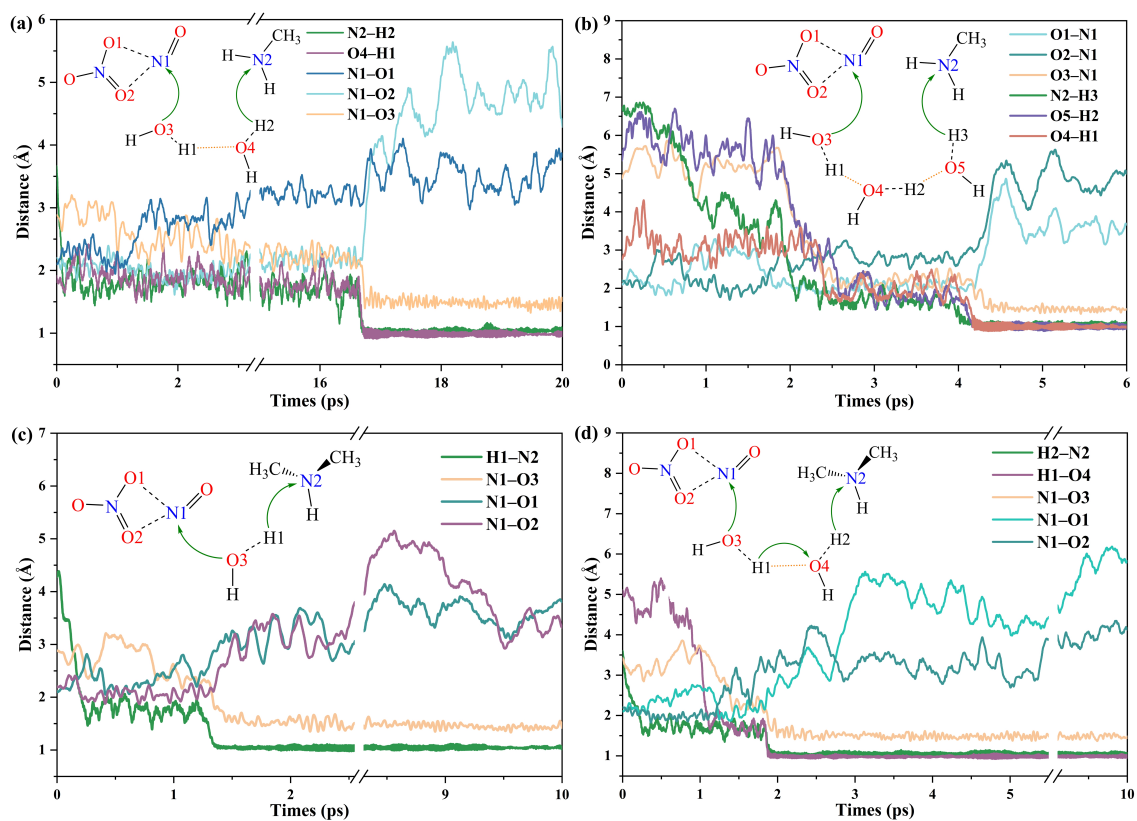


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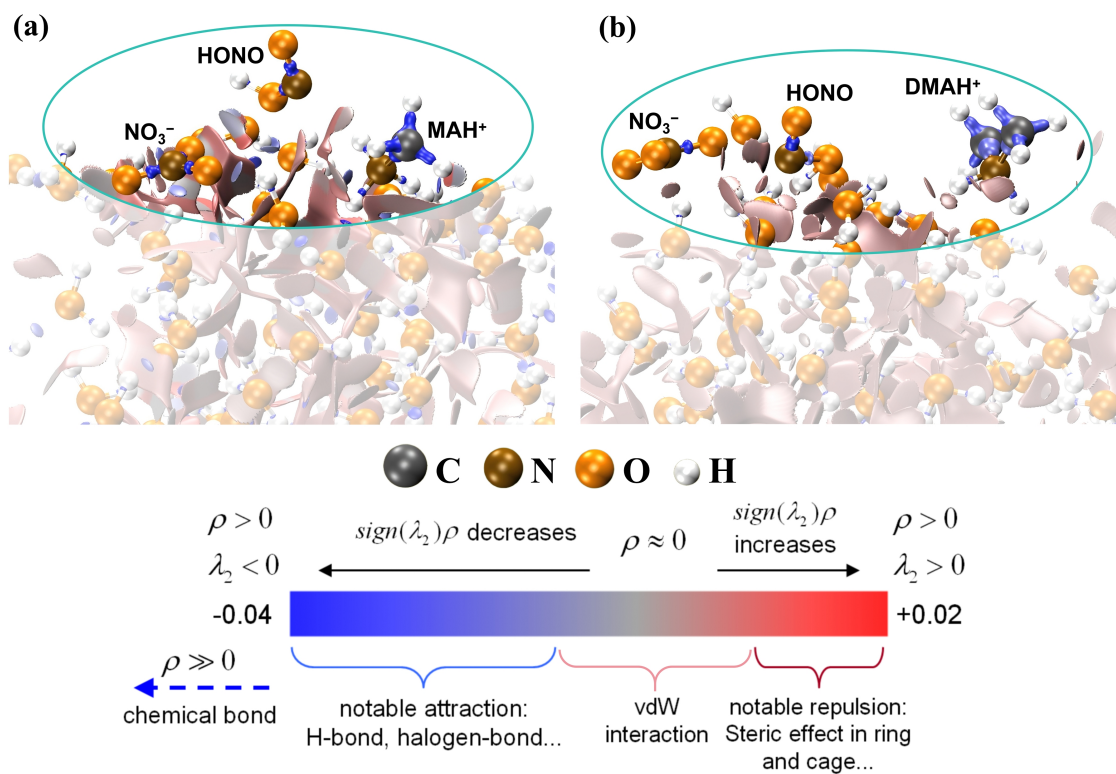
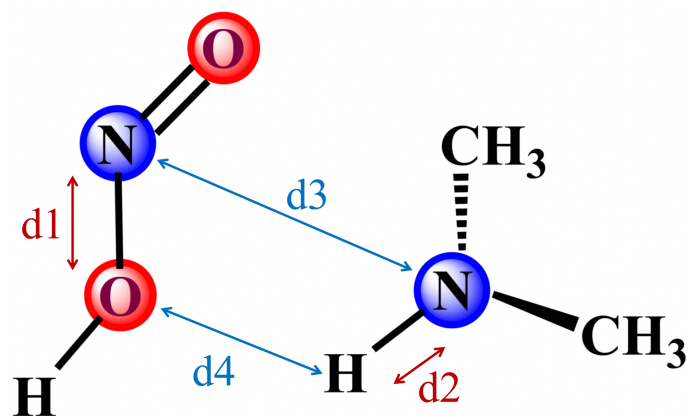


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$$d_{cv} = d1 + d2 - d3 - d4$$

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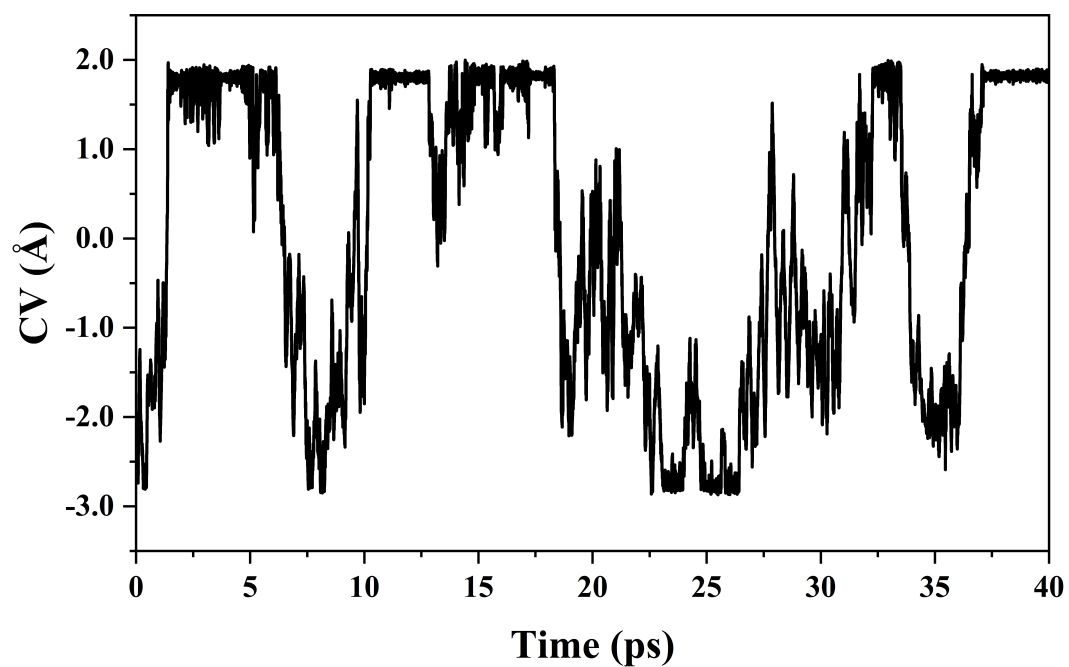


Figure S13. Convergence analysis of MetaD simulations for the N-nitrosation reaction between DMA and HONO at the air–water interface, based on the time evolution of the CV.

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