Supplemental information for:

Kinetics of associative detachment of O⁻ + N₂ and dissociative attachment of e⁻ + N₂O up to 1300 K: Chemistry relevant to modeling of transient luminous events

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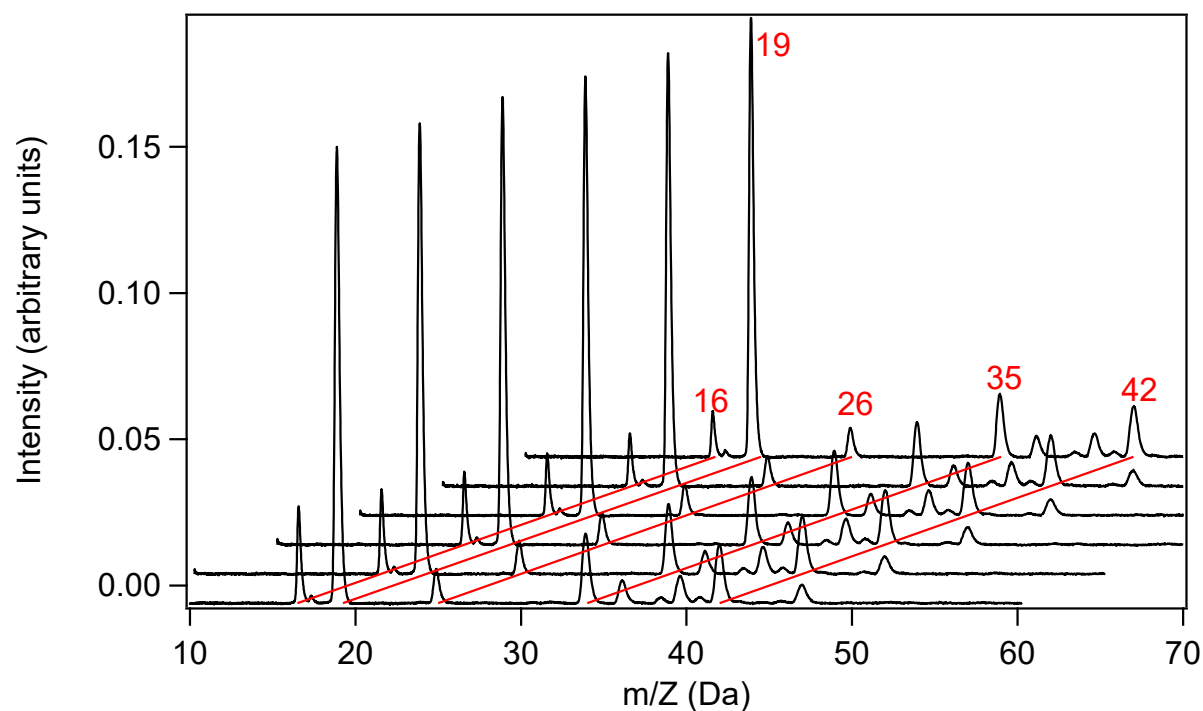*Corresponding author: rvborgmailbox@us.af.mil

Representative Data

Figure S1. Selected representative time-of-flight spectra corresponding to Figure 2 bottom at 1200 K. Spectra are offset for clarity. The N_2 concentration increases from 0 cm⁻³ to 1.0×10^{15} cm⁻³ from the bottom to the top spectrum.

Calculation of equilibrium constants

Calculating the thermodynamic equilibrium for a reaction such as $N_2O(g) + e^-(g) \rightarrow N_2(g) + O^-$ is both pretty straightforward and extremely frustrating. The fundamental relationship $\ln(K) = -\Delta G/kT$ requires calculation of ΔG, which in turn requires calculation of ΔH and ΔS to determine $\Delta G = \Delta H - T\Delta S$. We begin with the enthalpy change as a function of temperature.

The standard enthalpies of formation at 0K $\Delta_f H°_{0K}$ of all four species are extremely well-determined. The active thermochemical tables give the values for the molecular and atomic species listed in Table S1, while that of the electron and N_2 are by definition 0.

Table S1. Literature 0K enthalpies of formation

Species	$\Delta_f H°_{0K}$ (kJ mol^{-1})
N_2O	85.996 ±0.097
N_2	0
O^-	105.868 ±0.0021
e^-	0

Calculation of the enthalpy of reaction in the present case takes great care. If enthalpies of formation under the "ion convention" (e.g. from the Active Thermochemical Tables) are used, the enthalpy of the free electron must be explicitly accounted for in the calculation. i.e. for $N_2O + e^- \rightarrow O^- + N_2$

$$\Delta_r H°_T = \Delta_f H°_T(N_2) + \Delta_f H°_T(O^-) - \Delta_f H°_T(N_2O) - (H°_T - H°_{0K})(e^-)$$

Alternatively, if enthalpies of formation under the "electron convention" (e.g. from the JANAF tables or NIST Webbook) are used

$$\Delta_r H°_T = \Delta_f H°_T(N_2) + \Delta_f H°_T(O^-) - \Delta_f H°_T(N_2O).$$

Regardless of convention, compilations universally assign the enthalpy of the free electron as equal to 5/2kT, i.e. the translational enthalpy under Boltzmann statistics. Bartmess details that the electron should instead be treated under Fermi-Dirac statistics and calculates the enthalpy and entropy of the free electron assuming Fermi-Dirac statistics at discrete temperatures up to 1000 K. At temperatures not explicitly reported, the results may be parameterized using:

$$H(T) \text{ (kJ mol}^{-1}) = 5/2 \, RT - 5/2 \, RT \, [10.8/(5/2 \, RT + 10.8)]^{1.6}$$
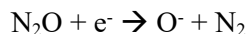
$$R = 0.00831446 \text{ kJ mol}^{-1} \text{ K}^{-1}$$

$$S(T) \text{ (J mol}^{-1} \text{ K}^{-1}) = f(0.08602 \, T - 0.00054) + (f - 1)(S_{trans}(e^-) + 6 \text{ J mol}^{-1} \text{ K}^{-1})$$

$$S_{trans}(e^-) = R[1.5 \ln(2\pi \, m_e/h^2) + 5/2 \ln(kT) - \ln(10^5 \text{ Pa}) + 2.5]$$

$$R = 8.31146 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$f = (1/[(1/(13.3e^{-0.012T}) + 0.7])^{1.11} (13.3e^{-0.012T})^{-0.11}$$

The enthalpy and entropy of the molecular species are reasonably calculated at an arbitrary temperature under harmonic oscillator and rigid rotor approximations by:

$$N_2O + e^- \rightarrow O^- + N_2$$

$\Delta_r H°_{0K} = \Delta_f H°_{0K}(O^-) - \Delta_f H°_{0K}(N_2O) = 105.868 ±0.0021 \text{ kJ mol}^{-1} - 85.996 ±0.097 \text{ kJ mol}^{-1} = 19.872 ±0.097 \text{ kJ mol}^{-1}$

as $\Delta_f H°_{0K}(N_2)$ and $\Delta_f H°_{0K}(e^-) = 0$.

$\Delta_r H^\circ_T = \Delta_r H^\circ_{0K} + (H^\circ_T - H^\circ_{0K})(N_2) + (H^\circ_T - H^\circ_{0K})(O^-) - (H^\circ_T - H^\circ_{0K})(N_2O) - (H^\circ_T - H^\circ_{0K})(e^-)$

$(H^\circ_T - H^\circ_{0K}) = H_{trans}(T) + H_{vib}(T) + H_{rot}(T) + H_{elec}(T) + pV$

Where for atomic and molecular species

$H_{trans}(T) = 3/2 \, kT$

$H_{vib}(T) = \Sigma^i \, \upsilon_i/(e^{\upsilon i/kT} - 1)$ where i indicates the vibrational mode and υ_i is the fundamental frequency

$(N_2 \, \upsilon = 2358.57 \text{ cm}^{-1}, N_2O \, \upsilon_{1-4} = 589, 589, 1285, 2224 \text{ cm}^{-1})$

$H_{rot}(T) = n/2 \, kT$ where n is the number of rotational degrees of freedom

$H_{elec}(T) = \Sigma^i \, P_i E_i$ where P_i is the population and E_i is the energy of electronic state i

$\Delta_r S_T = S_T(N_2) + S_T(O^-) - S_T(N_2O) - S_T(e^-)$

$S_T = S_{trans}(T) + S_{vib}(T) + S_{rot}(T) + S_{elec}(T)$

$S_{trans}(T) = R[3/2\ln(2\pi m/h^2) + 5/2\ln(kT) - \ln(P) + 2.5]$

$S_{vib}(T) = R[\Sigma^i \, \alpha e^{-\alpha} / (1-e^{-\alpha}) - \ln(1-e^{-\alpha})]$ where $\alpha = hc\upsilon_i/kT$

$S_{rot}(T) = R[\ln(\pi^{1/2}(kT)^n/(\sigma B)+n]$ where σ is the rotational symmetry number ($\sigma_{N2} = 2$; $\sigma_{N2O} = 1$), n is the number of rotational degrees of freedom, and B is the geometric means of the rotational constant(s) ($B_{N2} = 1.989581 \text{ cm}^{-1}$; $B_{N2O} = 0.41901 \text{ cm}^{-1}$).

The calculated enthalpies, entropies, free energies, and equilibrium constants appear in Table S2 and Figures S1 – S4.

Table S2. Calculated reaction enthalpies, entropies, free energies, and equilibrium constants for $O^- + N_2$ → $e^- + N_2O$

T(K)	$\Delta_r H^\circ_T$ (kJ mol^{-1})	$\pm$	$\Delta_r S_T$ (J mol^{-1} K^{-1})	$\pm$	$\Delta_r G_T$ (kJ mol^{-1})	$\pm$	K
300	-22.3312	0.2	-107.366	0.09	9.87871	0.2	0.0191
400	-21.5692	0.2	-104.805	0.12	20.353	0.2	0.00220
500	-20.3229	0.2	-101.952	0.15	30.65313	0.3	0.000628
600	-18.7384	0.2	-99.0546	0.18	40.69433	0.3	0.000287
700	-16.9159	0.2	-96.2433	0.21	50.45439	0.3	0.000172
800	-14.9241	0.2	-93.5874	0.24	59.94584	0.3	0.000122
900	-12.8103	0.2	-91.1102	0.27	69.18886	0.3	9.65E-05
1000	-10.6076	0.2	-88.8099	0.3	78.20228	0.4	8.23E-05
1100	-8.33903	0.2	-86.6739	0.33	87.00224	0.4	7.39E-05
1200	-6.02089	0.2	-84.6863	0.36	95.6027	0.4	6.9E-05
1300	-3.66498	0.2	-82.8315	0.39	104.016	0.4	6.62E-05
1400	-1.27991	0.2	-81.0951	0.42	112.2532	0.5	6.48E-05
1500	1.127943	0.2	-79.4642	0.45	120.3243	0.5	6.46E-05

| 1600 | 3.553784 | 0.2 | -77.9279 | 0.48 | 128.2384 | 0.5 | 6.51E-05 |
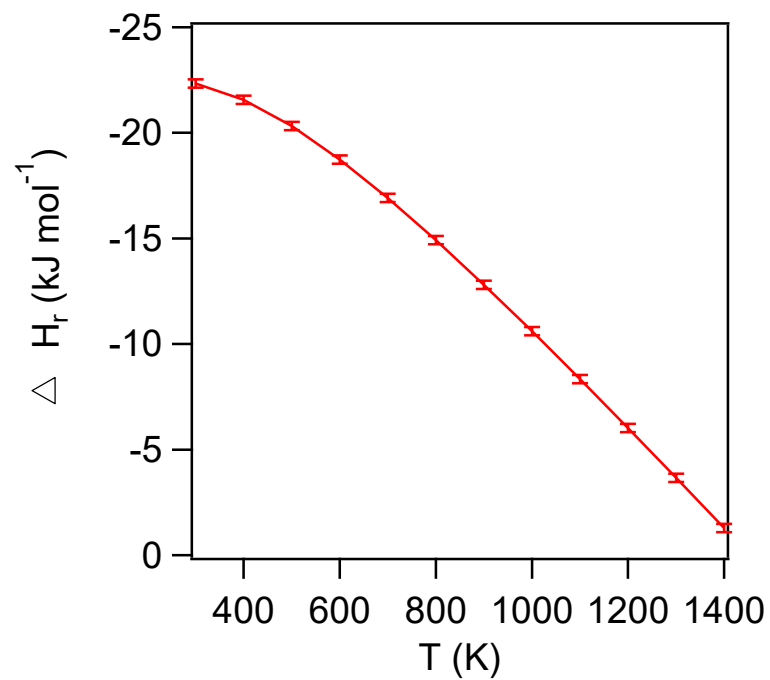
Figure S2. $O^- + N_2 \rightarrow N_2O + e^-$ enthalpy of reaction as a function of temperature.
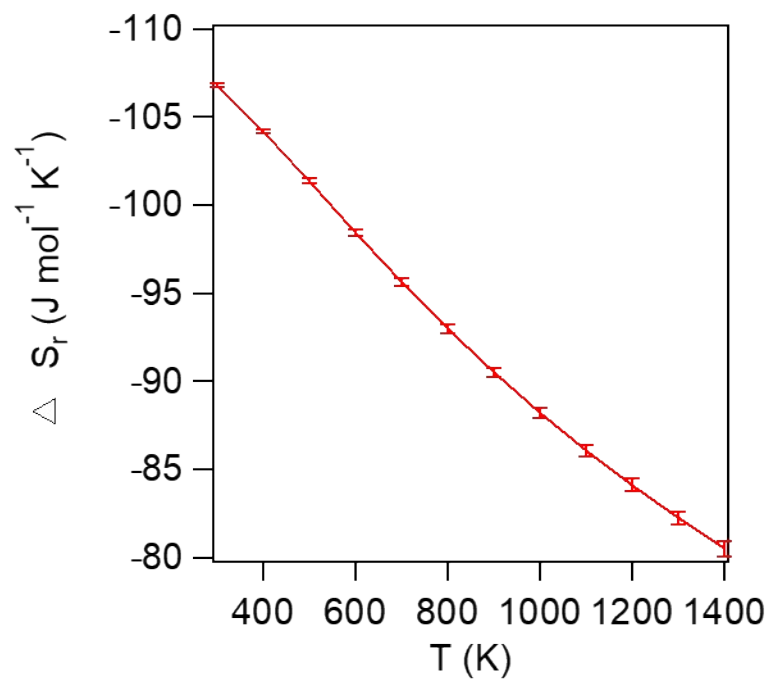
Figure S3. O⁻ + N₂ → N₂O + e⁻ entropy of reaction as a function of temperature.
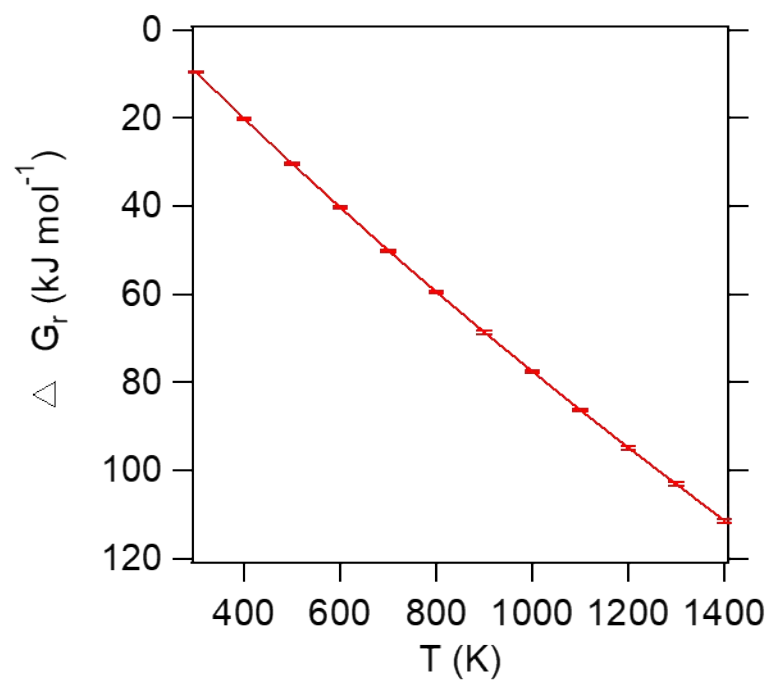
Figure S4. O⁻ + N₂ → N₂O + e⁻ free energy of reaction as a function of temperature.
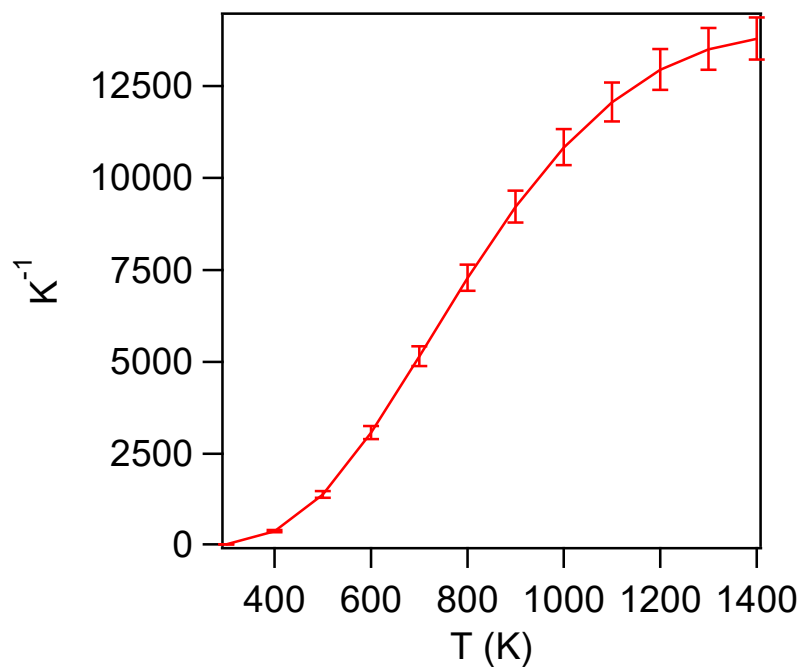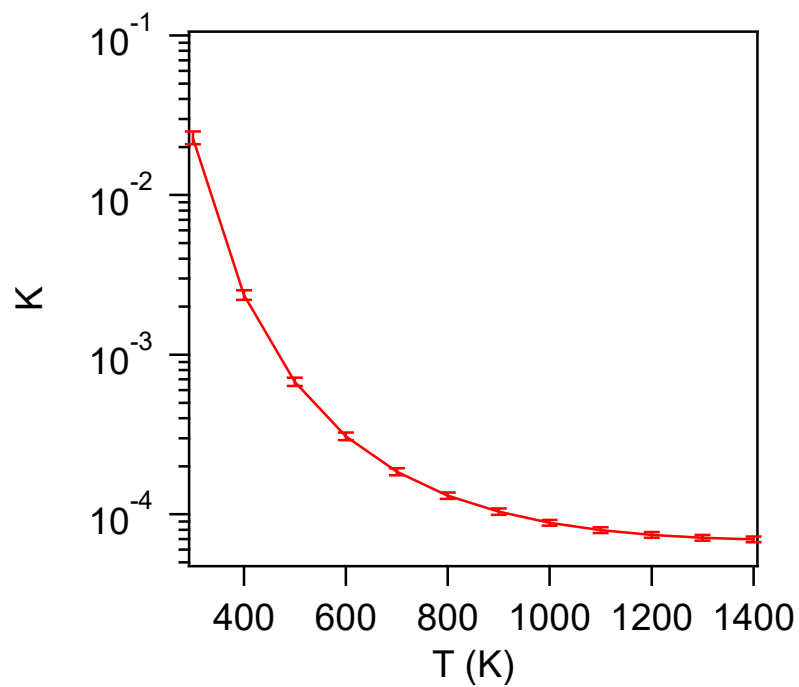
Figure S5. $O^- + N_2 \longleftrightarrow N_2O + e^-$ equilibrium constants (top) and their inverse (bottom) as a function of temperature.

Quantum Chemical Calculations
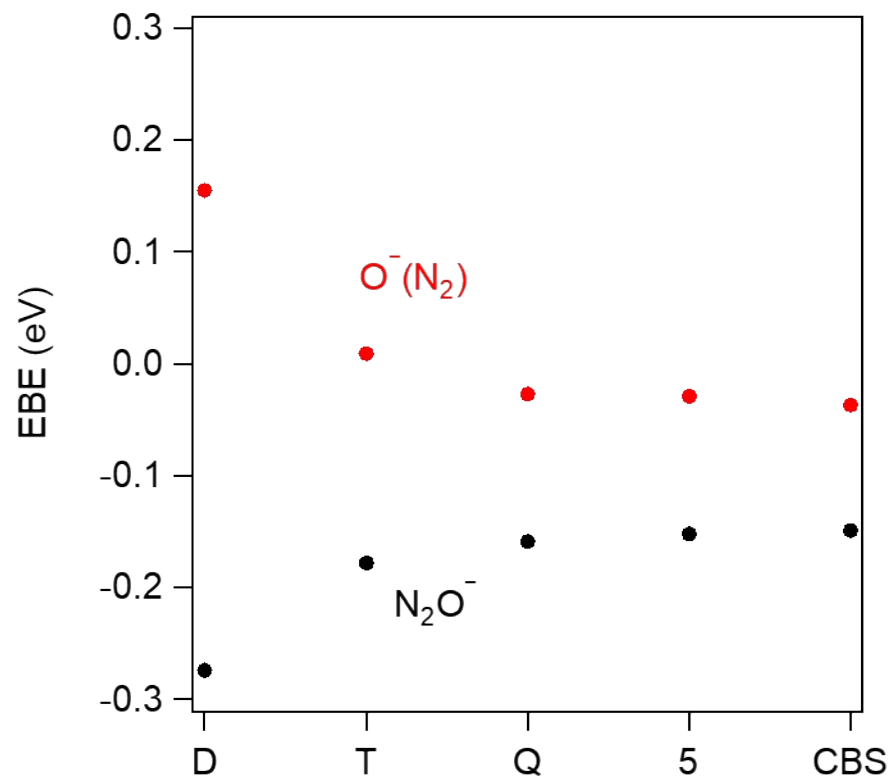
Figure S6. Zero-point corrected electron binding energies for N_2O^- (black) and $O^-(N_2)$ (red) calculated at the CCSD(T)/aug-cc-pVXZ level. Not shown is the higher energy c_2v structure, which extrapolates to -2.69 eV at the same CBS level.
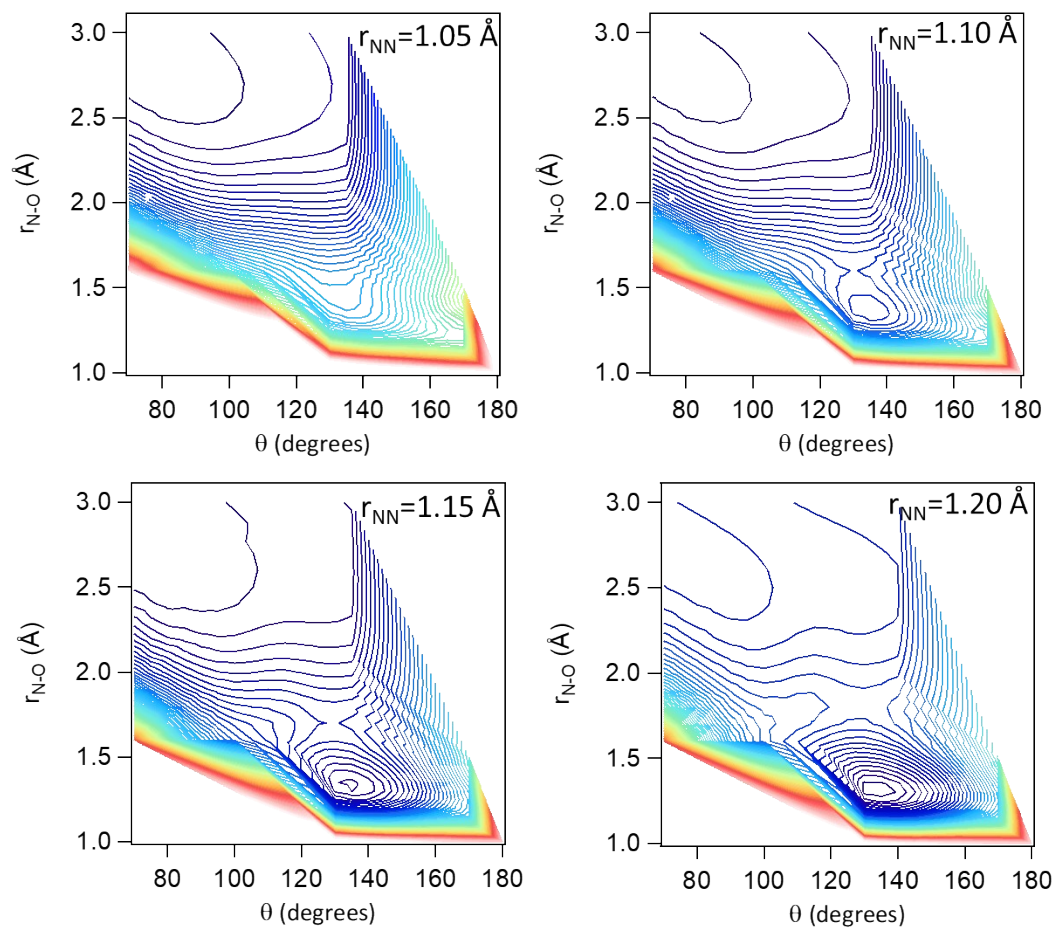
Figure S7. Slices of the N_2O^- potential surface at the indicated r_{NN} calculated at the CCSD(T)/aug-cc-pVTZ level. Color scale is the same as Figure 6. Contour spacing is 0.05 eV.
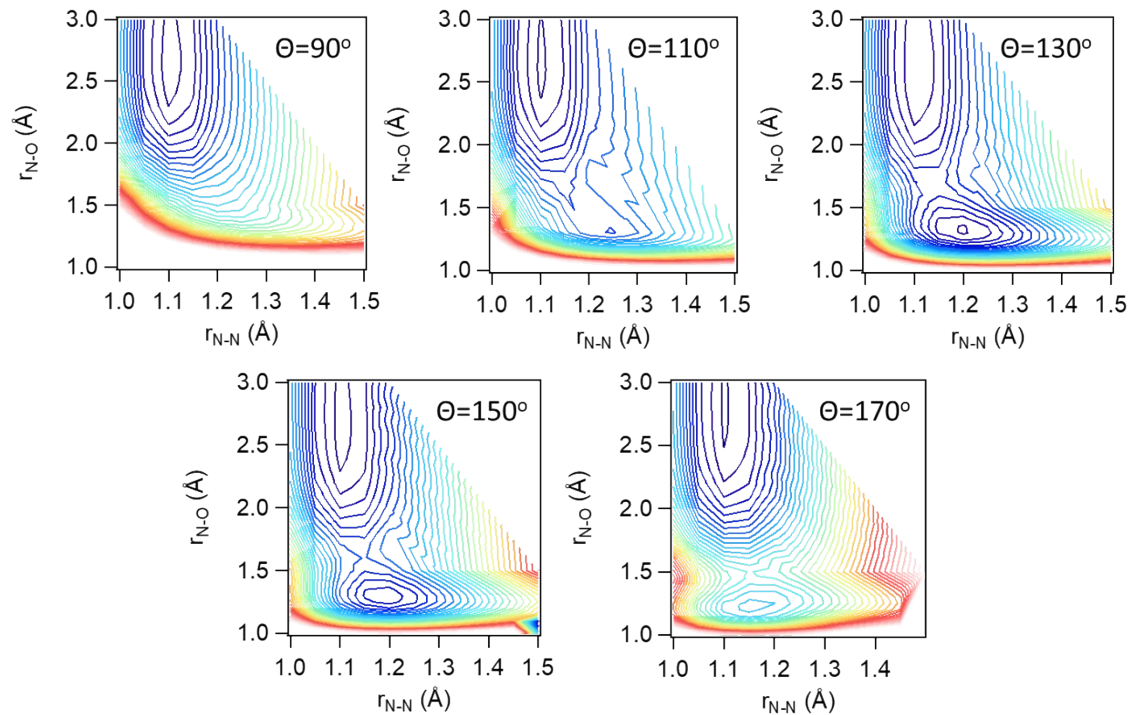
Figure S8. Slices of the N_2O^- potential surface at the indicated Θ calculated at the CCSD(T)/aug-cc-pVTZ level. Color scale is the same as Figure 6. Contour spacing is 0.1 eV.

$O^- + N_2$ vibrational model

The N_2O^- transition state energy is parameterized as:

$E(r,\Theta)$ (eV) $= (294907r^6 - 2002078r^5 + 5656687r^4 - 8514277r^3 + 7200720r^2 - 3244449r + 608493.58)f(\Theta)$

$f(\Theta) = e^{(\Theta_{TS} - \Theta)/29.7} \mid \Theta < \Theta_{TS}$

$\quad\quad = e^{(\Theta - \Theta_{TS})/17.9} \mid \Theta \geq \Theta_{TS}$

where $r = r_{NN}$ in Å, Θ is as defined in Figure 1, and $\Theta_{TS} = 135°$.

The probability distribution functions of r_{NN} in the entrance channel is approximated as that of an isolated N_2 molecule:

$P(r_{NN},n) = [(2^n n!)^{-0.5} (\mu_m\omega/\pi\hbar)^{0.25}\exp(-\mu_m\omega r_{NN}^2/2\hbar)H_n((\mu_m\omega/\hbar)^{0.5}r_{NN})]^2$

Where n is the vibrational state of N_2, μ_m is the reduced mass of N_2, ω is the harmonic frequency, and H_n are the physicist's Hermite polynomials.

The probability κ of crossing from the N_2O^- to the N_2O surface is calculated as a function of the collision velocity as

$\kappa(T) = e^{-cT^{1/2}}$

where T is the reaction temperature and c is a fitting parameter, determined here to be 0.075 $K^{-1/2}$.

The vibrational state-specific rate constant, where $E_v(n)$ is the vibrational energy in vibrational state n, is calculated as:

$k(n,T)=\kappa(T)\Sigma_{r_{NN}} \Sigma_\Theta P(r_{NN},n)\exp(-(E(r_{NN},\Theta)-E_v(n))/kT)$

Table S3. Vibrationally-resolved rate constants for $O^- + N_2$ derived via 'Model 2' as described in the text as a function of temperature.

T (K)	v = 0	v = 1	v = 2
		k (cm^3 s^{-1})	
200	2.3×10^{-20}	5.4×10^{-13}	1.7×10^{-11}
300	1.1×10^{-17}	9.9×10^{-13}	1.4×10^{-11}
400	2.2×10^{-16}	1.3×10^{-12}	1.2×10^{-11}
500	1.3×10^{-15}	1.5×10^{-12}	1.1×10^{-11}
600	4.6×10^{-15}	1.6×10^{-12}	9.4×10^{-12}
700	1.1×10^{-14}	1.6×10^{-12}	8.4×10^{-12}
800	2.0×10^{-14}	1.7×10^{-12}	7.6×10^{-12}
900	3.3×10^{-14}	1.7×10^{-12}	6.9×10^{-12}
1000	4.9×10^{-14}	1.7×10^{-12}	6.3×10^{-12}
1100	6.6×10^{-14}	1.7×10^{-12}	5.8×10^{-12}
1200	8.6×10^{-14}	1.6×10^{-12}	5.3×10^{-12}
1300	1.1×10^{-13}	1.6×10^{-12}	4.9×10^{-12}
1400	1.3×10^{-13}	1.6×10^{-12}	4.6×10^{-12}
1500	1.5×10^{-13}	1.5×10^{-12}	4.2×10^{-12}
1600	1.7×10^{-13}	1.5×10^{-12}	3.9×10^{-12}
1700	1.9×10^{-13}	1.5×10^{-12}	3.7×10^{-12}
1800	2.0×10^{-13}	1.5×10^{-12}	3.4×10^{-12}
1900	2.2×10^{-13}	1.4×10^{-12}	3.2×10^{-12}
2000	2.3×10^{-13}	1.3×10^{-12}	3.0×10^{-12}

Assuming the vibrationally-resolved rate constants in Table S3, the fraction of vibrationally excited N_2 in the experiment by R&M can be estimated. Under the simplifying assumption that only $N_2(v=0)$ and $N_2(v=1)$ were present

$$f(N_2(v=1)) = 1 - \frac{k(T_{eff})_{RM} - k(T_{eff})_{v=1}}{k(T_{eff})_{v=0} - k(T_{eff})_{v=1}}$$

where $f(N_2(v=1))$ is the fraction of vibrationally excited N_2, $k(T_{eff})_{RM}$ is the rate constant reported by R&M at a given effective temperature and $k(T_{eff})_{v=n}$ are the relevant rate constants interpolated from Table S3. R&M experimental values and derived vibrationally excited N_2 fraction are shown in Table S4 and Figure S9. The derived $f(N_2(v=1))$ increases linearly with the drift field strength (Figure S9). Assuming the $f(N_2(v=1)) = 0.0062(E/n)$ from the linear regression along with the vibrationally-resolved rate constant in Table S3, the expected rate constants agree well with the values reported by R&M (Figure S10).

Table S4. Experimental values from R&M and derived fraction of vibrationally excited N_2 present in that experiment.

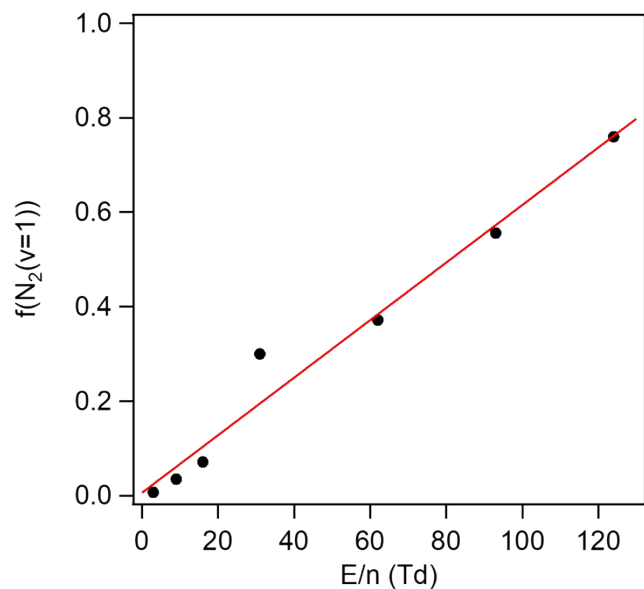| E/p (V cm^{-1} Torr^{-1})	E/n (Td)	κ_0 (cm^2 V^{-1} s^{-1})	T_{eff} (K)	k_{RM} (cm^3 s^{-1})	$k_{v=0}$ (cm^3 s^{-1})	$k_{v=1}$ (cm^3 s^{-1})	$f(N_2(v=1))$
1	3	3.00	301	6.9×10^{-15}	1×10^{-17}	1.0×10^{-12}	0.007
3	9	3.35	308	3.5×10^{-14}	2×10^{-17}	1.0×10^{-12}	0.035
5	16	3.37	322	7.8×10^{-14}	5×10^{-17}	1.1×10^{-12}	0.071
10	31	3.46	394	3.9×10^{-13}	2×10^{-16}	1.3×10^{-12}	0.30
20	62	4.00	801	6.3×10^{-13}	2×10^{-14}	1.7×10^{-12}	0.37
30	93	4.55	1758	8.9×10^{-13}	1.9×10^{-13}	1.5×10^{-12}	0.56
40	124	4.8	3185	9.9×10^{-13}	3.1×10^{-13}	1.2×10^{-12}	0.76

Figure S9. Derived fraction of vibrationally excited N_2 present in the R&M experiment as a function of the field strength in the drift tube (solid points). Line is a linear regession.
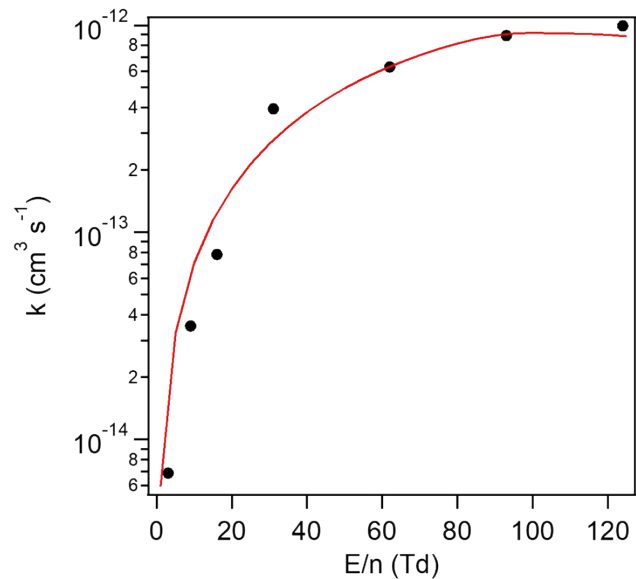
Figure S10. Reported rate constant of $O^- + N_2$ as a function of field strength reported by R&M (solid points) and predicted values using the vibrationally resolved rate constants reported in Table S3 and fraction of vibrationally excited N_2 $f(N_2(v=1)) = 0.0062(E/n)$ from the linear regression .
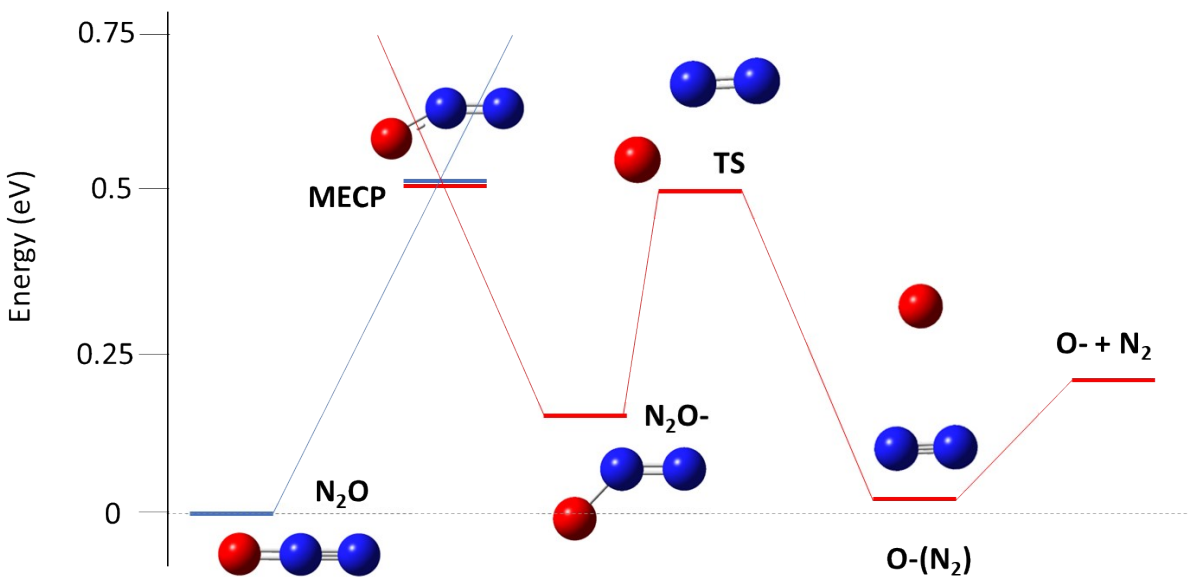

Figure S11. Low-lying stationary points in the N_2O (blue) and N_2O^- (red) systems optimized at the CCSD(T)/CBS(aug-pVXZ X=T,Q,5)//CCSD(T)/aug-cc-pVTZ level.

Table S5. Stationary point geometries CCSD(T)/aug-cc-pVTZ, electronic energies CCSD(T)/CBS(aug-pVXZ X=T,Q,5)//CCSD(T)/aug-cc-pVTZ, zero point energies, and harmonic frequencies.

	E(CBS) (Hartree)	ZPE (Hartree)	r_{NN} (Å)	r_{NO} (Å)	Θ (deg.)	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})
N_2O	-184.47933	0.01080	1.1326	1.1911	180.0	(593.3)x2	1287.06	2268.18
N_2O^-	-184.47386	0.00742	1.1917	1.3167	133.7	618.66	933.20	1704.95
$O^-(N_2)$	-184.47800	0.00581	1.1052	2.7315	78.3	92.78	133.79	2324.24
TS	-184.46562	0.00553	1.1379	1.6753	129.3	566.89i	423.48	2003.72
MECP	-184.46930	-	1.1500	1.2500	151.0	-	-	-