Spin-Orbit Charge Transfer & Nitrosation of Guanine Radical Cations by Nitric Oxide — Mechanisms, Kinetics, and Dynamics

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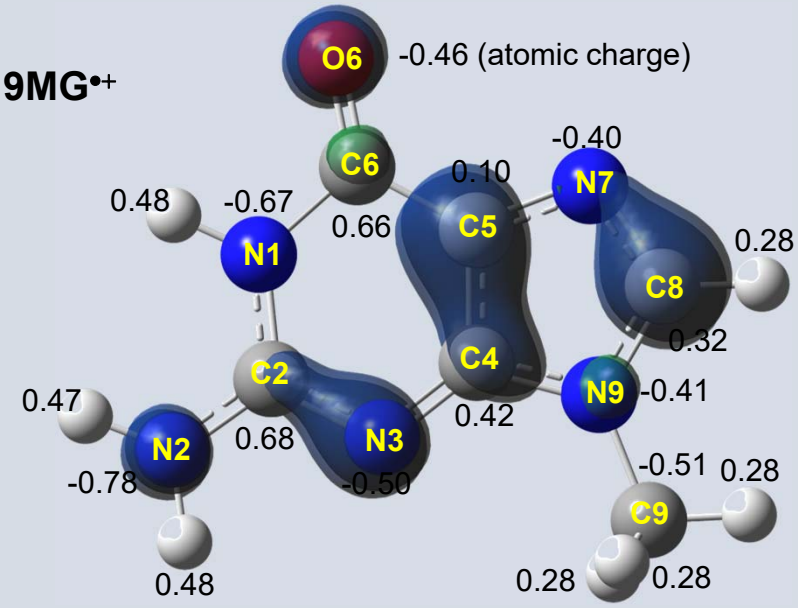
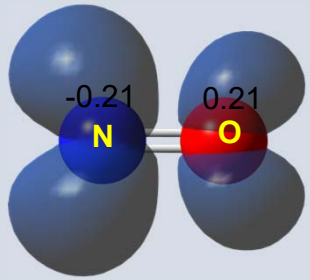
Biological Relevance of $G^{\bullet+}$ + $^{\bullet}NO$

9MG$^{\bullet+}$



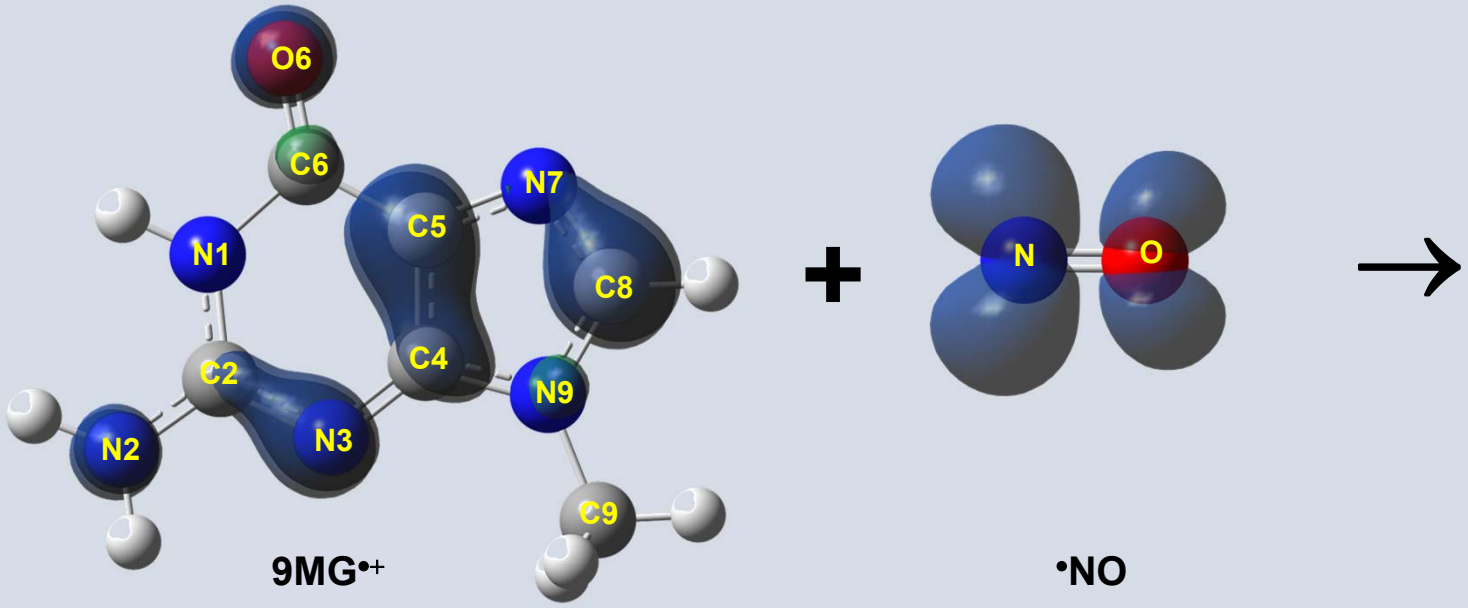
$^{\bullet}NO$



Formation of **9MG$^{\bullet+}$** (a guanosine-mimicking model compound) represents a consequence of DNA oxidative damages upon *ionization* and oxidation

$^{\bullet}NO$, a precursor to reactive nitrogen species (RNS) in biological systems, participates directly in numerous processes including enhancing DNA radiosensitivity in *ionizing radiation*-based radiotherapy.

Spin Dynamics of $9MG^{\bullet+}$ + $^{\bullet}NO$



Singlet (population: 25%)

$^{OS}[9MG^{\bullet+}(\uparrow) \cdots ^{\bullet} \mathrm{NO}(\downarrow) - 9MG^{\bullet+}(\downarrow) \cdots ^{\bullet} \mathrm{NO}(\uparrow)]/\sqrt{2}$

(or $^{CS}[9MG(\uparrow\downarrow) \cdots ^{+}\mathrm{NO}]$ with charge transfer)

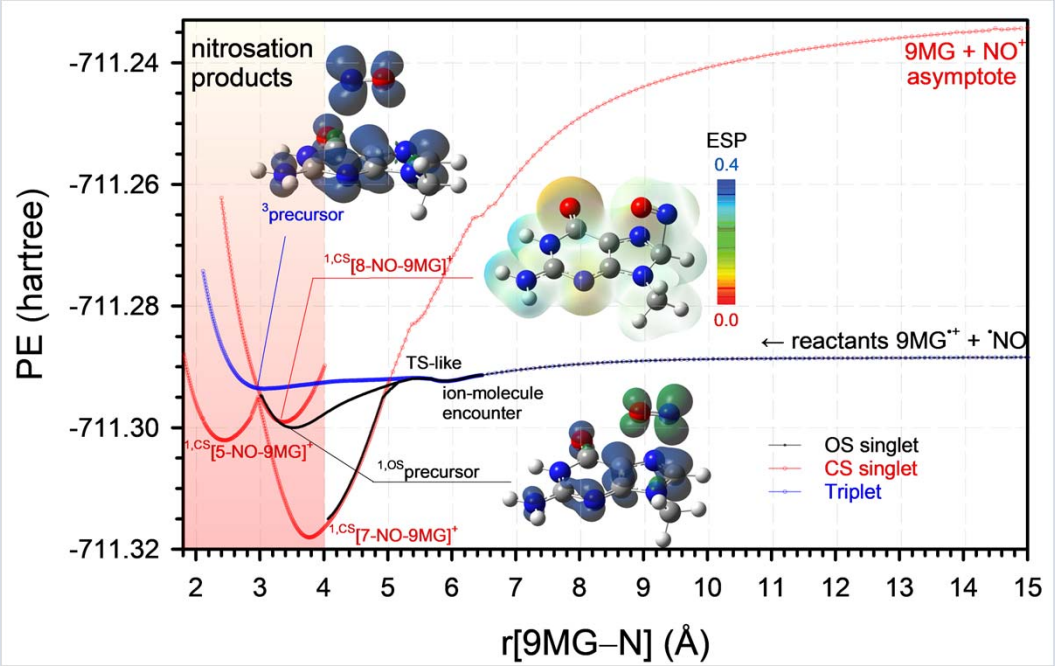
Triplet (75%)

$\mathbf{T_0}$: $[9MG^{\bullet+}(\uparrow) \cdots ^{\bullet} \mathrm{NO}(\downarrow) + 9MG^{\bullet+}(\downarrow) \cdots ^{\bullet} \mathrm{NO}(\uparrow)]/\sqrt{2}$

$\mathbf{T_+}$: $9MG^{\bullet+}(\uparrow) \cdots ^{\bullet} \mathrm{NO}(\uparrow)$

$\mathbf{T\_}$: $9MG^{\bullet+}(\downarrow) \cdots ^{\bullet} \mathrm{NO}(\downarrow)$

Influences of Spin Dynamics on Reaction

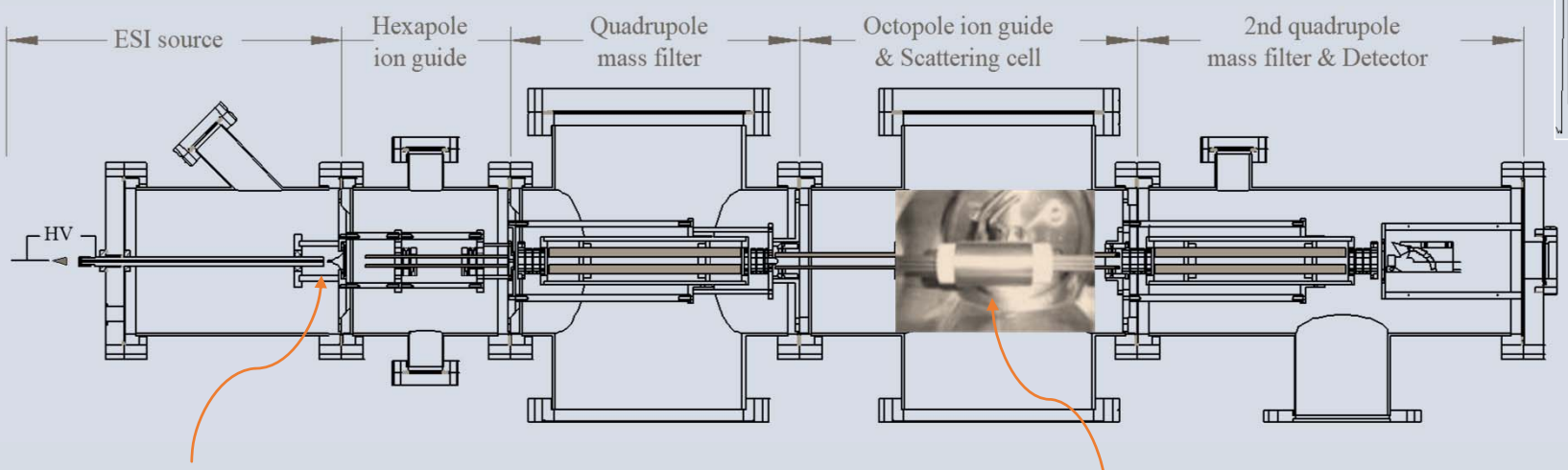


— open-shell (OS) singlet
— closed-shell (CS) singlet
— triplet

Critical processes: ion-molecule collision, ^{1,OS}precursor, ^{3}precursor, internal conversion, intersystem crossing

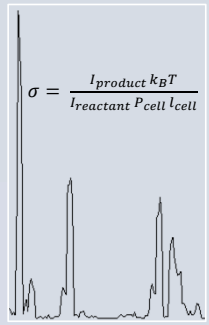
Products: charge transfer and $[X\text{-NO-9MG}]^{+}$

Explore Spin Dynamics and Products Using ESI Guided-Ion Beam Tandem MS



Beer-Lambert Law

$$\sigma = \frac{I_{product}\, k_B T}{I_{reactant}\, P_{cell}\, l_{cell}}$$



Data Interpretation

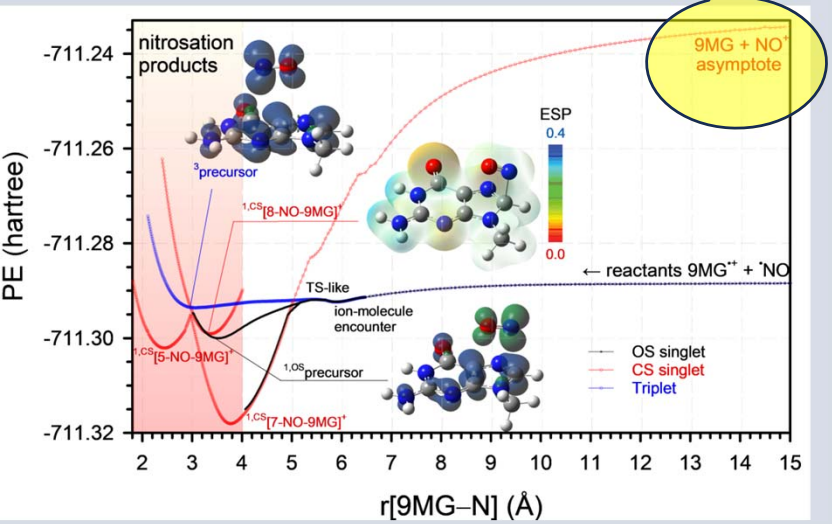
target gas
$^{\bullet}NO$

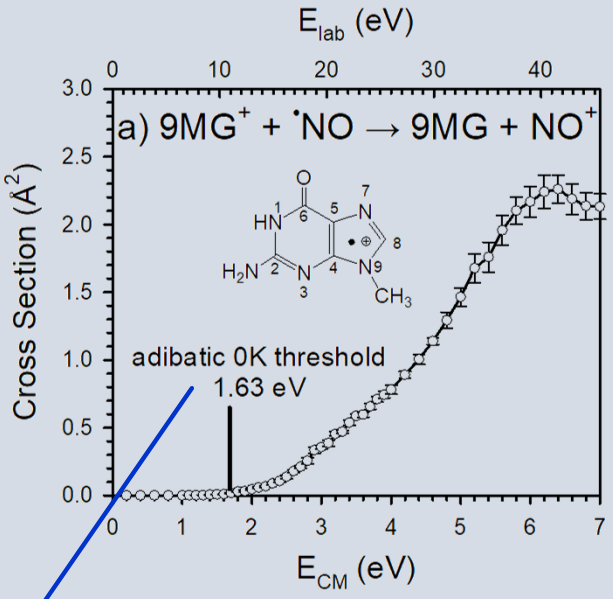
Y. Fang and J. Liu, *J. Phys. Chem. A*, 2009, ***113***, 11250

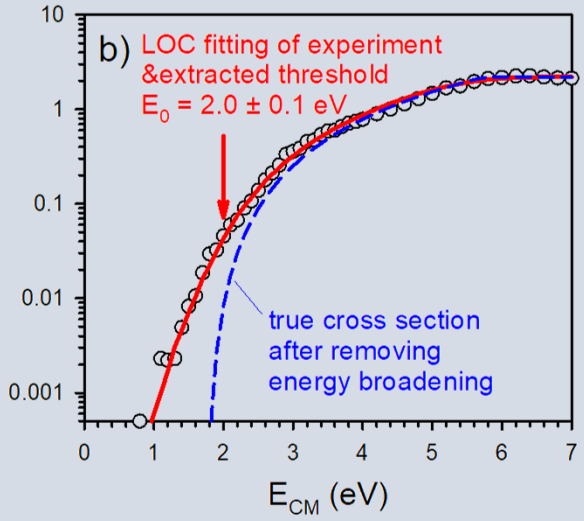
Formation of reactant radical cations via redox separation:

$[Cu^{II}9MG_3]^{\bullet 2+} \rightarrow [Cu^{I}9MG_2]^{+} + 9MG^{\bullet +}$

Experiment 1: Spin-Orbit Charge Transfer







= IP (•NO) – IP(9MG)

= 9.2643 – 7.63

= 1.63 eV

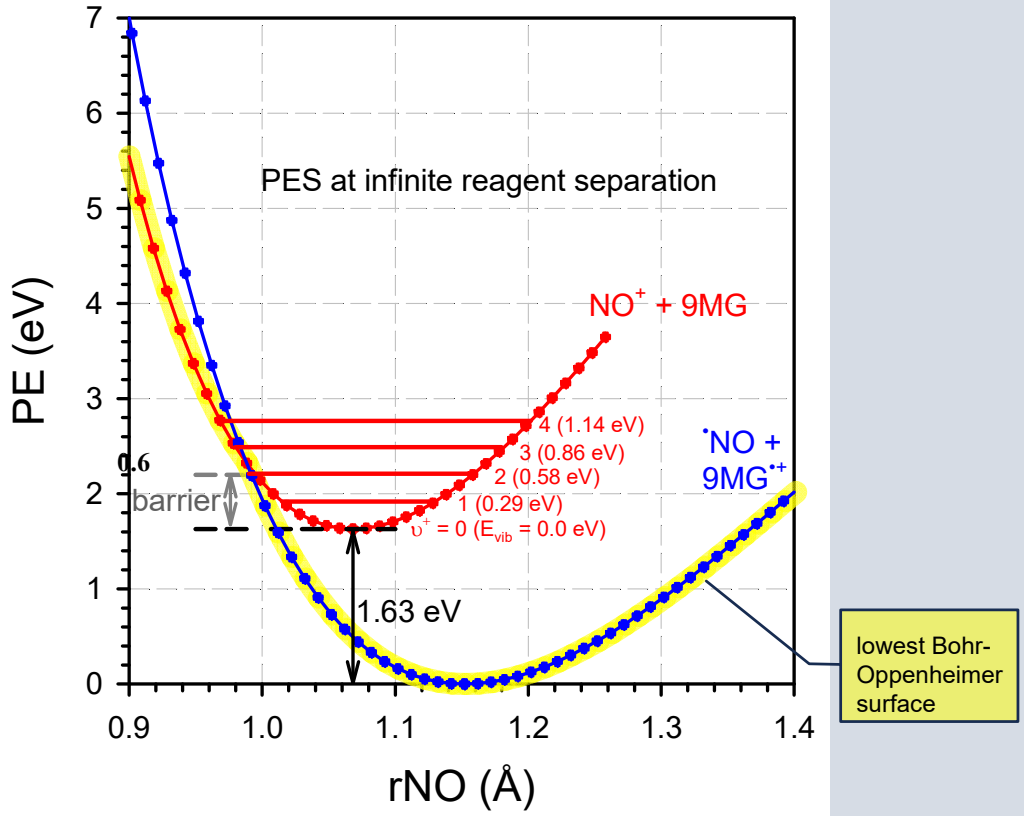
Line–of–Centers (LOC): $\sigma(E) = \sigma_0 \dfrac{(E_{\mathrm{CM}} + E_{\mathrm{vib}} + E_{\mathrm{rot}} - E_0)^n}{E_{\mathrm{CM}}}$

Exp E_0 (0 K) = 2.0 eV

ΔE (0 K adiabatic – Exp) = 0.36 eV

Benny and Liu, *J. Chem. Phys*, 2023, **159**, 085102

Rationalization of *Extra* Threshold Energy in a Frank-Condon Scheme



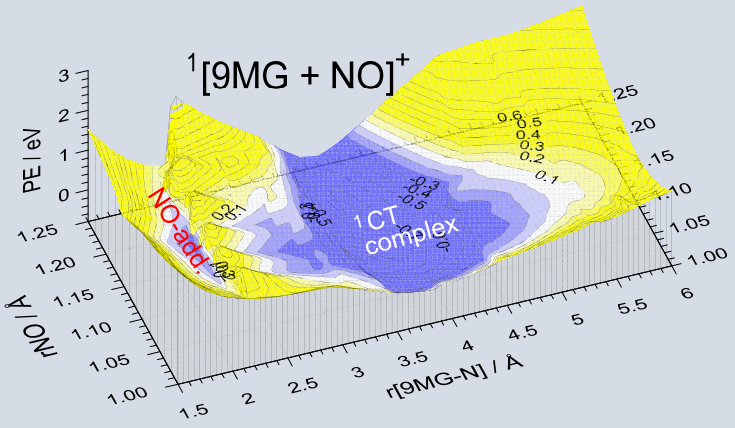
A qualitative PES at infinite reagent separation for (blue) $9MG^{\bullet+}$ + $^{\bullet}NO(X^2\Pi)$ vs. (red) 9MG + $NO^+(X^1\Sigma^+)$

2D-Surface Crossing toward Spin-Orbit Charge Transfer

Singlet

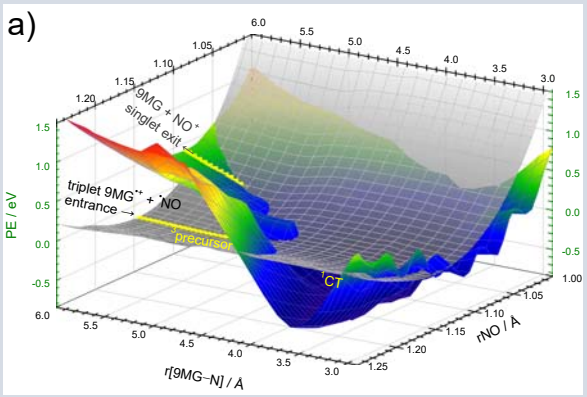
$9MG^{\bullet+}(\uparrow) + {}^{\bullet}NO(X^2\Pi, \downarrow) \xrightarrow{internal\ conversion} 9MG + NO^+(X^1\Sigma^+)$

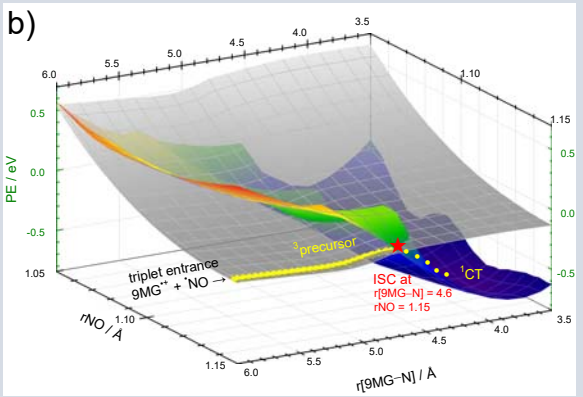
Singlet does not require extra barrier for CT, therefore is excluded!

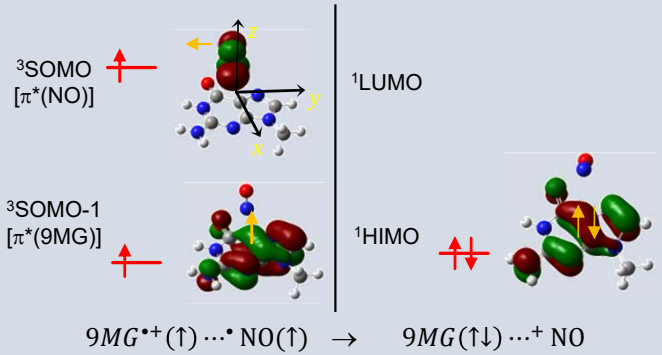


Triplet superimposed on singlet

$9MG^{\bullet+}(\uparrow) + {}^{\bullet}NO(X^2\Pi, \uparrow) \rightarrow {}^3precursor \xrightarrow{intersystem\ crossing} 9MG + NO^+(X^1\Sigma^+)$

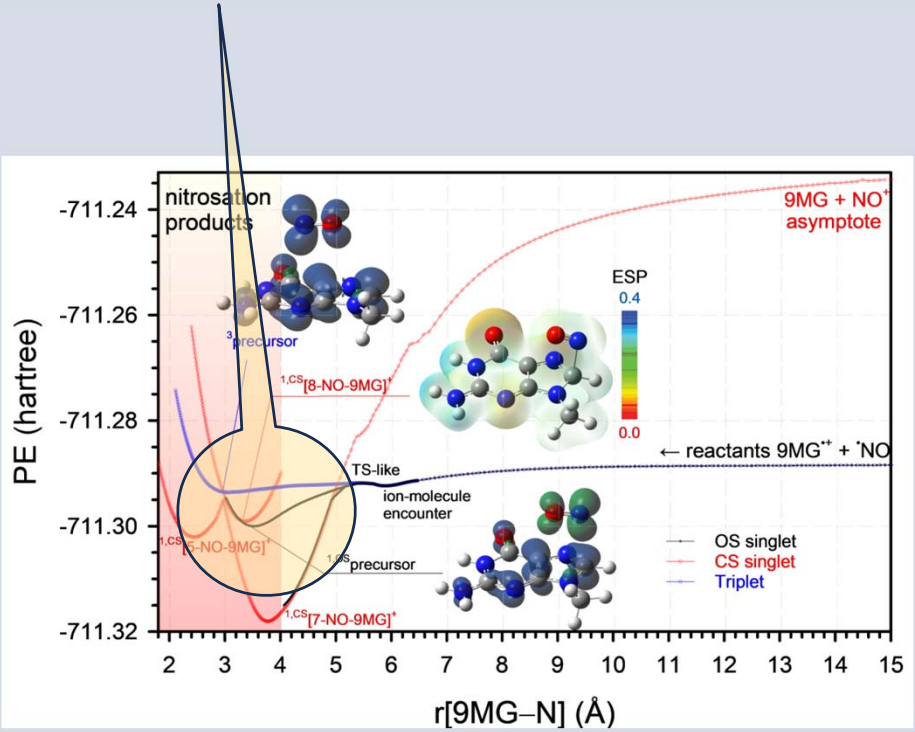






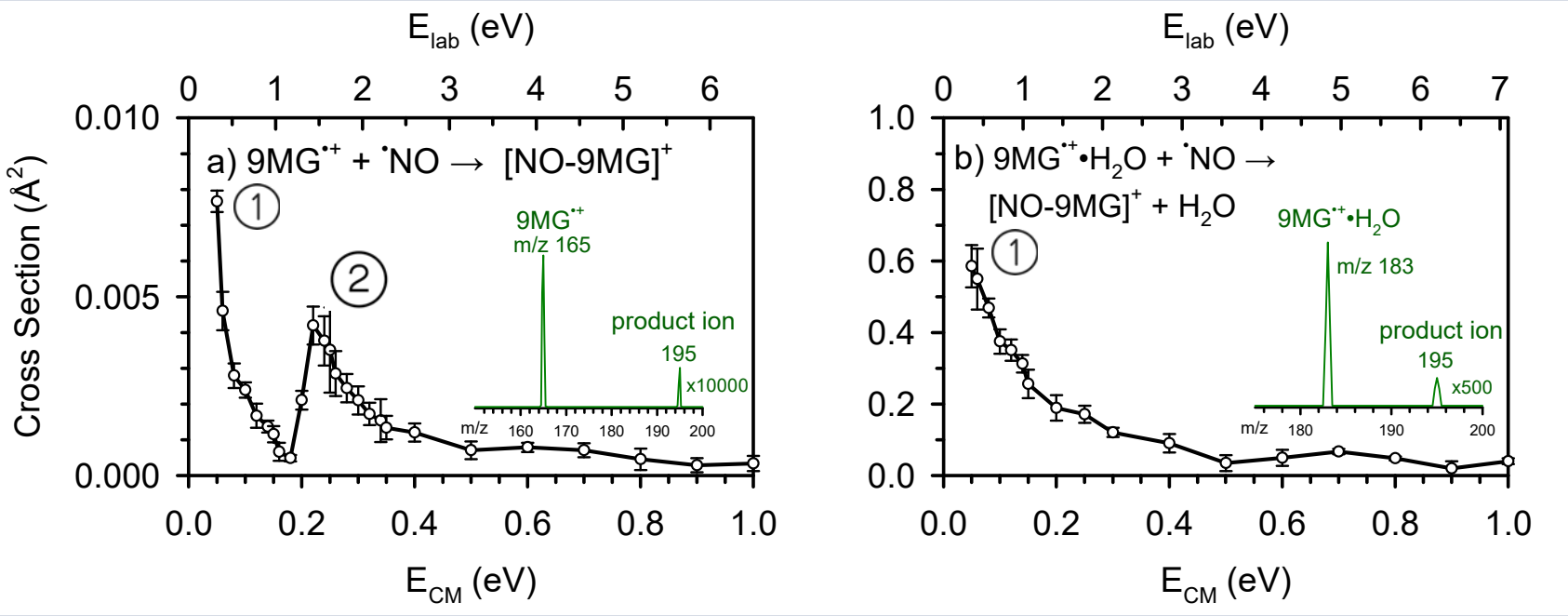
- The ***electron*** in ^{3}SOMO rephrases spin & merges to orthogonal ^{3}SOMO-1
- ***Spin*** momentum changes also induces ***orbit*** momentum change to conserve total angular momentum → ***spin-orbit charge transfer***
- **ISC** occurs at constant of rNO 1.15 Å, corresponding to NO^+ ($v^+ = 1$) → The amount that exceeds the 0 K threshold

Experiment 2: Nitrosation at Short-range Interaction and Different Spin States



Monitor dynamics,
as a function of collision energy,
from ^{1,3}precursor complexes
to various covalent adducts.

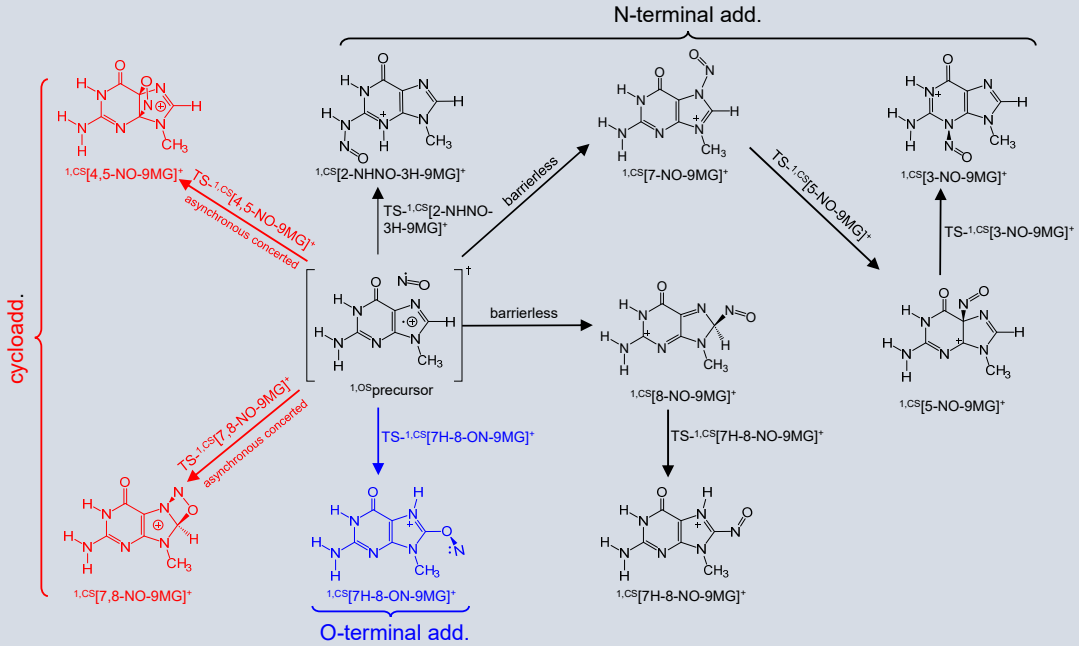
Nitrosation Product Cross Sections



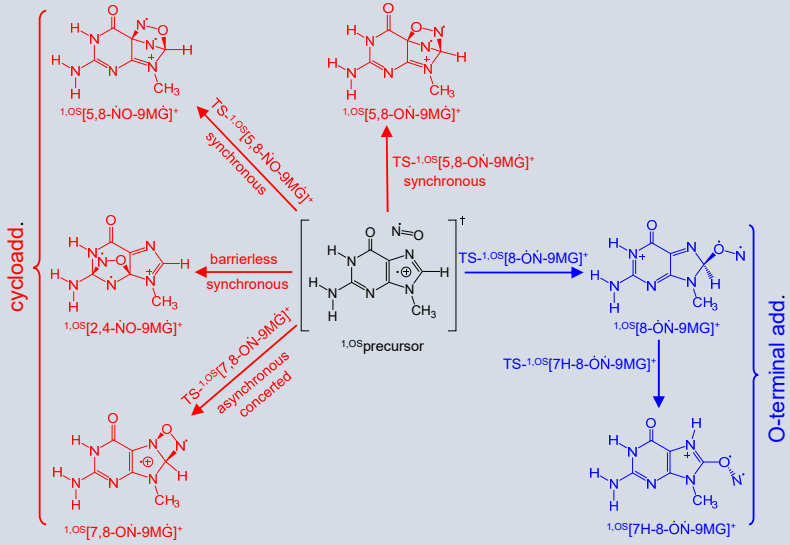
1) The first channel is exothermic with product heat release > 0.65 eV
   (calibrated using water-dissociation in nitrosation of hydrated $9MG^{\bullet+}$, see Fig. b)
2) The second channel is endothermic with product ΔH of approximate +0.6 eV

Numerous possible singlet reaction pathways/products predicted by DFT

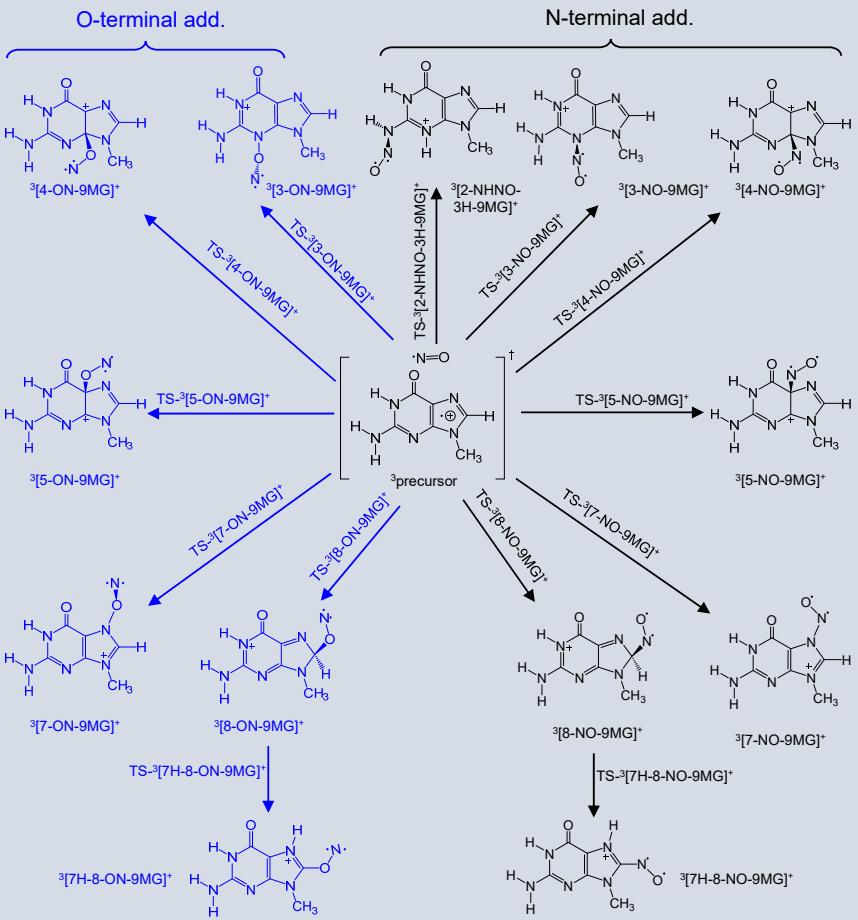
In the closed-shell singlet

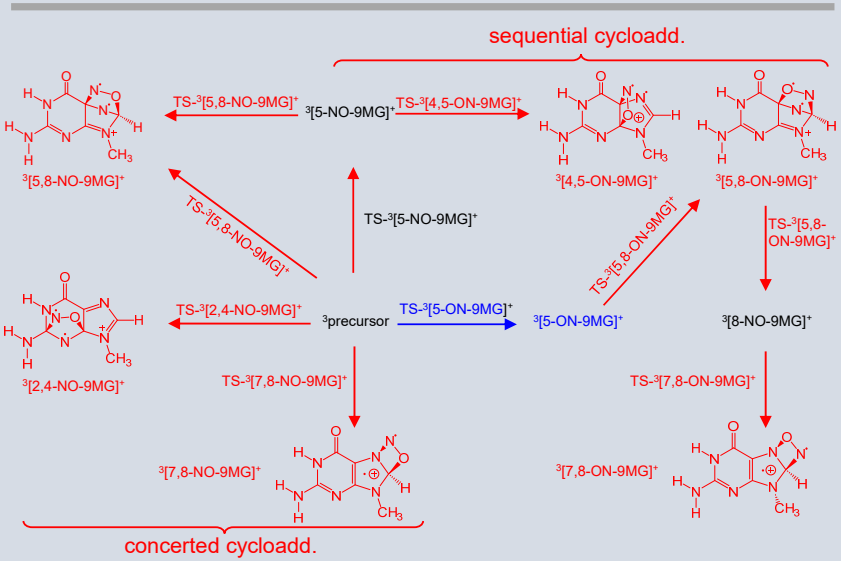


In the open-shell singlet

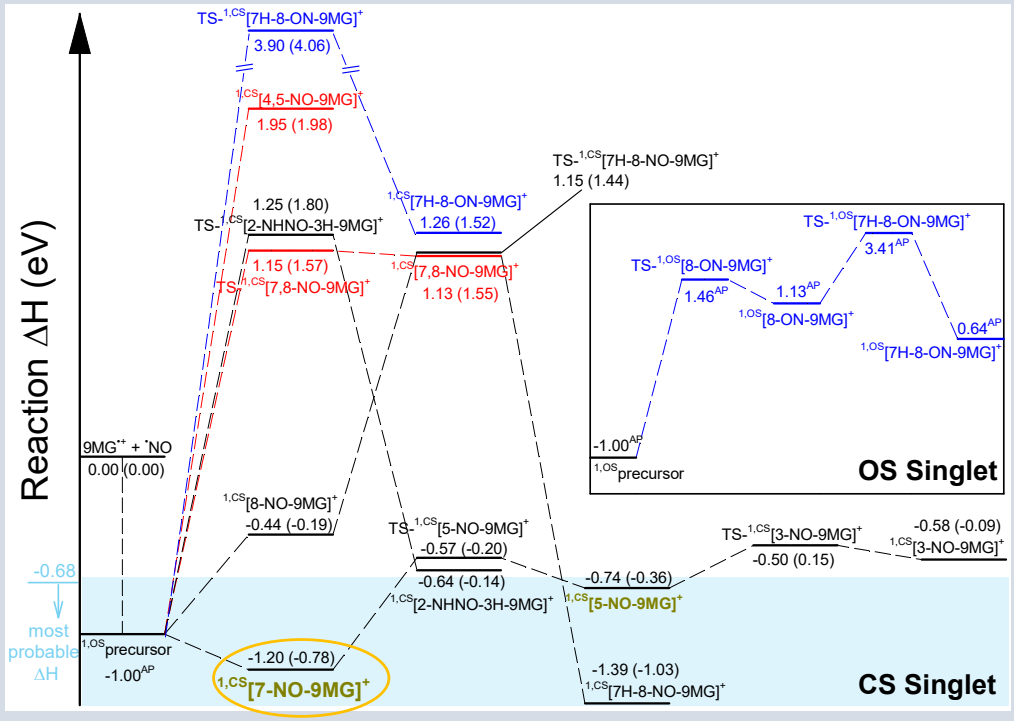


As well as in the triplet





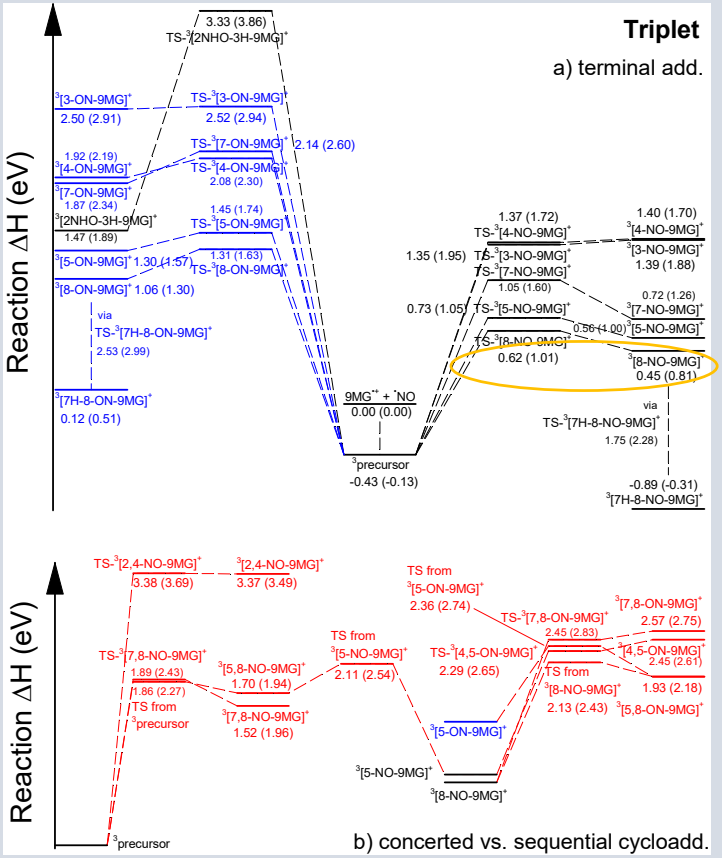
Identify Product Structures



Two possible exothermic products:

^{1,CS}[7-NO-9MG]$^+$ and ^{1,CS}[5-NO-9MG]

of which ^{1,CS}[7-NO-9MG]$^+$ is the most probable



Only product with endothermicity ~0.6 eV:

^{3}[8-NO-9MG]$^+$

Conclusions

Guided-ion beam mass spectrometry measurement of kinetic-energy resolved reactions, *combined with* electronic theory, advances the chemistry assessment between DNA nucleobase radicals and •NO:

Among > 30 potential reaction structures, we identified ^{1,CS}**[7-NO-G]**$^{+}$ as the only exothermic product and ^{3}**[9MG**$^{\bullet+}$**(↑)···(↑)•NO]** precursor that is responsible for the formation of endothermic ^{3}[8-NO-G]$^{+}$ at low energies and for spin-orbit charge transfer at high energies.

Biological implications
Synergistic damage of nucleobase in the presence of ionization, one-electron oxidation, and nitrosation.

Acknowledgements

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