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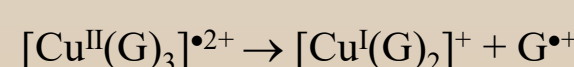
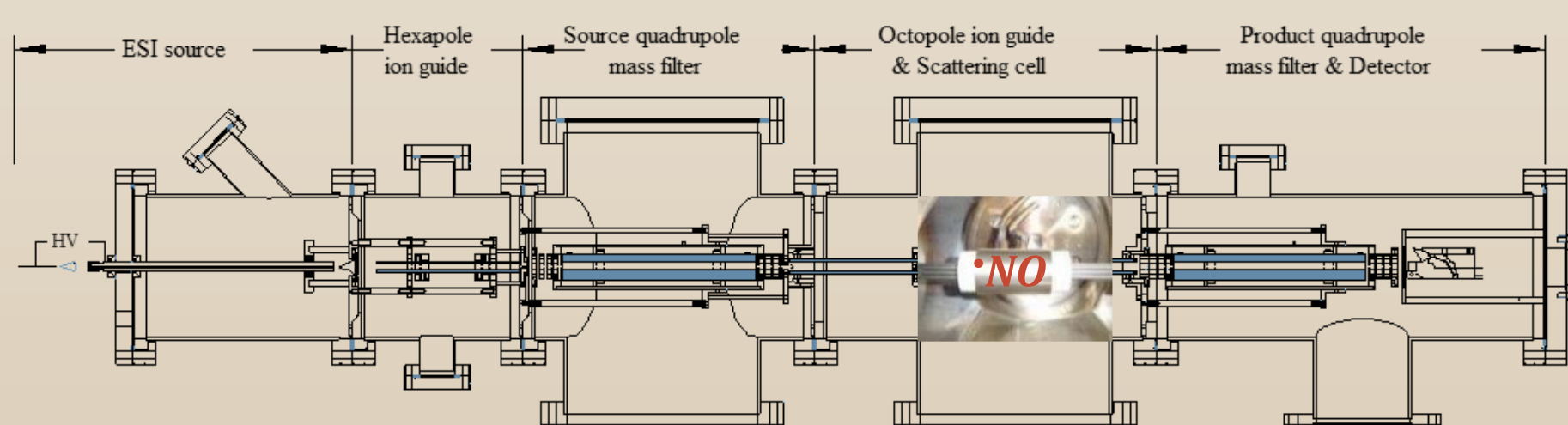
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Introduction

- Guanine is the dominant DNA target for one-electron oxidation and ionization.
- The Guanine radical cation ($G^{\bullet+}$) forms upon
 - Photoionization
 - Ionizing and ion-beam radiation
 - Oxidation by DNA-binding transitional metals
 - Electrocatalytic oxidation
 - Photooxidation
- The nitric oxide radical ($\cdot\text{NO}$), a reactive nitrogen species, is a precursor of DNA damage
- The overproduction of $\cdot\text{NO}$ can lead to oxidative and nitrative stress
 - DNA base deamination
 - Strand breaks and cross-links
 - Mutation
 - Carcinogenesis
 - Tumors
- The charge transfer reaction occurring in the collisions of $\cdot\text{NO}$ with the radical cations of guanine ($9\text{HG}^{\bullet+}$) and a model guanosine compound 9-methylguanine ($9\text{MG}^{\bullet+}$) was studied

Instrumentation & Ion-Molecule Reactions

Guided-Ion-Beam Tandem Mass Spectrometer for Generation of $G^{\bullet+}$ and Reaction with $\cdot\text{NO}$



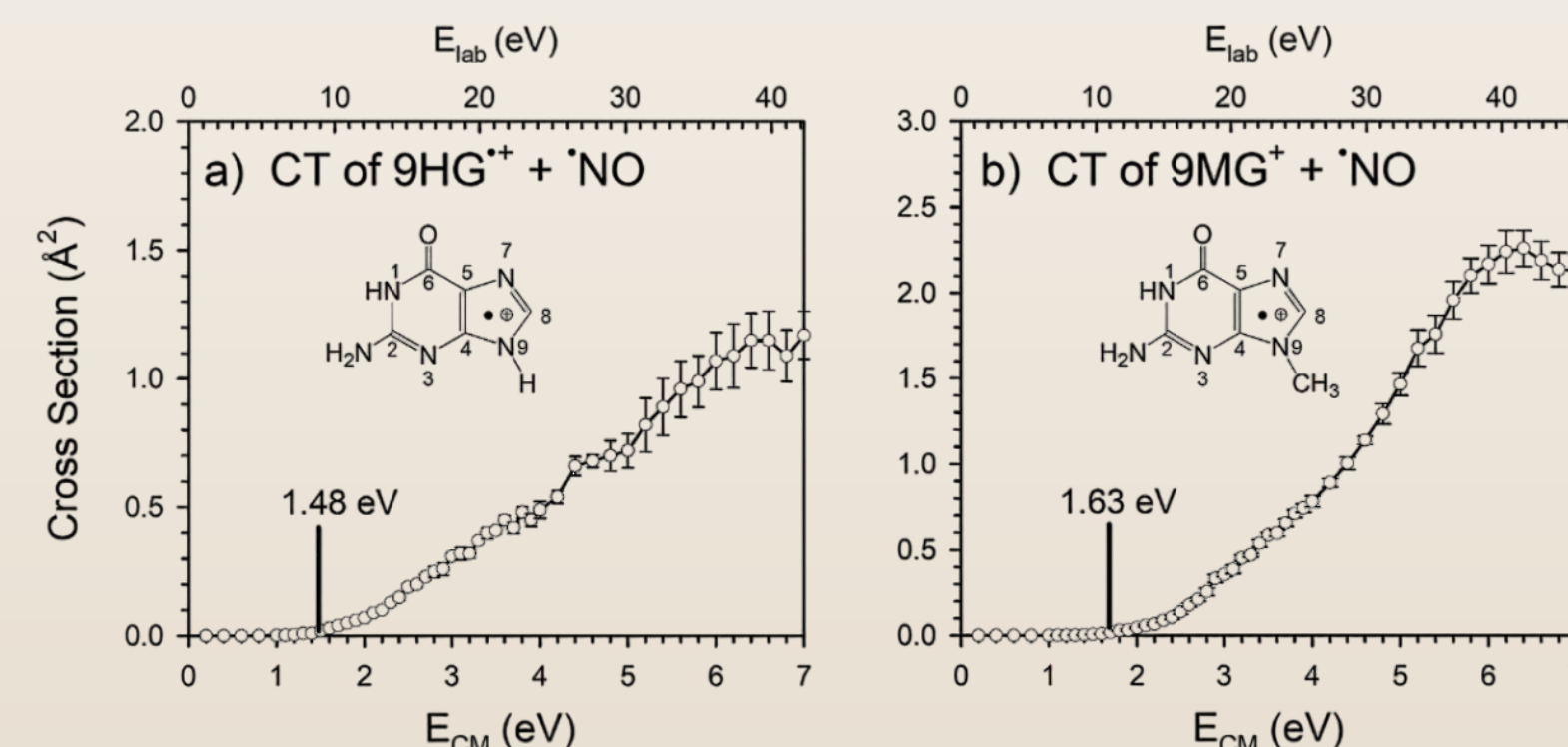
- Ion-molecule reactions were measured on a home-built guided-ion beam tandem mass spectrometer consisting of an electrospray ionization (ESI) source, radio-frequency (RF) hexapole ion guide, reactant quadrupole mass filter and electron multiplier detector
- Nucleobase radical ions of interest were mass selected by the reactant quadrupole mass filter and injected into the octopole ion guide that guided ions through a scattering cell filled with $\cdot\text{NO}$ gas
- In ion-molecule reactions, E_{lab} was converted to the center-of-mass collision energy (E_{CM})

$$E_{\text{CM}} = \frac{E_{\text{lab}} \times m_{\text{neutral}}}{(m_{\text{ion}} + m_{\text{neutral}})}$$

- Ion-molecule reactions studied over the range of E_{col} from 0.05 to 7 eV so that both exothermic and endothermic reactions could be detected
- Reaction cross sections are calculated from the ratio of reactant/product ion intensities, the gas pressure within the scattering cell and the effective cell length for collisions

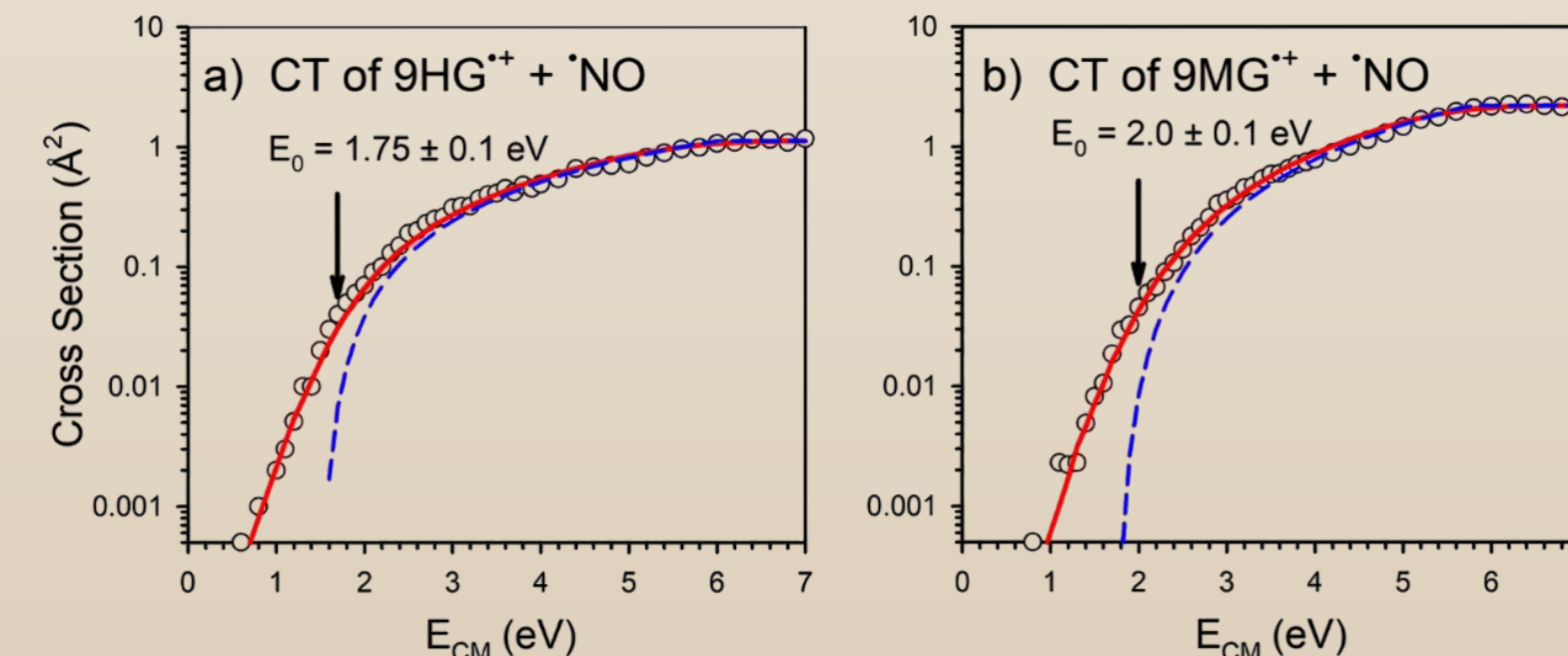
Experimental Results & Analysis

I. Product Ions & Cross Sections



- No obvious contribution from a triplet product channel at high collision energies
- Conversion to a singlet product channel is exclusive

II. Dissociation Threshold at 0 K



- To determine the exact value of E_0 , the E_{col} -dependent cross section was analyzed using a modified line-of-centers (LOC) function

$$\sigma(E) = \sigma_0 \frac{(E_{\text{CM}} + E_{\text{vib}} + E_{\text{rot}} - E_0)^n}{E_{\text{CM}}}$$

- The LOC model has accurately reproduced total cross sections from threshold to 7 eV for both systems

III. Thermochemistry Analysis

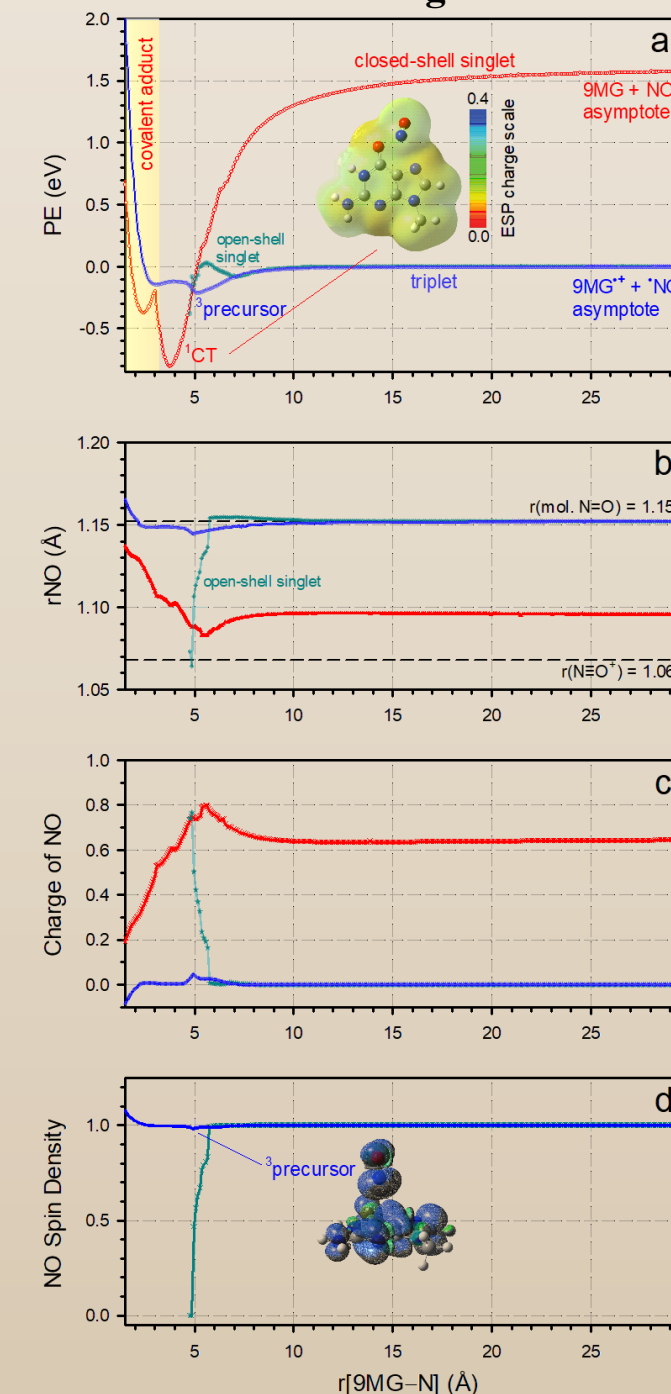


- The experimental charge transfer threshold was determined to be 1.75 eV for $9\text{HG}^{\bullet+} + \cdot\text{NO}$, which exceeds the asymptotic product energy (1.48 eV) by 0.27 eV; and is 2.0 eV for $9\text{MG}^{\bullet+} + \cdot\text{NO}$, which exceeds the asymptotic product energy (1.63 eV) by 0.37 eV
- Does this result imply the breakdown of the assumption in the LOC model that at least some collisions near threshold result in 100% $T \rightarrow E_{\text{int}}$?

Theoretical Modeling

- Geometries of reactants, intermediates and products were optimized using the ωB97XD functional and the 6-31+G(d,p) basis set (Gaussian 16)
- To combat spin contamination, reaction structures were subjected to T1 diagnostic and single-point energy calculations using DLPNO-CCSD(T) coupled with the aug-cc-pVTZ basis set (ORCA 4.2)

I. Triplet- and Open/Closed-Shell Singlet Intermediates and ISC for Charge Transfer

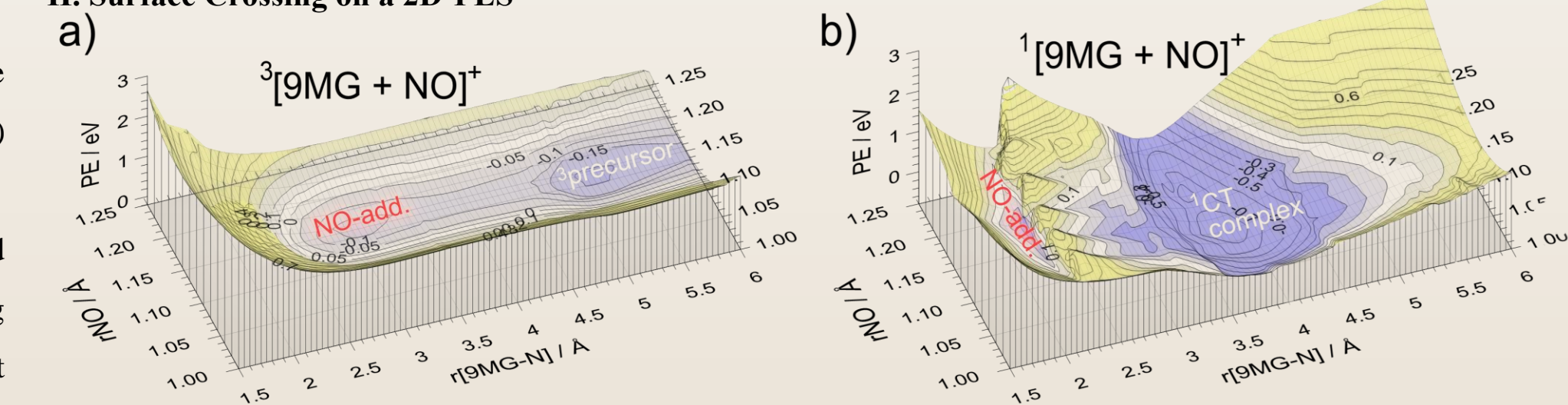


Relaxed PES scans along $r[9\text{MG}-\text{N}]$ for the total coupled spin multiplicities of closed-shell singlet, open-shell singlet, and triplet states

The charge transfer reaction starts by the formation of a collisionally-activated 3 precursor, followed by inter-system crossing towards a charge-transferred complex.

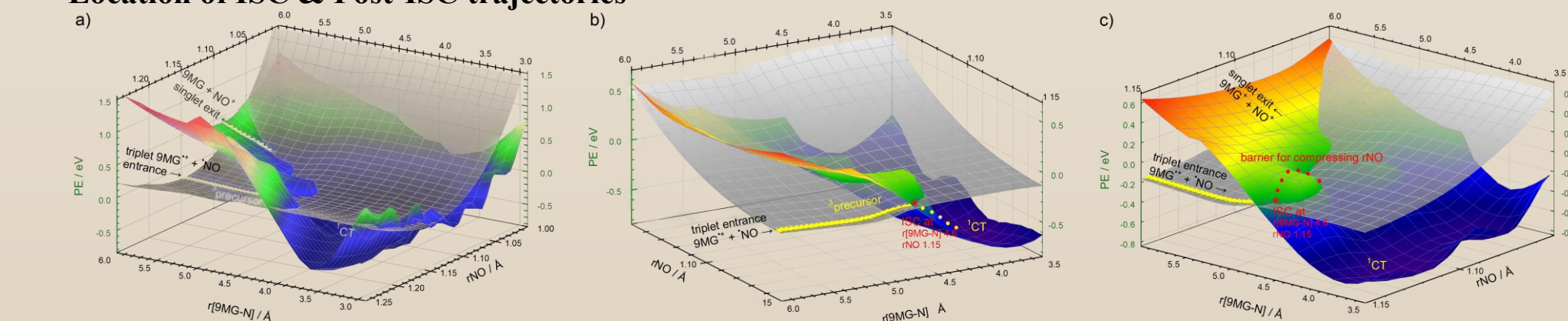
- Propagating along the product exit region of the closed-shell singlet PES, the complex separates to $9\text{MG} + \text{NO}^+$, as viewed by the evolution of NO bond length and charge
- There are no activation barriers for the approaching of $9\text{MG}^{\bullet+} + \cdot\text{NO}$ or the separation of $9\text{MG} + \text{NO}^+$ - barrier must be associated with other processes such as NO^+ internal energy or ISC

II. Surface Crossing on a 2D-PES



- The triplet surface presents a shallow reactant entrance where there exist two potential wells: the deep potential well at $r[9\text{MG} - \text{N}] = 5.2 \text{ \AA}$ represents the 3 precursor complex and the shallow potential well at $r[9\text{MG} - \text{N}] = 3 \text{ \AA}$ represents a covalently-bonded complex. There is no potential barrier leading to the formation of the 3 precursor
- The closed-shell singlet surface presents a large and deep potential well which corresponds to the formation of the 1 CT complex. Another narrower potential well at $r[9\text{MG} - \text{N}] = 2.3 \text{ \AA}$ corresponds to the formation of a covalently bonded $\text{NO}-9\text{MG}^+$. Both potential wells possess intra-complex charge transfer character. There is no reverse barrier at the product the product asymptote
- There exists a pathway(s) leading from the 1 CT complex to the covalently bonded $\text{NO}-9\text{MG}$ via a ridge peaked at $r[9\text{MG}-\text{N}]$ of 2.6 \AA .

Location of ISC & Post-ISC trajectories



- Bird's-eye view of the closed-shell singlet PES superimposed on triplet PES;
- NO^+ vibrational excitation;
- 3 precursor activation barrier and kinetic shift

Conclusions

- Product ion cross sections revealed that both reaction systems produce charge transfer products at the singlet spin multiplicity exclusively, and no triplet product is discernible.
- The reaction involves several steps:
 - Long-range ion-dipole attraction leads to the formation of a triplet $^3[G^{\bullet+}(\uparrow) \cdot (\uparrow)\cdot\text{NO}]$ precursor complex in ion-molecule collisions
 - The precursor complex may be sufficiently long lived such that spin orbital, charge transfer intersystem crossing occurs to form a closed-shell singlet, charge-transferred $^1[G(\uparrow\downarrow)\cdot\text{NO}^{\bullet+}]$ complex
 - With sufficient $T \rightarrow E_{\text{int}}$, the $^1[G(\uparrow\downarrow)\cdot\text{NO}^{\bullet+}]$ proceeds along the product exit channel to endothermic $G + \text{NO}^+$ asymptote. The dissociation of $^1[G(\uparrow\downarrow)\cdot\text{NO}^{\bullet+}]$ does not bear a reverse barrier
- Activation barrier due to the combination of kinetic shift of 3 precursor and vibrational excitation in NO^+
- Open-shell singlet \rightarrow Closed-shell singlet (internal conversion, not important in charge transfer)

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References

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