Multi-State Electronic Quenching: Non-Adiabatic Pathways in NO
2+ + O2 X 3g- Scattering

Citation for published version:
Soulié, C & Paterson, MJ 2022, 'Multi-State Electronic Quenching: Non-Adiabatic Pathways in NO 2+ +
O2 X 3g- Scattering', The Journal of Chemical Physics. https://doi.org/10.1063/5.0112556

Digital Object Identifier (DOI):
10.1063/5.0112556

Link:
Link to publication record in Heriot-Watt Research Portal

Document Version:
Peer reviewed version

Published In:
The Journal of Chemical Physics

Publisher Rights Statement:
© 2022 Author(s). This article has been accepted for publication and undergone full peer review but has not
been through the copyediting, typesetting, pagination, and proofreading process, which may lead to differences
between this version and the Version of Record.

General rights
Copyright for the publications made accessible via Heriot-Watt Research Portal is retained by the author(s) and /
or other copyright owners and it is a condition of accessing these publications that users recognise and abide by
the legal requirements associated with these rights.

Take down policy
Heriot-Watt University has made every reasonable effort to ensure that the content in Heriot-Watt Research
Portal complies with UK legislation. If you believe that the public display of this file breaches copyright please
contact open.access@hw.ac.uk providing details, and we will remove access to the work immediately and
investigate your claim.
Multi-State Electronic Quenching: Non-Adiabatic Pathways in NO $^2\Sigma^+ + O_2 X \ ^3\Sigma_g^-$ Scattering

Accepted Manuscript: This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination, and proofreading process, which may lead to differences between this version and the Version of Record.

Cite as: J. Chem. Phys. (in press) (2022); https://doi.org/10.1063/5.0112556
Submitted: 21 July 2022 • Accepted: 29 September 2022 • Accepted Manuscript Online: 04 October 2022

Clément Soulié and Martin J. Paterson
Multi-State Electronic Quenching: Non-Adiabatic Pathways in NO A $^{2\Sigma^+}$ + O$_2$ X $^{3\Sigma_g^-}$ Scattering

Clément Soulié$^1$ and Martin J. Paterson$^1$

Institute of Chemical Sciences, School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, Scotland, EH14 4AS.

(*Electronic mail: Corresponding author, m.j.paterson@hw.ac.uk)

(Dated: September 29, 2022)

The quenching of NO A $^{2\Sigma^+}$ with O$_2$ as a collisional partner is important for combustion and atmospheric processes. There is still a lack of theoretical understanding of this event, especially concerning the nature of the different quenching pathways. In this work we provide potential energy surfaces (PESs) of 20 electronic states of this system. We computed the spin-doublet and spin-quartet PESs using SA-CASSCF and XMS-CASPT2. We find two potential quenching pathways. The first one ($Q_1$) is a 2-step orientation-specific specific. The system first undergoes an electron transfer (NO$^+$ X $^{1\Sigma^+}$ + O$_2$ X $^{2\Pi_g}$) at short distances, before crossing to lower neutral states, such as NO X $^{2\Pi}$ + O$_2$ a $^{1\Delta_u}$, O$_2$ b $^{1\Sigma_g^+}$, O$_2$ X $^{3\Sigma_g^-}$ or even 2 O(3P). The second quenching pathway ($Q_2$) is less orientation-dependent, and should be sudden without requiring the proximity conditioning $Q_1$. The $Q_2$ cross-section will be enhanced with increasing initial vibrational level in both O$_2$ and NO. It is responsible for the production of NO X $^{2\Pi}$ with higher O$_2$ excited states, such as O$_2$ c $^{1\Sigma_g^+}$, A$^{3\Delta_u}$, or A$^{3\Sigma_g^+}$. Overall, the quenching of NO A $^{2\Sigma^+}$ by O$_2$ X $^{3\Sigma_g^-}$, as well as introducing a weighting scheme generally applicable to multireference, open-shell bimolecular systems. The effect of the spin-multiplicity on the different quenching pathways is also discussed.

I. INTRODUCTION

The nitric oxide radical has an important role in combustion$^1$ and atmospheric processes$^{2,3}$. As such researchers have grown increasingly interested in studying this radical species. They have utilised Laser Induced Fluorescence (LIF) to measure its atmospheric concentration, probing the $\gamma$ band transition NO X $^{3\Pi}$ $\leftarrow$ NO A $^{2\Sigma^+}$. However, these fluorescence measurements are impeded by a lack of radiative efficiency, which is due to quenching of NO A $^{2\Sigma^+}$ by different collisional partners$^4$.

To address this problem NO A $^{2\Sigma^+}$ quenching has been studied experimentally and computationally$^{5-13}$ with various quenchers, such as with NO X $^{3\Pi}$, N$_2$, O$_2$, CO, CO$_2$ and H$_2$O. Nevertheless, there is still a lack of theoretical work to explain the fate of NO A $^{2\Sigma^+}$ electronic energy during NO A $^{2\Sigma^+}$ + O$_2$ X $^{3\Sigma_g^-}$ quenching, which is of major interest since O$_2$ is the second most abundant species in the atmosphere.

From previous experiments, several quenching mechanisms are already hypothesized. Early work by Asscher and Haas$^{14}$ found the quenching efficiency of NO A $^{2\Sigma^+}$ to increase with the electron affinity of the quencher. Accordingly, they suggested that electron transfer can play an important role in the quenching process. This has been supported by the proposition of a harpoon mechanism by Paul et al.$^{15}$, in agreement with their following results$^{16}$ for NO A $^{2\Sigma^+}$ quenching at high temperatures. Such a mechanism is characterized by a two-step process, with the ionic state NO$^+$ X $^{1\Sigma^+}$ + O$_2$ X $^{2\Pi_g}$ as a quenching intermediate. Later, Nee et al.$^{17}$ also concluded that a charge transfer (CT) mechanism was responsible of the quenching of NO A $^{2\Sigma^+}$ by O$_2$. Then, Settersten et al.$^5$ observed a product distribution proportional to the Franck-Condon overlap between NO A $^{2\Sigma^+}$ and NO$^+$ X $^{1\Sigma^+}$. As a consequence, they also concluded that a harpoon mechanism was likely, but they also discussed the possibility of the formation of a collision complex.

Indeed, on the other hand, a negative temperature dependence of the quenching cross-section was observed by Settersten et al.$^6$, who proposed a well-depth of -41 cm$^{-1}$ for the collision complex. This prediction was supported by Sánchez-González et al.$^7$ who predicted a comparable well-depth of -39 cm$^{-1}$ for the collision complex. More recently, Few et al.$^8$ used Fourier Transformed IR spectroscopy to measure the vibrational population of NO X $^{3\Pi}$ and NO$_2$ quenching products. They found the non-reactive quenching of NO A $^{2\Sigma^+}$ to be consistent with two quenching channels, either producing high or low vibrational levels in NO X $^{3\Pi}$, being consistent with a long lived collision complex or a harpoon mechanism respectively. From all these experimental results, both quenching channels should be accessible at low energy collisions. It is very likely that their respective access should both be (essentially) barrierless. They also provided evidence to suggest the existence of different reactive quenching channels, producing NO$_2$ + O(3P) and supposedly NO X $^{3\Pi}$ + 2O(3P). Finally, Blackshaw et al.$^9$ recently supported the existence of a NO$_3$ collision complex due to long range attractive forces using velocity map imaging, and stressed on the importance of a conical intersection leading to NO X $^{3\Pi}$ (A') population. They also found that O$_2$ c $^{1\Sigma_g^-}$ could be formed in its vibrational ground-state, which agrees with Few et al.$^8$. The existence of a potential well on the NO A $^{2\Sigma^+}$ + O$_2$ X $^{3\Sigma_g^-}$ PES due to long-range attractive forces has also been supported by our own recent theoretical work$^{18}$.

To properly model such processes, it is important to investigate the shape of different regions on the PESs. First of all, the topology of the van der Waals (vdW) region on the excited state (NO A $^{2\Sigma^+}$ + O$_2$ X $^{3\Sigma_g^-}$) potential energy surface (PES) help in understanding which orientations are preferred during
the approach in a low-energy collision. Then, the short-range region of the initial excited-state describes which orientation will lead to the quenching event. Finally, the passage through a conical intersection will induce geometrical relaxations depending on the gradients and associated non-adiabatic couplings. The PESs involved in these quenching pathways define which products are accessible.

Following our previous work\(^\text{18}\) on the first step of this process, e.g. understanding the shape of the excited vdW PES of NO A \(^2\Sigma^+ + O_2 X ^3\Sigma_g^-\), we now focus on the next step: identifying potential quenching pathways and their associated products. To do this, we explored 20 spin-doublet (D) and 9 spin-quartet (Q) PESs at the SA-CASSCF level of theory. Differing spin-states are possible as \(O_2 X ^3\Sigma_g^-\) has two unpaired electrons and NO A \(^2\Sigma^+\) has one, NO A \(^2\Sigma^+ + \) \(O_2 X ^3\Sigma_g^-\) can therefore have a total spin of both a quartet and doublet. Additionally, we computed XMS-CASPT2 scans in the doublet manifold to describe important dynamic correlation effects on the accessibility and relaxation of the quenching event.

II. COMPUTATIONAL DETAILS

We performed our calculations using the MOLPRO 2021.3 \textit{ab initio} quantum chemistry package\(^\text{19,20}\), unless specified otherwise. The energy convergence threshold was \(1 \times 10^{-8}\) Hartree. In this paper, we use Jacobi\(^\text{21}\) coordinates as shown in Fig.1.

A. Active-space and excited states

The PESs were computed at the CASSCF level\(^\text{22,23}\). This is because it can accurately model non-adiabatic effects, as well as multi-configurational character. This active space is composed of NO and \(O_2 \; 2\sigma^*, 3\sigma, \pi_u, \pi_s, \pi_u^*, \pi_s^*\) orbitals, as well as NO \(4\sigma\) orbital, resulting in a CAS(19,13). A schematic representation of this active space at asymptotic inter-molecular separation is given in Figure 2.

To compute the PESs in different orientations, we used the C\(_1\) point group, unless specified otherwise. As a consequence, many excited states had to be included in the CASSCF calculation for two reasons. Firstly, \(O_2 \; d^1\Delta_g\) and \(b^1\Sigma_g^-\) states are lower in energy than NO A \(^2\Sigma^+\) state. In a vertical excitation framework at experimental bond-length for the states of interest, it means that NO \(X \; ^2\Pi\) degeneracy will couple with \(O_2 X, \; a\) and \(b\) states, leading to 8 doublet and 2 quartet surfaces lower in energy than NO A \(^2\Sigma^+ + O_2 X ^3\Sigma_g^-\). The state ordering in the asymptotic region \((R = 15 \; \text{Å})\) with fixed bond-length is presented in table I. Since Few \textit{et al.}\(^\text{8}\) suggested that \(O_2 \; c^1\Sigma_u^+\) could be a potential quenching product, the active-space/number of state combination was set for spin-doublet states first. Accordingly, the minimum number of spin-doublet states required is 9.

However, the NO A \(^2\Sigma^+ + O_2 X ^3\Sigma_g^-\) state was challenging to converge due to the Rydberg nature of NO A \(^2\Sigma^+\). The excited electron in NO A \(^2\Sigma^+\) populates the \(4\sigma\) orbital which is mostly composed of diffuse \(s\) functions. Amongst the first 9 states, the NO A \(^2\Sigma^+ + O_2 X ^3\Sigma_g^-\) is the only state with population in this orbital. The associated low-state-averaged density leads to instability in the active-space, replacing the NO \(4\sigma\) orbital by \(O_2 \; 3\sigma^+\) orbital, which persisted even when changing the weighting of the 9\(_{th}\) state.

It was not possible to include simultaneously the NO \(4\sigma\) and \(O_2 \; 3\sigma^+\) orbitals. Adding one extra virtual orbital led to the rotation of the \(NO \; 3\sigma^+\) orbital into the active space, while adding two extra virtuals led to higher NO Rydberg orbitals. Similarly, including \(O_2 \; 3\sigma^+\) also led to instabilities in the active space, with unwanted rotations. To solve this problem we computed more excited states until the NO \(4\sigma\) orbital was included in the active space. This technique works because to minimize the state average energy, it is better to include the NO \(4\sigma\) orbital in the active space and have co-excited-states (excited NO and \(O_2\)) than highly energetic excited states of \(O_2\). Including the first 20 doublet states stabilised the active space as required. These excited-states are listed in table I. Additionally, because the system can exist both in the spin-doublet or spin-quartet framework, we computed two set
of surfaces. However, all doublet states don’t have a quartet counterpart, as those need to be composed of $^{3}\text{O}_2$ states together with $^{3}\text{O}_2$ states only, i.e., no $^{1}\text{O}_2$ states coupled to $^{2}\text{NO}$ can give an overall quartet. As a result, a first set of surfaces (doublet and quartet) was computed at the SA(29)-CASSCF(19,13). Those surfaces will be referred to as SA-CASSCF surfaces. The second set of surfaces included spin-doublet states only, including a specific state weighting leading to SW(20)-CASSCF(19,13) calculations. These will be referred to as SW-CASSCF surfaces, and are discussed below. The experimental excitation energy of NO A $^{2}\Sigma^+$ (5.45 eV) compares well with the calculated adiabatic value of 5.44 eV) (energy difference difference including zero-point corrections) for the super molecule at 50 Å with SW-CASSCF optimized bond-lengths. Asymptotic adiabatic excited energies for the O$_2$ a $^{1}\Delta_g$ and O$_2$ b $^{1}\Sigma_g^+$ states (1.08 eV and 1.76 eV respectively) also compare well with experiment (0.98 eV and 1.64 eV respectively). We note that good agreement with experimental asymptotic energies can also be obtained from single molecule XMS-CASPT2 calculations for these states (1.139 eV and 1.845 eV respectively). Direct experimental comparison of adiabatic excitations for all states is problematic because of issues with stability of the active space for all states in the asymptotic region. We note however excellent agreement between CASPT2 and CCSD(T) state energies in intermediate regions, where applicable, and that CCSD(T) asymptotic excitation energies are in also good agreement with experiment.

### B. State-weighting

In a single-molecule system like NO, one would generally set-up the first 3 electronic states (2 NO X $^{2}\Pi$ micro-states, and NO A $^{2}\Sigma^+$ state) to have a weight of $\frac{1}{2}$, arising from state-averaging. However, a state-averaged CASSCF calculation of a bi-molecular system can introduce bias. Among the 20 bi-molecular doublet PESs we computed, the nitric oxide molecule is in its ground state in 16 surfaces, while NO A $^{2}\Sigma^+$ is only present in 4. Accordingly, optimizing the orbitals in a state-average fashion would introduce a bias toward bi-molecular states including NO X $^{2}\Pi$. To compensate for that, each bi-molecular state should be weighted so that the total weight of each single-molecule micro-state is equal within one molecule. The ideal weighting to provide a balanced description of each micro-state is given in table S2. Yet, it was not possible to use this ideal weighting for the SW-CASSCF surfaces, as it leads to root-flipping issues. Root-flipping arises when two states with different weighting are close in energy, and exchange their order, as well as their weight during an optimization step. As a solution, an identical weight was given to the upper states ($9^{th}$ state and above), as described in table S2. In that way, the orbital optimization is less biased in the SW-CASSCF surfaces than in the SA-CASSCF surfaces, and the weights don’t change the state ordering.

### C. Surfaces across the angle space

Initial surfaces were computed with fixed experimental bond-length for the states of interest, i.e. 1.0634 Å for NO A $^{2}\Sigma^+$ and 1.2075 Å for O$_2$ X $^{3}\Sigma_g^-$. We note that good agreement with experimental asymptotic energies can also be obtained from single molecule XMS-CASPT2 calculations for these states (1.08 eV and 1.76 eV respectively) also compare well with experiment (0.98 eV and 1.64 eV respectively). We note that good agreement with experimental asymptotic energies can also be obtained from single molecule XMS-CASPT2 calculations for these states (1.139 eV and 1.845 eV respectively). Direct experimental comparison of adiabatic excitations for all states is problematic because of issues with stability of the active space for all states in the asymptotic region. We note however excellent agreement between CASPT2 and CCSD(T) state energies in intermediate regions, where applicable, and that CCSD(T) asymptotic excitation energies are in also good agreement with experiment.

![Figure 3](image-url)

1.125 Figure 3 Angle space of NO + O$_2$. L: Linear; H: Hammer; LO: Linear-Oxygen; T: T-shape; P: Parallel; TO: T-shape-Oxygen; C: Cross

C. Surfaces across the angle space

Initial surfaces were computed with fixed experimental bond-length for the states of interest, i.e. 1.0634 Å for NO A $^{2}\Sigma^+$ and 1.2075 Å for O$_2$ X $^{3}\Sigma_g^-$. We note that good agreement with experimental asymptotic energies can also be obtained from single molecule XMS-CASPT2 calculations for these states (1.08 eV and 1.76 eV respectively) also compare well with experiment (0.98 eV and 1.64 eV respectively). We note that good agreement with experimental asymptotic energies can also be obtained from single molecule XMS-CASPT2 calculations for these states (1.139 eV and 1.845 eV respectively). Direct experimental comparison of adiabatic excitations for all states is problematic because of issues with stability of the active space for all states in the asymptotic region. We note however excellent agreement between CASPT2 and CCSD(T) state energies in intermediate regions, where applicable, and that CCSD(T) asymptotic excitation energies are in also good agreement with experiment.

To yield accurate energy values, we based our calculations on Dunning basis sets$^{25,27}$ as they are optimized to properly
model electronic correlation. We used the t-aug-cc-pVTZ basis set for both O₂ and NO as diffuse functions are necessary to represent both the 4σ orbital of NO [18], and possible ionic configurations with O₂⁻ and NO⁺. These calculations were obtained using the C₃ point group to keep our results comparable across all orientations.

D. XMS-CASPT2 scans

To explore the effect of dynamic correlation on the shape for the PESs, we performed multiple scans at the XMS-CASPT2 level in planar orientations [28-30]. These scans were performed using the internally contracted form of multi-reference Rayleigh-Schrödinger perturbation theory (RS2C) routine of Molpro 2022.2. The CASSCF wavefunction of the previous 20 states was computed within the C₃ point group, resulting in 10 A' and 10 A" states. The state weighting described above (section II B) was used for fig. 5, but not for section III B due to CASSCF root-flipping issues at short distances. A smaller active space (11,9) and basis set (t-aug-cc-pVQZ) were used due to the computational cost of the following XMS-CASPT2 calculation. This smaller active space only contains the π and π* orbitals, together with NO 4σ orbital. We used an IPEA (Ionisation Potential Electron Affinity) level shift of 0.25 to compensate for CASPT2 systematic error in excitation energies and avoid intruder states [31]. Only the 10 A" states were computed at the XMS-CASPT2 level as this is the symmetry of NO A 2Σ⁺ + O₂ X 3Σg⁻ state in a planar geometry.

E. Non-adiabatic couplings

The non-adiabatic coupling matrix elements (NACME) χiα of atom i on the axis α (α ∈ [x, y, z]) were computed analytically between NO A 2Σ⁺ + O₂ X 3Σg⁻ and NO X 2Π + O₂ c 1Σu⁺ (A") within the C₃ point group in planar geometries. The scans were performed with the SW-CASSCF/t-aug-cc-pVTZ basis set as described in section II D. We used fixed bond-length (1.0634 Å) for NO and O₂ (1.24 Å). Then, the full length of the non-adiabatic coupling vector (NACV) ε was computed as follows:

\[ ε = \sqrt{\sum_{i,α} \chi_{iα}^2} \]  

The full length of the non-adiabatic coupling vector is useful to understand non-radiative transition probabilities from one state to another. Indeed, this probability depends both on the energy difference between the 2 states, as well as the magnitude of their coupling. While the PESs in this work describe the former, the length of the NACV gives the latter.

III. RESULTS AND DISCUSSION

In this section, we first compare the doublet and quartet states across different orientations. We then investigate further the doublet PESs and identify a first quenching pathway Q₁ involving ionic configurations and discuss its accessibility. The associated geometrical relaxations are discussed, together with the possible quenching product. We also propose an alternative quenching channel Q₂ that doesn’t involve ionic configurations and evaluate the NAC for a potential product.

A. Exploring the PESs across the angular space

A total of 29 states, among which 20 doublets and 9 quartets, were plotted in 2 sets of 2D surfaces across the intermolecular distance R, and different set of angles with fixed bond-length as described in section II. The data points for all surfaces can be found in ESI material. Here we first discuss the SA-CASSCF surfaces, comparing the differences between the spin-quartet states and their spin-doublet counterpart. Furthermore, we describe the shape of the spin-doublet SW-CASSCF surfaces. We identify short-range geometries that present low-energy access to potential quenching pathways, and explain why those geometries provide such access by analysing the wave-function(s).

1. Comparison between doublet and quartet states

Firstly, the SA-CASSCF surfaces show that quartet states are degenerate with their spin-doublet counterpart in the asymptotic region. This is to be expected as the states are computed from the same orbital basis. However, this degeneracy is lifted in the short range region. This is due to spin-paired configurations stabilizing the spin-doublet states only. The c₁ coefficient of those spin-paired configurations increases as R decreases. Secondly, a common feature between all doublet and quartet surfaces, and across all orientations, is the repulsive wall at short distances, although, the shape and position along R are different.
1.125 Figure 4 Doublet states obtained from SW-CASSCF/t-aug-cc-pVTZ calculation in the scan going from geometry T to TO. The left plot (a) consist of a cut through the surfaces to observe the location of the entry to the quenching channel, and the right plot (b) corresponds to a zoom on the cut in polar coordinates. In polar coordinates, \( x = R \times \cos(\Theta_{NO}) \) and \( y = R \times \sin(\Theta_{NO}) \). The data point indicated corresponds to the maximum energy barrier discussed in III A 3. From bottom to top, the surfaces asymptotically correspond to NO \( \Pi_2^+ \) + \( \Omega_2^g \)(blue), NO \( \Pi_2^+ \) + \( \Omega_a^1 \Delta_g^+(cyan) \), NO \( \Pi_2^+ \) + \( \Omega_b^1 \Sigma_g^+(orange) \), NO \( \Pi_2^+ \) + \( \Omega_a^1 \Delta_g^+(cyan) \), NO \( \Pi_2^+ \) + \( \Omega_a^1 \Delta_u^+(dark \text{ green}) \), NO \( \Pi_2^+ \) + \( \Omega_a^1 \Delta_u^+(magenta) \), and NO \( \Pi_2^+ \) + \( \Omega_b^1 \Sigma_u^+(orange) \). The asymptotic (15 Å) energy of NO \( \Pi_2^+ \) + O \( 2 \) \( X_3^\Sigma_g^- \) is 4.3406 eV.

Thirdly, we observe a potential well on the 9th adiabatic doublet PES (Figure 4). It is centered at \( \Theta_{O_2} = 90^\circ \), \( \Theta_{NO} = 45^\circ \), \( \Phi = 0^\circ \) and \( R = 2.5 \text{ Å} \) which does not exist on the quartet surfaces. In this region, the main difference between the doublet and quartet state wave-functions is the increasing mixing of the charge-transfer configuration \( O^-_2 \Pi_2^+ + NO \Pi \) \( \Sigma_g^+ \) in the description of different adiabatic states with decreasing \( R \). The ion-pair character could be identified both because of the increasing \( C_t \) coefficient of the associated configurations, and because of large increase in the dipole moment of the state. Our results show that such configurations have an important role in the quenching process as proposed by earlier experimental studies. Yet, rather than a harpoon mechanism (direct crossing with a ionic surface), the smooth transition from neutral to ionic resembles a diffuse avoided crossing region. This long-range mixing is potentially due to the diffuseness of the electronic density of both NO \( \Pi_2^+ \) and \( O_2^\Xi_2^\Pi \). Since the quartet surfaces don’t show any potential quenching pathways accessible with low collision energy within these coordinates, we now focus our efforts on the doublet surfaces.

2. Weight-adapted doublet surfaces

To accurately describe the different quenching pathways, we calculated another set of surfaces only including spin-doublet states. For a better optimization of the orbitals, the bi-molecular states were weighted to avoid introducing a bias in excitation energies, as explained in section II B. As a consequence, the NO \( \Pi_2^+ \) state is largely stabilized, lowering the energies of \( \Pi_2^+ + \Omega_2^g \), \( \Pi_2^+ + \Omega_a^1 \Delta_g^+ \), \( \Pi_2^+ + \Omega_b^1 \Sigma_g^+ \), \( \Pi_2^+ + \Omega_a^1 \Delta_u^+ \) by almost 0.3 eV compared to the SA-CASSCF surfaces. Up to this point, only one 2D scan shows features that could lead to NO \( \Pi_2^+ \) quenching with low translational energy. It goes from the \( T \)-shaped geometry with the nitrogen of NO pointing toward the center of \( O_2 \), to the TO geometry, where the oxygen of NO points towards \( O_2 \). The surfaces of this scan are presented in fig. 4a. The PES asymptotically corresponding to NO \( \Pi_2^+ + O \times 3 \Sigma_g^+ \) shows 3 important
features with decreasing inter-molecular distance, in orientations centered around $\Theta_{NO}= 45^\circ$. Firstly, as $R$ decreases, the wave-function of this state is increasingly described by the $A''$ configuration of the $O_2^− X^2Π_g + NO^+ X^1Σ^+$ ionic state. Then, at short distances, approximately 2.6 Å, there is a conical intersection between the $9^{th}$ and $10^{th}$ adiabatic states. At this distance, they correspond to a crossing between the $A'$ and $A''$ states of $O_2^− X^2Π_g + NO^+ X^1Σ^+$. They do not couple in the plane, but the coupling is turned on by the dihedral angle, as it breaks the planar $C_s$ point group. The irreducible representations of $NO A^2Σ^+ + O_2 X^3Σ^-_e$ and $NO^+ X^1Σ^+ + O_2^− X^2Π_g$ depending on the dihedral angle are given in table S3. Finally, both $O_2^− X^2Π_g + NO^+ X^1Σ^+$ micro-states have a potential well at even shorter distances before hitting the repulsive wall.

3. **Accessibility of $Q_1$: CASSCF vs. CASPT2**

In fig. 4a, the $9^{th}$ adiabatic surface (green, asymptotically $NO A^2Σ^+ + O_2 X^3Σ^-_e$) shows a small potential energy barrier of approximately 1160 cm$^{-1}$, centered around 2.9 Å. Such a barrier could prevent access to the aforementioned potential well in a cold molecular beam experiment. However, as discussed below, we believe this potential energy barrier to be a computational artefact due to a lack of dynamical electronic correlation. Indeed, ion-pair states are more sensitive dynamical correlation than neutral states. This is the origin of the higher CASSCF barrier which is reduced at the CASPT2 level. Thus, we computed XMS-CASPT2 scans (see section IID) in the relevant orientation ($\Theta_{NO}= 45^\circ$, $\Theta_{O2}= 90^\circ$, $\Phi= 0^\circ$) to demonstrate the effect of increasing the amount of dynamical electronic correlation. Results in fig. 5 show two main differences compared to the CASSCF scan. Firstly, a long-range attractive potential is present in the CASPT2 scan. This has previously been noted when comparing CASPT2 to the accurate CCSD(T) in the VdW region. In addition, the potential energy barrier diminishes to approximately 20 cm$^{-1}$. Additionally, relaxing the NO bond-length along the approach does not decrease the barrier. This can be seen in Fig. S3 where we performed an XMS-CASPT2 scan with differing NO bond-lengths. This scan shows that the lowest energy barrier is obtained for the long-range optimized bond-length. This is to be expected as $NO A^2Σ^+$ and $NO^+ X^1Σ^+$ have very similar optimized bond-lengths (table S4). To summarise, these results indicate that lower translational energies will lead to an increased number of collisions thanks to the long-range attractive forces. Additionally, some specific orientations can lead to an *a priori*, small or barrierless quenching pathway.

4. **The role of orbital mixing in $Q_1$ quenching**

Before exploring further the details of the relaxation pathway we attempt to explain why the mixing between the neutral and ionic configurations is orientation specific. Indeed, an electron-transfer from $NO A^2Σ^+$ to $O_2 X^3Σ^-_e$ should only depend on $NO A^2Σ^+$ ionisation potential (IP) $(5.4906\pm0.0004\text{eV})$, $O_2 X^3Σ^-_e$ electron affinity (EA) $(0.448\pm0.006\text{eV})$, and the inter-molecular distance that defines the coulomb attraction (CA) between the resulting ions. An electron transfer should occur when $IP-CA\geq EA$, regardless of the orientation. Hence, we investigated which orbital mixing could explain this dependence.

With $\Theta_{NO}= 45^\circ$, $\Theta_{O2}= 90^\circ$ and $\Phi= 0^\circ$, the $O_2$ in-plane $\pi$ orbital (Figure S1) orbital has a strong mixing with NO in-plane $\pi^*$ orbital (fig. 6). A lobe of the NO in-plane $\pi^*$ orbital points directly to the middle of the $O_2$ in-plane $\pi$ orbital. An interpretation of this mixing is that in the $NO A^2Σ^+$ + $O_2 X^3Σ^-_e$ state, where NO $\pi^*$ orbitals are empty, $O_2$ can relax some of its electronic density into NO $\pi^*$, both increasing $O_2$ EA and decreasing NO IP to ultimately facilitate the electron transfer. According to this hypothesis, ionic configurations should be stabilised by this orbital overlap. To verify this, we scanned the PESs along the dihedral angle, rotating NO out of the plane, as this rotation should keep the former orbital mixing similar. The resulting surfaces are presented in fig. 6.

This deformation breaks the in-plane $C_s$ symmetry to produce orientations belonging to the $C_1$ point group, until it reaches $\Phi= 90^\circ$, which correspond to another $C_1$ geometry. The resulting PESs clearly display the same potential well along the dihedral rotation, which looks like a sink in polar coordinates. Hence, we consider this orbital overlap key to enter this quenching channel. With $\Phi= 90^\circ$, both micro-states of $NO^+ X^1Σ^+ + O_2 X^2Π$ belong to the $A''$ irreducible representation, while $NO A^2Σ^+ + O_2 X^3Σ^-_e$ is an $A'$ state (see table S3). Hence the coupling between $NO A^2Σ^+ + O_2 X^3Σ^-_e$ and $NO^+ X^1Σ^+ + O_2 X^2Π$ is turned off by turning on the dihedral angle. In planar geometries, the charge...
transfer can occur if there is an overlap between NO $4\sigma$ orbital and $O_2$ in-plane $\pi^*$ orbital. The NO $4\sigma$ orbital is a diffuse $s$-type Rydberg orbital, and so this overlap is non-zero at long-range in most of the angle space. The mixing between these two orbitals is anti-bonding. The associated rise in energy during the approach also facilitates the electron transfer. Then, because of associated changes in the wave-function (neutral to ionic) at short inter-molecular distances, further geometrical relaxation may occur along the different bond-lengths.

B. 2D PESs along $O_2$ bond-length

The experimental bond-length of each electronic states discussed in this paper are presented in table S4. From there, one can see that NO $A^2\Sigma^+$ and NO$^+ X^1\Sigma^+$ have similar optimized bond-length. This is not surprising since NO $A^2\Sigma^+$ state can be seen as NO$^+$ with a surrounding diffuse Rydberg electron. However, $O_2$ $X^2\Pi_g$ has a much larger optimized bond-length than $O_2$ $X^3\Sigma_g^-$. This is because of the extra electron that populates one of the two $\pi^*$ orbitals, weakening the bond. Hence, we explored this relaxation pathway. We calculated the PESs at the XMS-CASPT2 level across the stretching of $O_2$ with $\Theta_{NO} = 45^\circ$, $\Theta_{O_2} = 90^\circ$, and $\Phi = 0^\circ$. To discriminate between the states that couple together at a planar geometry, this scan was computed within the $C_1$ point group. Since NO $A^2\Sigma^+$ belongs to the $A'$ irreducible representation, only $A'$ states are plotted in section III B. On fig. 7a, one can see the evolution of the gradient along $O_2$ bond-length for asymptotic NO $A^2\Sigma^+ + O_2 X^3\Sigma_g^-$ state. When $R > 3.5$ Å, as the main configuration for $O_2$ corresponds to $O_2 X^3\Sigma_g^-$, the computed optimized bond-length is approximately 1.2 Å. However, at short distances, the gradient of the PES evolves and drives the system towards longer $O_2$ bond-length. At the XMS-CASPT2 level, the short-range potential well described in fig. 7a is more pronounced than at the SW-CASSCF level (Fig. S2). Such shape of the PES has the effect of locking the two molecules in a temporary NO$^+_3$ complex while it relaxes through $O_2$ stretch.

As $O_2 X$, $a$ and $b$ states have similar optimized bond-length (table S4), extending $O_2$ bond-length destabilises those states, and stabilises $O_2 X^2\Pi_a$ as well as $O_2 c^1\Sigma_u^+$ excited states. This deformation closes the energetic gap between NO $A^2\Sigma^+ + O_2 X^3\Sigma_g^-$ and NO $X^2\Pi + O_2 X, a$ and $b$ states (8 micro-states). All of those 8 micro-states are purely repulsive between the two molecules, which can lead to the dissociation of the complex. Alternatively, the dissociation limit of $O_2$ into two O$^3P$ is energetically accessible as well, given the initial potential energy of NO $A^2\Sigma^+ + O_2 X^3\Sigma_g^-$. Finally, the surfaces also seems to show that NO$^+_2$ could be formed by an insertion of the nitrogen in the middle of the $O_2$ bond, eventually going through the $D_3h$ geometry. Although, such process would require a relaxation of NO bond-length, $\Theta_{NO}$, as well as $O_2$ stretch, which would be better described by dynamic calculations. A qualitative graphical description of this quenching pathway, denoted as $Q_1$, is available in fig. 7a.

These results let us propose that $Q_1$ can then be described as follows:

\[
\begin{align*}
\text{NO} & \ A^2\Sigma^+ + O_2 \ X^3\Sigma_g^- & \rightarrow & \ NO^+ \ X^1\Sigma^+ + O_2^- \ X^2\Pi_g \\
\text{NO}^+ \ X^1\Sigma^+ + O_2^- \ X^2\Pi_g & \rightarrow & \ NO \ X^2\Pi + O_2 \ a^1\Sigma_g^+ \\
& & \ NO \ X^2\Pi + O_2 \ a^1\Delta_g \\
& & \ NO \ X^2\Pi + O_2 \ X^3\Sigma_g^- \\
& & \ NO \ X^2\Pi + 2 \ O^3P \\
\text{NO}_2 & + O
\end{align*}
\]

Regarding the vibrational distribution in the products, it is very likely that $O_2$ will be highly vibrationally excited. Concerning NO, the Franck-Condon (FC) overlap NO $A^2\Sigma^+ (v' = 0)$ to NO $X^2\Pi (v'' = 0)$ is known to be large. Since NO $A^2\Sigma^+$ and NO$^+ X^1\Sigma^+$ have similar optimized bond-length, it is very likely that NO$^+ X^1\Sigma^+$ displays similar FC overlap, which would result in low vibrational level in quenched NO $X^2\Pi$. However, due to the proximity between
Figure 7 (a): 5 A'' states across stretching of O₂ bond-length in planar geometry. Computed with XMS-CASPT2/t-aug-cc-pVDZ. From bottom to top, at O₂ bond = 1.2 Å, the surfaces asymptotically correspond to NO X ²Π + O₂ X ³Σ⁻ (blue), NO X ²Π + O₂ a ¹Δg (cyan), NO X ²Π + O₂ b ¹Σ⁺ (orange), NO A ²Σ⁺ + O₂ X ³Σ⁻ (green). The arrows correspond to the presumed pathway the system would undergo while being quenched through Q₁. (b): 10 A'' states across stretching of O₂ bond-length in planar geometry at R = 15 Å. Computed with XMS-CASPT2/t-aug-cc-pVDZ. From bottom to top, at O₂ bond = 1.2 Å, the surfaces asymptotically correspond to NO X ²Π + O₂ X ³Σ⁻ (blue), NO X ²Π + O₂ a ¹Δg (cyan), NO X ²Π + O₂ b ¹Σ⁺ (orange), NO A ²Σ⁺ + O₂ a ¹Δg (cyan), NO X ²Π + O₂ c ¹Σ⁺ (red), NO X ²Π + O₂ A' ³Δu (dark green) and NO X ²Π + O₂ A' ³Σ⁺ (magenta). The dotted lines correspond to the presumed pathway the system would undergo while being quenched through Q₂.

NO and O₂ required by this quenching channel, it is very likely that there is some vibrational energy transfer from O₂ to NO. This would fit the experimental results concerning the first quenching channel described by Few et al.⁸.

Alternatively, fig. 7b shows a cut of the A'' PESs at the XMS-CASPT2 level along O₂ stretch. At the top, the cyan state (NO A ²Σ⁺ + O₂ a ¹Δg) rise in energy with the stretch until it crosses with NO X ²Π + O₂ c ¹Σ⁺ (green), NO A ²Σ⁺ + O₂ a ¹Δg (cyan), NO X ²Π + O₂ b ¹Σ⁺ (orange), NO X ²Π + O₂ X ³Σ⁻ (blue), NO X ²Π + O₂ a ¹Δg (cyan), NO X ²Π + O₂ c ¹Σ⁺ (red), NO X ²Π + O₂ A' ³Δu (dark green) and NO X ²Π + O₂ A' ³Σ⁺ (magenta). The same crossing is observed just below with the green surface (NO A ²Σ⁺ + O₂ X ³Σ⁻) when O₂ bond-length is greater than 1.32 Å. This is the second quenching channel, Q₂, proposed in this paper. The crossing between these PESs is not orientation specific, and doesn’t depend on R. It only depends on the bond-length of the two molecules. This quenching can also happen on the quartet surfaces as long as the O₂ final electronic state is a spin-triplet state (A' ³Δu or A' ³Σ⁺). However, population transfer between different electronic states does not only depend on their energy difference, but also on their non-adiabatic couplings (NACs). The

Figure 8 Length of the non-adiabatic coupling vector between NO A ²Σ⁺ + O₂ X ³Σ⁻ and NO X ²Π + O₂ c ¹Σ⁺ in planar geometries, at an inter-molecular distance of 5 Å. Computed with SW-CASSCF/t-aug-cc-pVTZ.
NACME between NO $^2\Sigma^+ \rightarrow O_2 \times ^3\Sigma_g^-$ and NO $^2\Pi + O_2 \times ^1\Sigma_g^-$ were computed in planar orientations, as described in section II E. Figure S3 shows that the coupling exponentially increase with decreasing inter-molecular distance in different geometries. Also, the length of the non-adiabatic vector was computed in different orientations, at a fixed inter-molecular distance of 5 Å. Different maxima are found across the planar orientation, as shown in fig. 8, meaning that the quenching could happen in different orientations. The maximum in fig. 8 correspond to an orientation of $\Theta_{NO} = 60^\circ$ with $\Theta_{O2} = 130^\circ$. The associated NAC vector are plotted in Figure S4, together with the gradient difference vector in Figure S5. Both correspond to a synchronised stretching of NO and $O_2$, but are not perfectly parallel. They thus form a linearly independent basis for the branching space; the most physical representation being the separate stretching modes on each collision partner. Overall, $Q_2$ could lead to the following products:

$$\text{NO A} \times ^2\Sigma^+ + O_2 \times ^3\Sigma_g^- \rightarrow \text{NO X} \times ^2\Pi + O_2 \times ^1\Sigma_u^-$$
$$\text{NO A} \times ^2\Sigma^+ + O_2 \times ^3\Sigma_g^- \rightarrow \text{NO X} \times ^2\Pi + O_2 \times ^3\Sigma_u^+$$

### IV. CONCLUSIONS

Overall, we computed several sets of spin-doublet and spin-quartet PESs at the CASSCF and XMS-CASPT2 level. From our results, we propose two potential quenching pathways, $Q_1$ and $Q_2$, that can lead to NO $^2\Sigma^+$ quenching when colliding with $O_2 \times ^3\Sigma_g^-$. While $Q_1$ is limited to the spin-doublet framework, $Q_2$ can occur between both spin-doublet and spin-quartet states. The ionic quenching pathway ($Q_1$) has an orientation-specific energetic access, but it shouldn’t have an energy barrier. The gradient on the PES should lead to it because of long-range attractive forces. $Q_2$ should be favored by concerted vibrations of the two diatomic molecules, and high initial vibrational level of $O_2$ and NO. The cross-section of these quenching pathways will largely depends on the distribution of the collision energy, and should be estimated quantitatively only through dynamic calculations. $Q_1$ could lead to NO $^2\Pi$ with either $O_2 \times ^3\Sigma_g^-$, or even $O_2 \times ^3\Pi$, with high vibrational levels in $O_2$ due to the neutral - anion - neutral transition. Some of $O_2$ vibrational energy could be transferred to NO due to the proximity between the two molecules required by this quenching process. $Q_2$ should create mainly NO $^2\Pi$ with high excited states in $O_2$, like $^1\Sigma_u^-$, $^3\Delta_u^-$, and $^3\Sigma_u^+$ with probably lower vibrational level in NO, as this pathway does not require as much proximity as $Q_1$. These two quenching channels are consistent with earlier experimental results.

### SUPPLEMENTARY INFORMATION

Potential energy surface data points are available as attached files in the Electronic Supplementary Information. These are in the folder `surface` which contains a sub-folder for each surface. Each sub-folder contains 2D arrays of energies labeled as `Xi_surface.out`, where X can be D or Q for spin-doublet and spin-quartet respectively, and i corresponds to the number of the state. Those sub-folders also contain the list of inter-molecular distances (`R_list.out`), the list of angles (`param.out`), and pictures of the corresponding surface.

### CONFLICTS OF INTEREST

There are no conflicts to declare.

### ACKNOWLEDGMENTS

MJP thanks the EPSRC for funding through grants EP/P001459, EP/T021675, and EP/V006746. CS thank Heriot-Watt University for the award of a James-Watt scholarship, Prof. M. L. Costen for fruitful discussions, as well as Dr Jeremy Coe for help with HPC.

### REFERENCES

1. T. Li, Ø. Skreiberg, T. Løvås, and P. Glarborg, Fuel 254, 115569 (2019).
2. P. Crutzen, Canadian Journal of Chemistry 52, 1569 (1974).
3. P. S. Monks, Chemical Society Reviews 34, 376 (2005).
4. P. H. Paul, J. A. Gray, J. L. Durant, and J. W. Thoman, AIAM Journal 32, 1670 (1994), https://doi.org/10.2514/3.12158.
5. T. B. Settersten, B. D. Patterson, H. Kronenmayer, V. Sick, C. Schulz, and J. W. Daily, Phys. Chem. Chem. Phys. 8, 5328 (2006).
6. T. B. Settersten, B. D. Patterson, and C. D. Carter, The Journal of Chemical Physics 130, 204302 (2009), https://doi.org/10.1063/1.3138178.
7. R. Sánchez-González, W. D. Eveland, N. A. West, C. L. N. Mai, R. D. W. Bowserox, and S. W. North, The Journal of Chemical Physics 141, 074313 (2014), https://doi.org/10.1063/1.4892980.
8. J. Few, J. D. Fletcher, G. Hancock, J. L. Redmon, and G. A. D. Ritchie, Phys. Chem. Chem. Phys. 19, 11289 (2017).
9. K. J. Blackshaw, N.-K. Quartey, R. T. Korb, D. J. Hood, C. D. Hettwer, and N. M. Kidwell, The Journal of Chemical Physics 151, 104304 (2019), https://doi.org/10.1063/1.5109112.
10. B. F. Parsons, C. J. Jayson, D. E. Szpunar, and M. M. Cook, The Journal of Physical Chemistry A 125, 3406 (2021), pMID: 33852318, https://doi.org/10.1021/acs.jpca.1c01920.
11. L. Guardado, D. J. Hood, K. Luong, N. M. Kidwell, and A. S. Petit, The Journal of Physical Chemistry A 125, 8803 (2021), doi: 10.1021/acs.jpca.1c05653.
12. Pajón-Suárez, M. Valentin-Rodríguez, and R. Hernández-Lamoned, Chemical Physics Letters 658, 176 (2016).
13. J. Lozeille, S. E. Daire, S. D. Gamblin, T. G. Wright, and E. P. F. Lee, The Journal of Chemical Physics 113, 10952 (2000), https://doi.org/10.1063/1.1326068.
14. M. Asscher and Y. Haas, The Journal of Chemical Physics 76, 2115 (1982), https://doi.org/10.1063/1.443306.
15. P. H. Paul, J. A. Gray, J. L. Durant, and J. W. Thoman, Applied Physics B 57, 249 (1993).
16. P. Paul, J. Gray, J. Durant, and J. Thoman, Chemical Physics Letters 259, 508 (1996).
17. J. Nee, C. Juan, J. Hsu, J. Yang, and W. Chen, Chemical Physics 300, 85 (2004).
18. C. Soulié and M. J. Paterson, Phys. Chem. Chem. Phys. 24, 7983 (2022).
19. H.-J. Werner, P. J. Knowles, G. Knizia, F. R. Manby, and M. Schütz, WIREs Computational Molecular Science 2, 242 (2012), https://wires.onlinelibrary.wiley.com/doi/pdf/10.1002/wcms.82.
20. H.-J. Werner, P. J. Knowles, F. R. Manby, J. A. Black, K. Doll, A. Hellelmann, D. Kats, A. Köhn, T. Korona, D. A. Kreplin, Q. Ma, T. F. Miller, A. Mitrushchenkov, K. A. Peterson, I. Polyak, G. Rauhut, and M. Sibaev, The Journal of Chemical Physics 152, 144107 (2020), https://doi.org/10.1063/5.0005081.
21. R. Krivec, Few-Body Systems 25, 199 (1998).
22. P. J. Knowles and H.-J. Werner, Chemical Physics Letters 115, 259 (1985).
23. D. A. Kreplin, P. J. Knowles, and H.-J. Werner, The Journal of Chemical Physics 150, 194106 (2019), https://doi.org/10.1063/1.5094644.
24. K. P. Huber and G. Herzberg, “Constants of diatomic molecules,” in Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules (Springer US, Boston, MA, 1979) pp. 8–689.
25. T. H. Dunning, The Journal of Chemical Physics 90, 1007 (1989), https://doi.org/10.1063/1.456153.
26. D. E. Woon and T. H. Dunning, The Journal of Chemical Physics 100, 2975 (1994), https://doi.org/10.1063/1.466439.
27. R. A. Kendall, T. H. Dunning, and R. J. Harrison, The Journal of Chemical Physics 96, 6796 (1992), https://doi.org/10.1063/1.462569.
28. H.-J. WERNER, Molecular Physics 89, 645 (1996), https://doi.org/10.1080/002689796173967.
Scan along $\Theta_{\text{NO}} / \Theta_{\text{O}_2} = 90^\circ$, $\Phi = 0^\circ$.
XMS-CASPT2 scan NO $A^2\Sigma^+ + O_2 X^3\Sigma^-$

R = 3.9
E = 17.69

Energy (wavenumber/cm)

R (Angstroms)
Scan along $\Phi / \Theta_{O_2} = 90^\circ \quad \Theta_{NO} = 45^\circ$
$5 \text{ A}''$ states / $\Theta_{\text{NO}} = 45^\circ$ / $\Theta_{\text{O}_2} = 90^\circ$ / $\Phi = 0^\circ$
10 A'' states \( R = 15 \text{ Å} \) / \( \Theta_{\text{NO}} = 45^\circ \) / \( \Theta_{\text{O}_2} = 90^\circ \) / \( \Phi = 0^\circ \)

Energy (eV)

O\(_2\) Bond (Angstrom)
