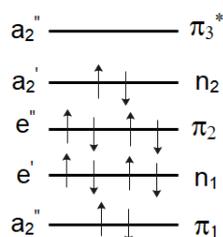


## Supporting Information

### S.1 Symmetry analysis

The transition from the ground state ( $A_1'$ ) to the  $n \rightarrow \pi^*$  state ( $A_1''$ ) (Figure S.1) in the gas phase nitrate anion ( $D_{3h}$ ) is highly forbidden by symmetry which can be rationalized by an analysis of the symmetry of the transition.



**Figure S.1:** Energy diagram for the nitrate anion electronic ground-state including orbital symmetries and labels

**Table S.1** Character table for the  $D_{3h}$  point group

$D_{3h}$	E	$\sigma_h$	$2C_3$	$2S_3$	$3C_2'$	$3\sigma_v$	h=12
$A_1'$	1	1	1	1	1	1	$z^2, x^2+y^2$
$A_2'$	1	1	1	1	-1	-1	$R_z$
$A_1''$	1	-1	1	-1	1	-1	
$A_2''$	1	-1	1	-1	-1	1	$z$
$E'$	2	2	-1	-1	0	0	$(x, y), (xy, x^2-y^2)$
$E''$	2	-2	-1	1	0	0	$(xz, yz), (R_x, R_y)$

The selection rule for electronic transitions states that the integrand in Equation 1 or its equivalents for  $x$ ,  $y$  or  $z$  must span the totally symmetric symmetry species ( $A_1'$  in the  $D_{3h}$  point group) for the transition dipole moment,  $\mu_{z,fi}$ , if it is not to vanish.

$$\mu_{z,fi} = -e \cdot \int \psi_i^* \cdot z \cdot \psi_f d\tau \quad (1)$$

Within the  $D_{3h}$  point group (Table S.1)  $x$  and  $y$  have the  $E'$  symmetry, while  $z$  has  $A_2''$ . Considering the  $\pi \rightarrow \pi^*$  transition corresponding to a transition from  $A_1'$  to  $E'$  symmetry, the symmetries of the transition dipole moment components are:

$$\mu_{x,y}^s = A_1' \times E' \times E' = A_1' + A_2' + E'$$

$$\mu_z^s = A_1' \times E' \times A_2'' = E''$$

Here the superscript,  $s$ , indicates that it is the symmetry of the component. For  $x$  and  $y$  the product contains the  $A_1'$  symmetry, thus the  $\pi \rightarrow \pi^*$  transition is allowed for  $x$  or  $y$  polarized light.

Similarly for the  $n \rightarrow \pi^*$  transition corresponding to a transition from  $A_1'$  to  $A_1''$ :

$$\mu_{x,y}^s = A_1' \times A_1'' \times E' = E''$$

$$\mu_z^s = A_1' \times A_1'' \times A_2'' = A_2'$$

As neither of the above contain  $A_1'$ , no orientation of light immediately allows the  $n \rightarrow \pi^*$  transition. Vibronic coupling to one or more vibrational modes of appropriate symmetry can result in symmetrically forbidden electronic transitions becoming allowed. It was just seen that the transition dipole moment for the  $n \rightarrow \pi^*$  transition in the  $x$  or  $y$  and the  $z$  direction spans  $E''$  and  $A_2'$  respectively. Hence vibronic coupling to a vibration of symmetry  $E''$  or  $A_2'$  is required:

$$E'' \times E'' = A_1' + A_2' + E'$$

$$A_2' \times A_2' = A_1'$$

The nitrate anion has six vibrational modes of which two pairs are degenerate, giving four vibrational frequencies of symmetries  $a_1'$ ,  $a_2''$ ,  $e'$  and  $e'$ , respectively. The symmetries of vibrational modes are given as lower-case letters to distinguish them from electronic states. None of the vibrational modes have the appropriate symmetry to allow the  $n \rightarrow \pi^*$  transition on their own. From the three vibrational symmetries of the nitrate normal modes four possible combinations can be made:

$e' \times a_2'' = e''$	<b>allowed for x and y</b>
$e' \times a_1' = e'$	not allowed
$e' \times e' = a_1' + a_2' + e'$	<b>allowed for z</b>
$a_1' \times a_2'' = a_2''$	not allowed

As vibronic coupling to  $e''$  or  $a_2'$  is required to make the transition dipole moment non-vanishing, vibronic coupling to vibrational modes with symmetries  $e'$  and  $a_2''$  or  $e'$  and  $e'$  can make the transition allowed in the  $x$  or  $y$  and  $z$  direction respectively.

**Table 0.2** Character table for the  $C_{2v}$  point group

$C_{2v}$	E	$C_2$	$\sigma_v$	$\sigma_v'$	h=4
$A_1$	1	1	1	1	$z, z^2, x^2+y^2$
$A_2$	1	1	-1	-1	$xy, R_z$
$B_1$	1	-1	1	-1	$x, xz, R_y$
$B_2$	1	-1	-1	1	$y, yz, R_x$

In solution the symmetry of the nitrate anion is reduced to  $C_{2v}$ . Within the  $C_{2v}$  framework (Table 0.2) the  $n \rightarrow \pi^*$  state has the  $A_2$  symmetry and the ground-state has  $A_1$  symmetry. The transition dipole moment in the  $x$ ,  $y$  and  $z$  directions including no vibronic coupling have  $B_2$ ,  $B_1$  and  $A_2$  symmetries:

$$\mu_x^s = A_1 \times A_2 \times B_1 = B_2$$

$$\mu_y^s = A_1 \times A_2 \times B_2 = B_1$$

$$\mu_z^s = A_1 \times A_2 \times A_1 = A_2$$

Again none of the components contain  $A_1$ , making all three components forbidden. Considering first vibronic coupling to one vibrational mode it is clear that vibrations of symmetry  $b_2$ ,  $b_1$  or  $a_2$  can make the transition allowed in the  $x$ ,  $y$  and  $z$  direction. The  $C_{2v}$  nitrate anion has six vibrational modes of symmetries  $a_1$ ,  $a_1, a_1$ ,  $b_1$ ,  $b_2$  and  $b_2$ . Thus, three vibrational modes have the correct symmetry in them self to allow the transition. Furthermore 11 combinations give the right symmetry.

To a first approximation the oscillator strength is proportional to the norm square of the transition dipole moment. However, given the low intensity of  $n \rightarrow \pi^*$  state, higher order terms such as the magnetic transition dipole moment or the electric quadrupole moment could potentially contribute to the observed intensity. Within the  $D_{3h}$  point group the quadratic terms  $z^2$  and  $x^2 + y^2$  have  $A_1'$  symmetry,  $xy$  and  $x^2 - y^2$  have  $E'$  symmetry and  $xz$  and  $yz$  have  $E''$  symmetry. As the products of all of these with the involved states do not contain  $A_1'$  the quadrupole moment for the  $n \rightarrow \pi^*$  ( $A_1' \rightarrow A_1''$ ) in the gas phase is zero:

$$A_1' \times A_1'' \times A_1' = A_1''$$

$$A_1' \times A_1'' \times E' = E''$$

$$A_1' \times A_1'' \times E'' = E'$$

Similarly the magnetic transition dipole moment is zero as the linear rotations  $R_x$ ,  $R_y$  and  $R_z$  spans  $E''$ ,  $E'$  and  $A_2'$  respectively and:

$$A_1' \times A_1'' \times A_2' = A_2''$$

Thus, the electric transition quadrupole moment and the magnetic transition dipole moment are forbidden in the zeroth order approximation. Vibronic coupling to vibrational modes of symmetries  $A_2''$  or  $E'$  could potentially result in contributions from these terms, however these are assumed to be negligible.

In the  $C_{2v}$  geometry the electric transition quadrupole moment and the magnetic transition dipole moment of the  $n \rightarrow \pi^*$  transition ( $A_1 \rightarrow A_2$ ) are allowed as  $xz$  and  $R_z$  both have the  $A_2$  symmetry. However it was found that the small structural change going from  $D_{3h}$  to  $C_{2v}$  was insufficient to make the first order vibronic coupling terms non-zero, although symmetry considerations show that these could potentially be non-zero. Hence it is assumed that also the electric transition quadrupole moment and the magnetic transition dipole moment terms can be neglected.

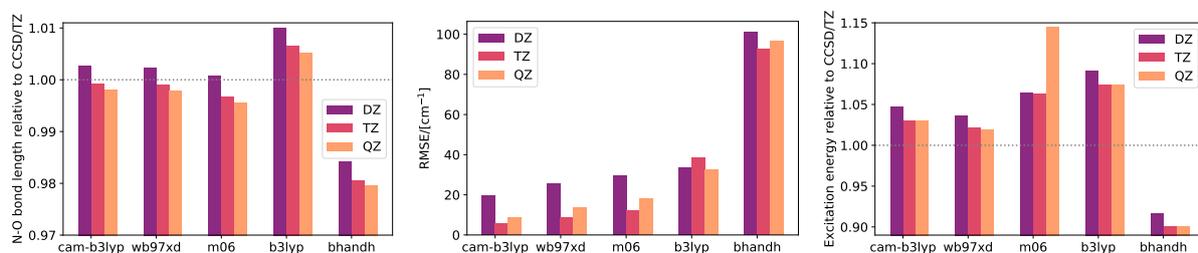
## S.2 Benchmark

Three parameters that are important for the calculation of oscillator strengths are chosen as benchmark parameters, namely the N-O bond length, the vibrational frequencies and the excitation energy. Five DFT methods and three basis sets (aug-cc-pVDZ (DZ), aug-cc-pVTZ (TZ) and aug-cc-pVQZ (QZ)) have been tested and compared with CCSD/aug-cc-pVTZ values.

The ground state N-O bond length,  $r_{N-O}$  in the left panel of Figure S.2, for the free nitrate anion optimized at the CCSD/aug-cc-pVTZ level of theory is 1.249870 Å. For all five methods the bond length decreased with increasing zeta value, resulting in an overestimated bond length for DZ for the long-range corrected functionals, CAM-B3LYP and  $\omega$ B97XD,

whereas for TZ these two methods predicts a bond length that is 99% of the CCSD value. The meta gga functionals B3LYP and BHandH both completely fail to reproduce the correct bond lengths with all three basis sets.

The central panel of Figure S.2 shows the root mean square deviation for the vibrational frequencies. The long-range corrected performs the best. The same trend is observed for the excitation wavelength (Figure S.2 right panel), namely, CAM-B3LYP and  $\omega$ B97XD perform the best with  $\omega$ B97XD giving slightly better excitation energies while especially BHandH severely underestimates the excitation energy.



**Figure S.2:** N-O bond length (left panel), vibrational frequency (central panel) and excitation energy (right panel)

### S.3 Coordinates for Optimized Structures

**Table S.3** Coordinates in Å for gas phase  $\text{NO}_3^-$  calculated at the  $\omega$ B97XD/aug-cc-pVTZ level of theory

Atomic number	X	Y	Z
7	0.000000	0.000000	0.000000
8	0.000000	1.248745	-0.000000
8	1.081445	-0.624372	-0.000000
8	-1.081445	-0.624372	-0.000000

**Table S.4** Coordinates in Å for aqueous phase  $\text{NO}_3^-$  calculated at the  $\omega$ B97XD/aug-cc-pVTZ level of theory

Atomic number	X	Y	Z
7	-0.000000	0.000000	-0.000060
8	0.000000	-0.000000	1.246685
8	0.000000	1.079798	-0.623317
8	-0.000000	-1.079798	-0.623317