Supplementary Material

Each element of the potential matrix (Eq. 1) is written as an expansion of the form

$$V_{pq} = \sum_k F_i^{pq} q_i + \frac{1}{2} \sum_{kl} F_{kl}^{pq} q_k q_l + \frac{1}{6} \sum_{klm} F_{klm}^{pq} q_k q_l q_m + \frac{1}{24} \sum_{klmn} F_{klmn}^{pq} q_k q_l q_m q_n, \tag{A1}$$

where the q_n are reduced (dimensionless) normal coordinates of the nitrate anion. In NO_3, q_1 is the symmetric stretching mode, q_2 the out-of-plane umbrella mode, and q_3 and q_4 are the degenerate stretching and bending modes of e' symmetry. The complete parametrization of this Hamiltonian is embedded in the file below, which is part of an input for the XSIM simulation program of Stanton. Comments in the file should serve to help the reader understand the connection between the input values and the constants in Eq. A1. All constants here are the *ab initio* values; the off-diagonal terms (in the state basis, *i.e.* $p \neq q$ were scaled by a factor of 0.975 in the computations here. All values are in cm^{-1}.

```
Mode numbering scheme
1 = q1
2 = q2
3 = q3a
4 = q4a
5 = q3b
6 = q4b
Vertical Energies  ! Gaps between X and B state at q=0
0 15406. 15406.
Frequencies ! Anion frequencies that define the reduced normal coordinates
1 1060.6
2  858.1
3 1432.4
4  716.4
5 1432.4
6  716.4
0 0 0 0 0 0 0 0
Linear ! linear constants; three indices are pqi in Eq. A1
1 1 1     -868.2
2 2 1      440.5
3 3 1      440.5
2 2 3      440.7
3 3 3     -440.7
2 3 5      440.7
2 2 4      762.2
3 3 4     -762.2
2 3 6      762.2
1 3 3     2855.5
1 2 5     2855.5
1 3 4    -1095.5
```

```
1 2 6    -1095.5
0 0 0 0 0 0 0 0
Quadratic ! quadratic constants; four indices are pqij in Eq. A1
1 1 1 1         960.300000000000
2 2 1 1        1070.800000000000
3 3 1 1        1070.800000000000
1 1 3 3        1482.947899571595
1 1 5 5        1482.947899571595
1 1 4 4         562.386556917565
1 1 6 6         562.386556917565
1 1 3 4          -0.088084787745
1 1 5 6          -0.088084787745
2 2 3 3         819.100000000000
3 3 5 5         819.100000000000
3 3 3 3         968.452100428404
2 2 5 5         968.452100428404
2 3 3 5          74.676050214202
2 2 4 4         677.500000000000
3 3 6 6         677.500000000000
3 3 4 4         570.413443082435
2 2 6 6         570.413443082435
2 3 4 6         -53.543278458782
2 2 3 4          83.000000000000
3 3 5 6          83.000000000000
3 3 3 4         121.688084787745
2 2 5 6         121.688084787745
2 3 3 6          19.344042393872
2 3 5 4          19.344042393872
2 2 1 3         -61.300000000000
3 3 1 3          61.300000000000
2 3 1 5         -61.300000000000
2 2 1 4          66.400000000000
3 3 1 4         -66.400000000000
2 3 1 6          66.400000000000
1 3 1 3         130.560000000000
1 2 1 5         130.560000000000
1 3 1 4        -121.920000000000
1 2 1 6        -121.920000000000
1 3 3 3         120.960000000000
1 3 5 5        -120.960000000000
1 2 3 5        -120.960000000000
1 3 4 4        -135.360000000000
1 3 6 6         135.360000000000
1 2 4 6         135.360000000000
1 3 3 4          38.400000000000
1 3 5 6         -38.400000000000
```

```
1 2 3 6         -38.400000000000
1 2 5 4         -38.400000000000
0 0 0 0 0 0 0 0
Cubic ! cubic constants; five indices are pqijk in Eq. A1
1 1 1 1 1         197.300000000000
1 1 1 3 3         289.400000000000
1 1 1 5 5         289.400000000000
1 1 1 4 4          50.200000000000
1 1 1 6 6          50.200000000000
1 1 1 3 4          72.200000000000
1 1 1 5 6          72.200000000000
1 1 3 3 3        -210.800000000000
1 1 3 5 5         210.800000000000
1 1 4 4 4          41.700000000000
1 1 4 6 6         -41.700000000000
1 1 3 3 4         -37.300000000000
1 1 5 5 4          37.300000000000
1 1 3 5 6          37.300000000000
1 1 3 4 4         -26.000000000000
1 1 3 6 6          26.000000000000
1 1 5 4 6          26.000000000000
2 2 1 1 1         204.700000000000
3 3 1 1 1         204.700000000000
2 2 1 1 3         -12.000000000000
3 3 1 1 3          12.000000000000
2 3 1 1 5         -12.000000000000
2 2 1 3 3         231.400000000000
3 3 1 5 5         231.400000000000
3 3 1 3 3         243.800000000000
2 2 1 5 5         243.800000000000
2 3 1 3 5           6.200000000000
2 2 3 3 3        -414.800000000000
3 3 3 3 3        -101.400000000000
2 2 3 5 5         205.866666666667
3 3 3 5 5         310.333333333333
2 3 5 5 5        -156.700000000000
2 3 3 3 5         -52.233333333333
2 2 1 1 4           7.500000000000
3 3 1 1 4          -7.500000000000
2 3 1 1 6           7.500000000000
2 2 1 4 4          63.600000000000
3 3 1 6 6          63.600000000000
3 3 1 4 4          45.600000000000
2 2 1 6 6          45.600000000000
2 3 1 4 6          -9.000000000000
2 2 4 4 4          45.400000000000
```

```
3 3 4 4 4          34.800000000000
2 2 4 6 6         -38.333333333333
3 3 4 6 6         -41.866666666667
2 3 6 6 6           5.300000000000
2 3 4 4 6           1.766666666667
2 2 1 3 4          81.200000000000
3 3 1 5 6          81.200000000000
3 3 1 3 4          80.400000000000
2 2 1 5 6          80.400000000000
2 3 1 3 6          -0.400000000000
2 3 1 4 5          -0.400000000000
2 2 3 3 4         -66.800000000000
3 3 3 3 4         -60.800000000000
2 2 4 5 5          63.800000000000
3 3 4 5 5          63.800000000000
2 2 3 5 6          62.300000000000
3 3 3 5 6          65.300000000000
2 3 5 5 6          -3.000000000000
2 3 3 4 5          -1.500000000000
2 2 4 4 3           0.000000000000
3 3 4 4 3           9.000000000000
2 2 3 6 6          -4.500000000000
3 3 3 6 6          -4.500000000000
2 2 4 6 5          -6.750000000000
3 3 4 6 5          -2.250000000000
2 3 6 6 5          -4.500000000000
2 3 4 3 6          -2.250000000000
1 2 5 5 5         -90.000000000000
1 2 3 3 5         -30.000000000000
1 3 3 3 3         -90.000000000000
1 3 3 5 5         -30.000000000000
0 0 0 0 0 0 0 0 0
Quartic ! quartic constants; six indices are pqijkl in Eq. A1
1 1 1 1 1 1          32.900000000000
1 1 1 1 3 3          43.700000000000
1 1 1 1 5 5          43.700000000000
1 1 1 1 4 4           0.400000000000
1 1 1 1 6 6           0.400000000000
1 1 1 1 3 4          20.600000000000
1 1 1 1 5 6          20.600000000000
1 1 1 3 3 3         -74.200000000000
1 1 1 3 5 5          74.200000000000
1 1 1 4 4 4          -1.500000000000
1 1 1 4 6 6           1.500000000000
1 1 1 3 3 4          -4.000000000000
1 1 1 5 5 4           4.000000000000
```

1 1 1 3 5 6	4.000000000000
1 1 1 3 4 4	-0.600000000000
1 1 1 3 6 6	0.600000000000
1 1 1 5 6 4	0.600000000000
1 1 3 3 3 3	115.900000000000
1 1 5 5 5 5	115.900000000000
1 1 3 3 5 5	38.633333333333
1 1 3 3 3 4	31.900000000000
1 1 5 5 5 6	31.900000000000
1 1 3 5 5 4	10.633333333333
1 1 3 3 5 6	10.633333333333
1 1 3 4 4 4	-5.700000000000
1 1 5 6 6 6	-5.700000000000
1 1 3 4 6 6	-1.900000000000
1 1 5 4 4 6	-1.900000000000
1 1 4 4 4 4	-1.400000000000
1 1 6 6 6 6	-1.400000000000
1 1 4 4 6 6	-0.466666666667
1 1 3 3 4 4	22.600000000000
1 1 5 5 6 6	22.600000000000
1 1 3 3 6 6	-10.404800000000
1 1 5 5 4 4	-10.404800000000
1 1 3 5 4 6	16.502400000000
2 2 1 1 1 1	32.700000000000
3 3 1 1 1 1	32.700000000000
2 2 1 1 1 3	-1.000000000000
3 3 1 1 1 3	1.000000000000
2 3 1 1 1 5	-1.000000000000
2 2 1 1 3 3	40.400000000000
3 3 1 1 5 5	40.400000000000
3 3 1 1 3 3	40.400000000000
2 2 1 1 5 5	40.400000000000
2 3 1 1 3 5	0.000000000000
2 2 1 3 3 3	-72.200000000000
3 3 1 3 3 3	-24.900000000000
2 2 1 3 5 5	40.666666666667
3 3 1 3 5 5	56.433333333333
2 3 1 5 5 5	-23.650000000000
2 3 1 3 3 5	-7.883333333333
2 2 3 3 3 3	134.200000000000
3 3 3 3 3 3	52.200000000000
2 2 5 5 5 5	52.200000000000
3 3 5 5 5 5	134.200000000000
2 2 3 3 5 5	31.066666666667
3 3 3 3 5 5	31.066666666667
2 3 3 3 3 5	-20.500000000000

2 3 3 5 5 5	-20.500000000000
2 2 1 1 1 4	1.000000000000
3 3 1 1 1 4	-1.000000000000
2 3 1 1 1 6	1.000000000000
2 2 1 1 4 4	5.600000000000
3 3 1 1 6 6	5.600000000000
3 3 1 1 4 4	7.000000000000
2 2 1 1 6 6	7.000000000000
2 3 1 1 4 6	0.700000000000
2 2 1 4 4 4	3.300000000000
3 3 1 4 4 4	6.800000000000
2 2 1 4 6 6	-5.633333333333
3 3 1 4 6 6	-4.466666666667
2 3 1 6 6 6	-1.750000000000
2 3 1 4 4 6	-0.583333333333
2 2 4 4 4 4	1.300000000000
3 3 4 4 4 4	-0.500000000000
2 2 6 6 6 6	-0.500000000000
3 3 6 6 6 6	1.300000000000
2 2 4 4 6 6	0.133333333333
3 3 4 4 6 6	0.133333333333
2 3 4 4 4 6	-0.450000000000
2 3 4 6 6 6	-0.450000000000
2 2 1 1 3 4	15.800000000000
3 3 1 1 5 6	15.800000000000
3 3 1 1 3 4	10.700000000000
2 2 1 1 5 6	10.700000000000
2 3 1 1 3 6	-2.550000000000
2 3 1 1 4 5	-2.550000000000
2 2 4 3 3 3	36.000000000000
3 3 4 3 3 3	54.000000000000
2 2 6 5 5 5	36.000000000000
3 3 6 5 5 5	54.000000000000
2 2 4 3 5 5	24.000000000000
3 3 4 3 5 5	6.000000000000
2 2 3 3 6 5	24.000000000000
3 3 3 3 6 5	6.000000000000
2 3 3 3 3 6	-9.000000000000
2 3 4 5 5 5	9.000000000000
2 3 4 3 3 5	-9.000000000000
2 3 3 6 5 5	9.000000000000
2 2 3 4 4 4	3.200000000000
3 3 3 4 4 4	16.100000000000
2 2 5 6 6 6	3.200000000000
3 3 5 6 6 6	16.100000000000
2 2 3 4 6 6	9.666666666667

```
3 3 3 4 6 6          -3.233333333333
2 2 4 4 5 6           9.666666666667
3 3 4 4 5 6          -3.233333333333
2 3 4 4 4 5          -6.450000000000
2 3 3 6 6 6           6.450000000000
2 3 3 4 4 6          -6.450000000000
2 3 4 5 6 6           6.450000000000
2 2 1 3 3 4          -5.200000000000
3 3 1 3 3 4          -5.000000000000
2 2 1 4 5 5           5.100000000000
3 3 1 4 5 5           5.100000000000
2 2 1 3 5 6           5.050000000000
3 3 1 3 5 6           5.150000000000
2 3 1 5 5 6          -0.100000000000
2 3 1 3 4 5          -0.050000000000
2 2 1 4 4 3          -2.000000000000
3 3 1 4 4 3          -6.000000000000
2 2 1 3 6 6           4.000000000000
3 3 1 3 6 6           4.000000000000
2 2 1 4 6 5           5.000000000000
3 3 1 4 6 5           3.000000000000
2 3 1 6 6 5           2.000000000000
2 3 1 4 3 6           1.000000000000
2 2 3 3 4 4          10.100000000000
3 3 3 3 4 4         -25.700000000000
2 2 3 3 6 6         -26.000000000000
3 3 3 3 6 6         -26.000000000000
2 2 4 4 5 5         -26.000000000000
3 3 4 4 5 5         -26.000000000000
2 2 5 5 6 6         -25.700000000000
3 3 5 5 6 6          10.100000000000
2 2 3 5 4 6           9.100000000000
3 3 3 5 4 6           9.100000000000
2 3 3 3 4 6          -8.950000000000
2 3 3 5 4 4          -8.950000000000
2 3 3 5 6 6          -8.950000000000
2 3 5 5 4 6          -8.950000000000
0 0 0 0 0 0 0 0
```