

Supporting Material

MRCI investigation of Ni₂O₂ and Ni₂O₂⁺

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Results for Ni₂O₂

Figure S1 shows the energetic order of the different terms of Ni₂O₂ according to the MRCI calculations (without Davidson correction) that use the orbitals from the CASSCF calculations with the smaller active space (8 or 10 orbitals) at the Davidson corrected MRCI minimum structure of the ¹A_g ground term. The other two terms that form the lowest-lying spin ladder together with the ground term are ³B_{1u} and ⁵A_g at relative energies of 0.10 and 0.26 eV. With respect to the results that include the Davidson correction, there are only small differences. The relative energies (of the singlet terms) of the different spin ladders change by at most 0.07 eV, the inclusion of the Davidson correction increases the singlet quintet splitting by at most 0.05 eV.

The occupation of the natural orbitals for selected terms by the CASSCF calculations is given in Tables S1 and S2. Taking as an example the terms of the lowest-lying spin ladder, it can be seen that the terms of different multiplicity of a given ladder have similar occupation patterns. The results with the larger active space that includes a part of the 2p orbitals of O indicate that the open shell domain in principle contains only the 3d orbitals. The occupation numbers of those active orbitals that are essentially oxygen 2p orbitals with minor contributions from the nickel 3d orbitals amount to values close to 2, between 1.97 and 1.99. Concerning the ⁵B_{1u} term it is noticeable that there are larger differences between the results with both active spaces. In this case, indeed the inclusion of the 2p orbitals has a larger effect.

Table S3 contains the term energies, equilibrium distances and harmonic vibrational frequencies (of both totally symmetric modes) of the optimised structures of selected terms, using the CASSCF orbitals of the calculations with the smaller active space. The structure optimisations yield values for the term energies of the excited states that are lower by up to 0.06 eV than at the structure of the ground state. For the higher-lying terms of the lowest-energy spin ladder, ³B_{1u} and ⁵A_g, the term energies amount to 0.11 and 0.28 eV including the Davidson correction.

The structure determination yield values for Ni–Ni distances of the ¹A_g ground term of 231.1 and 229.3 pm (without and with Davidson correction) and corresponding values for the O–O distance of 275.5 and 275.8 pm. Therefore, the values for the Ni–O distance amount to 178.8 and 179.3 pm (without and with Davidson correction). For all considered excited states the optimised structures are similar to that of the ground term. The Ni–Ni distances are elongated by at maximum 7 pm with respect to the ground state, the O–O distances by at maximum 3 pm. In case of the ¹B_{3u} term the O–O distance is shortened, namely by less than 1 pm. For the low-lying excited states ³B_{1u} and ⁵A_g, the Ni–Ni distances amount to 231.0 and 233.3 pm with Davidson correction, and the O–O distances amount to 277.0 and 278.4 pm with Davidson correction. Hence, the step to a state of higher spin multiplicity comes along with a slight expansion of the structure. In general,

the inclusion of the Davidson correction induces a decrease of the Ni–Ni distance by less than 2 pm and an increase of the O–O distance by up to 1 pm.

The calculated values of the harmonic vibrational frequencies of both totally symmetric modes of the 1A_g term amount to 719 and 338 cm^{-1} without Davidson correction and to 705 and 341 cm^{-1} with Davidson correction. For the other terms of the lowest-energy spin ladder, $^3B_{1u}$ and 5A_g , the values for the higher-frequency mode are 710 and 711 cm^{-1} with Davidson correction, and the values for the lower-frequency mode are 329 and 308 cm^{-1} with Davidson correction. Thus, the step from 1A_g to $^3B_{1u}$ leads to an increase of the higher-frequency mode by about 5 cm^{-1} and to a decrease of the lower-frequency mode by about 10 cm^{-1} , and the step to the 5A_g term leads to corresponding changes by 1 cm^{-1} and 20 cm^{-1} . Especially for the lower-frequency mode there is a pronounced change accompanying the step from $^3B_{1u}$ to 5A_g . The calculated frequencies of the other singlet terms, except for the high-lying $^1B_{1u}$ term, differ from the result for the ground state in the case of the higher-frequency mode by at most 10 cm^{-1} and in the case of the lower-frequency mode by at most 20 cm^{-1} . The inclusion of the Davidson correction in general shifts the values for the higher-frequency mode by about 15 cm^{-1} but hardly affects the lower-frequency mode.

Results for Ni_2O_2^+ (D_{2h})

Figure S2 shows the energetic order of the different terms of Ni_2O_2^+ according to the MRCI calculations (without Davidson correction) at the Davidson corrected MRCI structure of the $^2B_{2g}$ term using the orbitals from the CASSCF calculations with the smaller active space (14 or 16 orbitals). The lowest term according to the calculations is a $^2B_{2g}$ term. The associated $^4B_{3u}$ term is found only 0.007 eV higher in energy. With respect to the results that include the Davidson correction, the size of the splitting between the $^2B_{2g}$ ground term and the $^4B_{3u}$ term is reduced by 0.047 eV. The relative positions of the other terms is changed by at maximum 0.05 eV.

The occupation of the natural orbitals from the CASSCF calculations for selected states is shown in Tables S4 and S5. For all doublet and quartet terms, the two valence orbitals of b_{3u} symmetry are composed by about equal amounts of oxygen 2p and nickel 3d orbitals. Furthermore, there are 5 valence orbitals with the main contribution from the oxygen 2p orbitals and minor contributions from nickel 3d orbitals, and further 9 orbitals with the main contribution from the nickel 3d orbitals and minor contributions from oxygen. The occupation number of the higher occupied b_{3u} orbital amounts to about 1.7, that of the other b_{3u} orbital amounts to from 0.4 to 0.7, depending on the state. Then, the sum for both orbitals adds up to between 2.1 and 2.4, and therefore, about 1.1 to 1.2 electrons can be assigned to oxygen and nickel. The occupation numbers of the 5 essentially oxygen 2p orbitals are close to 2, between 1.92 and 2.00. Hence, Ni_2O_2^+ can be characterised by an occupation of the oxygen 2p orbitals by about 11 electrons. This means, compared to the neutral, that one electron is removed from the 2p shells.

Taking as an example some of the doublet quartet pairs ($^4B_{1u}$ and 2A_g , 4A_g and $^2B_{1u}$, $^4B_{2g}$ and $^2B_{3u}$, $^4B_{3u}$ and $^2B_{2g}$) it can be seen that the two terms of a pair exhibit similar orbital occupations. They differ essentially in the spin coupling between the Ni centres. For the calculated states, with the exception of the $^4B_{2g}$ and $^2B_{3u}$ terms, the Ni 3d b_{2g} orbital is basically singly occupied. The lowest two terms, $^2B_{2g}$ and $^4B_{3u}$, are characterised by two further singly occupied orbitals, b_{1u} and a_u , whereas the other 6 3d orbitals are essentially doubly occupied. The next pairs of terms,

in energetical order, with the quartet terms $^4B_{1u}$, 4A_g , $^4B_{3g}$, $^4B_{2u}$, 4A_u , $^4B_{1g}$, are characterised by 4 3d orbitals with an occupation of about 1.5 electrons and further 4 orbitals that are essentially doubly occupied. For the higher lying terms, $^4B_{2g}$ and $^2B_{3u}$, the orbitals cannot be classified simply according to their occupations: the occupation numbers of the 3d orbitals vary between 1.4 and 1.9. For the sextet terms of the Table, in principle 6 orbitals can be assigned to oxygen 2p orbitals. The occupation of the b_{1g} orbital amounts to about 1.2. Hence, these sextet terms too are characterised by not completely filled oxygen 2p shells. Concerning the further sextet terms, the situation is rather less clear, but there are always orbitals with essential oxygen contribution that have occupation numbers clearly smaller than two. The results of the calculations with the larger active space (Ni 4s orbitals) essentially agree with those relying on the smaller active space. The additional active orbitals are occupied by at most 0.05 electrons.

Table S6 shows the term energies, equilibrium distances, and harmonic vibrational frequencies (of the totally symmetric modes) for selected terms of $Ni_2O_2^+$ by MRCI calculations that use the orbitals of the CASSCF calculations with the large active space. Compared to the results that are based on the smaller active space orbitals, there are only small changes, except for the $^2B_{2u}$ term. The changes in relative term energies amount to at most 0.03 eV, the changes in Ni–Ni and O–O distances to at most 2 pm, and the changes in vibrational frequencies amount to at most 14 or 20 cm^{-1} , depending on the mode. In case of the Davidson corrected results for the $^2B_{2u}$ term, the Ni–Ni distance is shortened by 16 pm, the O–O distance elongated by 11 pm, and the harmonic frequencies increase by 50 and 165 cm^{-1} . The reason for this discrepancy is found in the fact that the Davidson corrected results yield an additional minimum of the potential energy hyper surface, which does not correspond to the results with the smaller active space orbitals. But another (corresponding) minimum is still found at an energy higher by 0.05 eV.

Table S1: Occupation of the natural orbitals of selected terms of Ni₂O₂ by the CASSCF calculations with the small active space (8 or 10 orbitals) at the Davidson corrected structure of the ¹A_g ground term (7s6p4d3f2g/5s4p3d2f ANO basis set).

Ni ₂ O ₂ Term	Ni-3d									
	8a _g	10a _g	6b _{3u}	4b _{2u}	2b _{1g}	6b _{1u}	8b _{1u}	4b _{2g}	3b _{3g}	1a _u
¹ A _g	2	1.95	0.91	1.95	0.97	2	1.95	1.19	1.95	1.13
³ B _{1u}	2	1.95	0.97	1.95	1.01	2	1.94	1.14	1.94	1.10
⁵ A _g	2	1.94	1.05	1.94	1.06	2	1.94	1.06	1.94	1.06
¹ B _{1u}	1.76	1.50	1.14	1.77	1.75	1.72	1.50	1.34	1.76	1.78
³ A _g	1.77	1.52	1.16	1.76	1.75	1.71	1.48	1.32	1.76	1.77
⁵ B _{1u}	1.96	1.57	1.47	1.47	1.50	1.95	1.46	1.60	1.48	1.55
¹ B _{3u}	1.97	1.92	0.99	1.54	1.42	1.97	1.92	1.23	1.56	1.48
¹ B _{2g}	1.97	1.92	0.99	1.58	1.40	1.97	1.90	1.25	1.54	1.48
¹ B _{2u}	1.98	1.48	0.96	1.58	1.90	1.97	1.44	1.22	1.56	1.92
¹ B _{3g}	1.98	1.47	0.96	1.57	1.91	1.97	1.45	1.21	1.57	1.92
¹ B _{1g}	1.99	1.50	0.90	1.96	1.50	1.98	1.50	1.18	1.96	1.54
¹ A _u	1.99	1.53	0.90	1.96	1.48	1.98	1.48	1.18	1.96	1.55

Table S2: Occupation of the natural orbitals of selected terms of Ni₂O₂ by the CASSCF calculations with the large active space (14 or 16 orbitals) at the Davidson corrected structure of the ¹A_g ground term (7s6p4d3f2g/5s4p3d2f ANO basis set).

Ni ₂ O ₂ Term	O-2p						Ni-3d								Ni-4s			
	9a _g	5b _{3u}	3b _{2u}	1b _{1g}	7b _{1u}	3b _{2g}	8a _g	10a _g	6b _{3u}	4b _{2u}	2b _{1g}	6b _{1u}	8b _{1u}	4b _{2g}	3b _{3g}	1a _u	11a _g	9b _{1u}
¹ A _g	1.99	1.98	2	2	1.99	1.98	2	1.95	0.88	1.95	0.96	2	1.95	1.22	1.95	1.14	0.03	0.03
³ B _{1u}	1.99	1.98	2	2	1.99	1.98	2	1.95	0.94	1.95	1.01	2	1.95	1.17	1.95	1.10	0.03	0.03
⁵ A _g	1.99	1.98	2	2	1.99	1.98	2	1.95	1.05	1.94	1.05	2	1.94	1.06	1.94	1.06	0.03	0.03
¹ B _{1u}	1.99	1.97	2	2	1.98	1.98	1.72	1.49	1.03	1.82	1.80	1.66	1.51	1.35	1.81	1.82	0.04	0.04
³ A _g	1.99	1.97	2	2	1.98	1.98	1.73	1.53	1.06	1.82	1.80	1.64	1.47	1.32	1.81	1.82	0.04	0.04
⁵ B _{1u}	1.99	1.98	2	2	1.99	1.98	1.76	1.55	1.19	1.79	1.77	1.67	1.45	1.25	1.78	1.80	0.03	0.04
¹ B _{3u}	1.99	1.97	2	2	1.99	1.98	1.97	1.94	0.92	1.52	1.44	1.97	1.94	1.27	1.54	1.50	0.03	0.04
¹ B _{2g}	1.99	1.97	2	2	1.99	1.98	1.97	1.94	0.92	1.56	1.42	1.97	1.92	1.28	1.52	1.50	0.04	0.04
¹ B _{2u}	1.99	1.97	2	2	1.98	1.98	1.98	1.49	0.88	1.57	1.93	1.98	1.44	1.26	1.54	1.94	0.04	0.04
¹ B _{3g}	1.99	1.97	2	2	1.98	1.97	1.98	1.48	0.88	1.55	1.94	1.98	1.45	1.25	1.55	1.94	0.04	0.04
¹ B _{1g}	1.99	1.98	2	2	1.99	1.98	1.98	1.49	0.85	1.97	1.50	1.98	1.50	1.23	1.97	1.54	0.03	0.04
¹ A _u	1.99	1.98	2	2	1.99	1.98	1.98	1.53	0.85	1.97	1.48	1.98	1.47	1.23	1.96	1.56	0.03	0.04

Table S3: Term energies, equilibrium distances, and harmonic vibrational frequencies of both totally symmetric modes for selected terms of Ni₂O₂ by MRCI calculations (7s6p4d3f2g/5s4p3d2f ANO basis set). The reference space is the complete active space of the 10 3d orbitals of Ni and the 6 2p orbitals of O. The active space of the CASSCF calculations consists of 8 or 10 of the 3d orbitals of Ni. Davidson corrected results in parenthesis.

Term	T_e/eV	$r_e^{\text{Ni-Ni}}/\text{pm}$	$r_e^{\text{O-O}}/\text{pm}$	$\tilde{\nu}_e^{(1)}/\text{cm}^{-1}$	$\tilde{\nu}_e^{(2)}/\text{cm}^{-1}$
¹ A _g	0.0 (0.0)	231.1 (229.3)	275.5 (275.8)	719 (705)	338 (341)
³ B _{1u}	0.090 (0.113)	232.5 (231.0)	276.3 (277.0)	724 (710)	328 (329)
⁵ A _g	0.228 (0.282)	234.5 (233.3)	277.3 (278.4)	724 (711)	312 (308)
¹ B _{1u}	1.056 (1.106)	237.3 (235.7)	277.3 (278.3)	692 (674)	323 (322)
¹ B _{3u}	0.468 (0.495)	236.2 (234.7)	274.8 (275.4)	710 (696)	330 (331)
¹ B _{2g}	0.437 (0.457)	234.9 (233.2)	275.6 (276.3)	715 (701)	326 (326)
¹ B _{2u}	0.662 (0.715)	237.5 (236.0)	276.0 (276.9)	710 (696)	321 (321)
¹ B _{3g}	0.667 (0.722)	237.8 (236.4)	275.8 (276.7)	709 (694)	323 (323)
¹ B _{1g}	0.313 (0.352)	233.7 (232.2)	276.9 (277.7)	720 (705)	331 (332)
¹ A _u	0.285 (0.317)	233.0 (231.4)	276.9 (277.5)	718 (703)	330 (332)
² ¹ A _g	0.466 (0.536)	235.2 (233.8)	277.7 (278.7)	716 (701)	324 (324)

Table S4: Occupation of the natural orbitals of selected terms of Ni₂O₂⁺ by the CASSCF calculations with the smaller active space (14 or 16 orbitals) at the Davidson corrected structure of the ²B_{2g} term (7s6p4d3f2g/5s4p3d2f ANO basis set).

Ni ₂ O ₂ ⁺ Term	O-2p					Ni-3d-O-2p		Ni-3d								
	9a _g	3b _{2u}	1b _{1g}	7b _{1u}	3b _{2g}	5b _{3u}	6b _{3u}	8a _g	10a _g	4b _{2u}	2b _{1g}	6b _{1u}	8b _{1u}	4b _{2g}	3b _{3g}	1a _u
⁴ B _{1u}	1.96	1.98	1.97	1.99	1.97	1.71	0.44	1.99	1.95	1.44	1.41	1.98	1.96	1.05	1.61	1.59
² A _g	1.98	1.99	1.97	1.99	1.96	1.69	0.53	1.96	1.91	1.57	1.40	1.97	1.92	1.09	1.54	1.52
⁴ A _g	1.96	1.99	1.98	1.99	1.97	1.70	0.45	1.99	1.95	1.57	1.44	1.97	1.93	1.09	1.50	1.52
² B _{1u}	1.96	1.99	1.96	1.99	1.96	1.70	0.54	1.98	1.90	1.55	1.33	1.97	1.86	1.13	1.64	1.52
⁴ B _{2g}	1.98	1.97	1.93	1.99	1.99	1.78	0.66	1.85	1.60	1.55	1.53	1.84	1.47	1.39	1.71	1.77
² B _{3u}	1.98	1.97	1.92	1.99	1.99	1.77	0.70	1.88	1.51	1.57	1.49	1.89	1.52	1.38	1.67	1.76
⁴ B _{3u}	1.98	1.99	1.97	1.99	1.97	1.69	0.43	2	1.94	1.95	1.06	2	1.95	1.05	1.95	1.07
² B _{2g}	1.98	1.99	1.96	1.99	1.96	1.69	0.48	2	1.94	1.95	0.90	2	1.95	1.01	1.95	1.25
⁴ B _{3g}	1.97	2.00	1.98	1.99	1.97	1.69	0.41	1.99	1.45	1.97	1.49	1.99	1.53	1.02	1.97	1.58
⁴ B _{2u}	1.97	2.00	1.98	1.99	1.97	1.70	0.41	1.99	1.58	1.97	1.45	1.99	1.42	1.02	1.97	1.61
⁴ A _u	1.97	1.99	1.99	1.99	1.97	1.69	0.42	1.99	1.46	1.55	1.93	1.98	1.47	1.07	1.56	1.96
⁴ B _{1g}	1.96	1.99	1.99	1.99	1.97	1.69	0.43	1.99	1.53	1.51	1.95	1.98	1.43	1.05	1.60	1.95
Ni ₂ O ₂ ⁺ Term	O-2p						Ni-3d									
	9a _g	5b _{3u}	3b _{2u}	2b _{1g}	7b _{1u}	3b _{2g}	8a _g	10a _g	6b _{3u}	4b _{2u}	1b _{1g}	6b _{1u}	8b _{1u}	4b _{2g}	3b _{3g}	1a _u
⁶ B _{3u}	1.99	1.90	1.95	1.22	1.98	1.97	1.98	1.62	1.08	1.39	1.91	1.99	1.40	1.10	1.67	1.84
⁶ B _{2g}	1.99	1.94	1.96	1.15	1.99	1.98	2	1.44	1.06	1.46	1.93	2	1.54	1.07	1.60	1.90
⁶ B _{1g}	1.99	1.91	1.95	1.16	1.99	1.98	2.00	1.95	1.10	1.07	1.91	2.00	1.94	1.13	1.10	1.85

Table S5: Occupation of the natural orbitals of selected terms of Ni_2O_2^+ by the CASSCF calculations with the larger active space (16 or 18 orbitals) at the Davidson corrected structure of the $^2\text{B}_{2g}$ term (7s6p4d3f2g/5s4p3d2f ANO basis set).

Ni ₂ O ₂ ⁺ Term	O-2p					Ni-3d-O-2p				Ni-3d						Ni-4s		
	10a _g	3b _{2u}	1b _{1g}	7b _{1u}	3b _{2g}	5b _{3u}	6b _{3u}	8a _g	9a _g	4b _{2u}	2b _{1g}	6b _{1u}	8b _{1u}	4b _{2g}	3b _{3g}	1a _u	11a _g	9b _{1u}
⁴ B _{1u}	1.93	1.98	1.96	1.98	1.95	1.71	0.45	1.98	1.95	1.41	1.39	1.98	1.96	1.04	1.63	1.62	0.04	0.04
² A _g	1.90	1.99	1.97	1.98	1.93	1.68	0.54	1.97	1.95	1.56	1.41	1.97	1.93	1.07	1.53	1.54	0.04	0.04
⁴ A _g	1.92	1.99	1.97	1.98	1.95	1.70	0.47	1.98	1.96	1.58	1.44	1.97	1.93	1.08	1.49	1.53	0.04	0.04
² B _{1u}	1.95	1.98	1.96	1.98	1.94	1.70	0.55	1.97	1.89	1.54	1.32	1.97	1.87	1.12	1.65	1.54	0.04	0.04
⁴ B _{2g}	1.96	1.96	1.92	1.98	1.97	1.79	0.72	1.88	1.60	1.49	1.45	1.89	1.46	1.40	1.69	1.78	0.04	0.04
² B _{3u}	1.96	1.96	1.91	1.98	1.97	1.78	0.74	1.89	1.50	1.54	1.43	1.91	1.54	1.39	1.65	1.77	0.04	0.04
⁴ B _{3u}	1.93	1.99	1.97	1.98	1.95	1.68	0.45	2	1.95	1.94	1.07	2	1.95	1.04	1.95	1.07	0.03	0.04
² B _{2g}	1.93	1.99	1.95	1.98	1.93	1.69	0.49	2	1.95	1.95	0.88	2	1.95	1.00	1.95	1.28	0.04	0.04
⁴ B _{3g}	1.93	1.99	1.97	1.98	1.95	1.68	0.43	1.99	1.43	1.97	1.48	1.99	1.54	1.02	1.98	1.59	0.03	0.04
⁴ B _{2u}	1.93	1.99	1.97	1.98	1.95	1.69	0.43	1.99	1.58	1.97	1.44	1.99	1.41	1.02	1.97	1.62	0.04	0.04
⁴ A _u	1.93	1.99	1.99	1.98	1.95	1.68	0.45	1.99	1.45	1.55	1.93	1.98	1.48	1.07	1.57	1.96	0.04	0.04
⁴ B _{1g}	1.92	1.99	1.99	1.97	1.95	1.68	0.45	1.98	1.53	1.50	1.95	1.98	1.43	1.05	1.60	1.96	0.04	0.04

Ni ₂ O ₂ ⁺ Term	O-2p					Ni-3d								Ni-4s				
	9a _g	5b _{3u}	3b _{2u}	2b _{1g}	7b _{1u}	3b _{2g}	8a _g	10a _g	6b _{3u}	4b _{2u}	1b _{1g}	6b _{1u}	8b _{1u}	4b _{2g}	3b _{3g}	1a _u	11a _g	9b _{1u}
⁶ B _{3u}	1.97	1.89	1.93	1.24	1.97	1.95	1.99	1.62	1.07	1.38	1.91	1.99	1.39	1.10	1.68	1.84	0.04	0.04
⁶ B _{2g}	1.98	1.92	1.93	1.18	1.98	1.95	2	1.43	1.05	1.45	1.93	2	1.54	1.06	1.62	1.89	0.04	0.05
⁶ B _{1g}	1.98	1.90	1.92	1.17	1.98	1.95	2.00	1.94	1.09	1.07	1.91	2.00	1.94	1.12	1.10	1.85	0.04	0.05

Table S6: Term energies, equilibrium distances, and harmonic vibrational frequencies of both totally symmetric modes for selected terms of Ni_2O_2^+ by MRCI calculations (7s6p4d3f2g/5s4p3d2f ANO basis set). The reference space is the complete active space of the 10 3d orbitals of Ni and the 6 2p orbitals of O. The active space of the CASSCF calculations consists of 8 or 10 of the 3d orbitals of Ni, the two 4s orbitals of Ni, and the 6 2p orbitals of O. Davidson corrected results in parenthesis.

Term	T_e/eV	$r_e^{\text{Ni-Ni}}/\text{pm}$	$r_e^{\text{O-O}}/\text{pm}$	$\tilde{\nu}_e^{(1)}/\text{cm}^{-1}$	$\tilde{\nu}_e^{(2)}/\text{cm}^{-1}$
² B _{1u}	0.308 (0.138)	224.1 (219.0)	267.9 (269.9)	796 (809)	299 (365)
² B _{2g}	0.023 (0.0)	250.8 (247.1)	247.3 (249.1)	717 (713)	268 (271)
² B _{2u}	0.288 (0.260)	256.6 (237.3)	246.9 (260.5)	708 (748)	247 (402)
⁴ A _g	0.206 (0.225)	257.7 (254.9)	246.2 (248.7)	710 (706)	259 (251)
⁴ B _{1u}	0.076 (0.069)	257.1 (254.6)	242.9 (244.2)	706 (700)	282 (286)
⁴ B _{3u}	0.0 (0.028)	255.1 (253.1)	247.6 (249.5)	720 (710)	272 (269)
⁴ B _{2g}	0.571 (0.452)	235.2 (230.3)	262.7 (265.1)	766 (770)	283 (325)
⁴ B _{2u}	0.055 (0.075)	254.0 (251.1)	247.9 (250.1)	716 (708)	256 (251)
⁴ B _{3g}	0.122 (0.159)	257.6 (255.6)	246.4 (248.3)	709 (699)	267 (269)
⁴ B _{1g}	0.301 (0.350)	262.8 (260.7)	242.9 (245.2)	699 (690)	264 (259)
⁴ A _u	0.323 (0.375)	263.1 (260.9)	243.4 (245.9)	700 (689)	259 (256)
⁶ B _{3u}	0.724 (0.626)	252.5 (248.9)	254.6 (258.2)	722 (703)	236 (228)

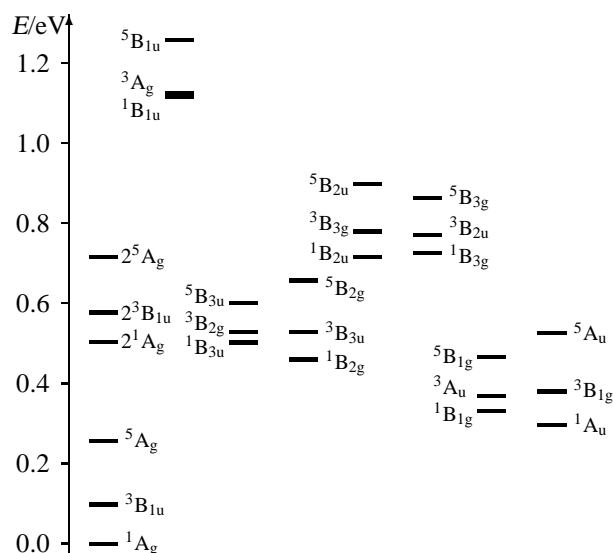


Figure S1: Relative energetical position of different terms of Ni_2O_2 according to MRCI calculations with a reference space of 16 orbitals (Ni 3d, O 2p) at the corresponding Davidson corrected MRCI structure of the $^1\text{A}_g$ ground term, using the orbitals from the CASSCF calculations with the smaller active space (Ni 3d only).

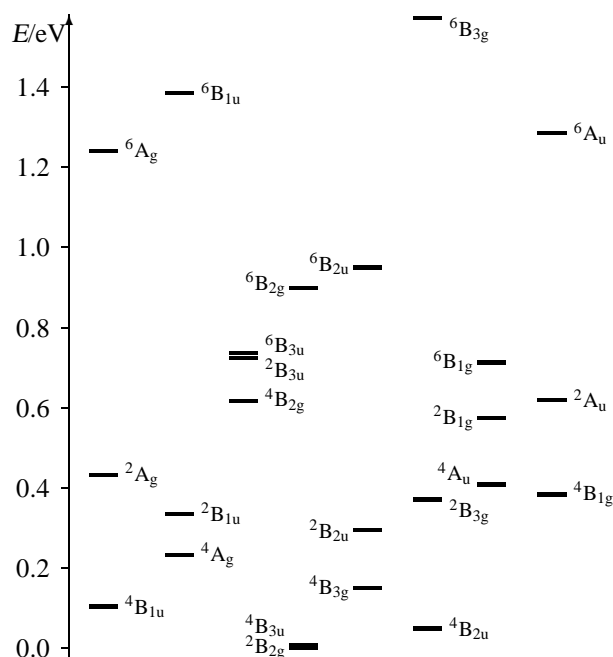


Figure S2: Relative energetical position of different terms of Ni_2O_2^+ according to MRCI calculations with a reference space of 16 orbitals (Ni 3d, O 2p) at the corresponding Davidson corrected MRCI structure of the $^2\text{B}_{2g}$ term, using the orbitals from the CASSCF calculations with the smaller active space (Ni 3d, O 2p).