

MRCI investigation of different isomers of $\text{Ni}_2\text{O}_2\text{H}_2^+$

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Details of the active spaces and reference spaces of the different sections of the energy profile for the approach of H_2 to Ni_2O_2^+

Table S1: Details of the CASSCF and MRCI calculations for the different sections of the path from $\text{Ni}_2\text{O}_2^+\cdots\text{H}_2$ to $\text{Ni}_2(\text{OH})_2^+$: (1) Number, (2) symmetries, and (3) main atomic contributions of the orbitals of the active space, (4) number of states optimised within the CASSCF calculations and (5) selection criterion for the reference space of the subsequent MRCI calculations.

section	no	symmetries	main atomic contributions*	states	reference
0.0–0.1	14	21–27a' / 8–14a''	2×2p 3×3d 1×1s 1×4s / 2×2p 4×3d 1×1s	2	0.05
0.1–0.3	14	21–27a' / 8–14a''	2×2p 3×3d 1×1s 1×4s / 2×2p 4×3d 1×1s	2	0.05
0.3–0.38335	13	21–27a' / 9–14a''	3×2p 2×3d 1×1s 1×4s / 3×2p 2×3d 1×1s	1	0.05
0.38335–0.4	15	20–27a' / 8–14a''	3×2p 3×3d 1×1s 1×4s / 3×2p 3×3d 1×1s	2	0.05
0.4–0.5	13	21–27a' / 9–14a''	2×2p 3×3d 1×1s 1×4s / 2×2p 3×3d 1×1s	1	0.05
0.5–0.9	11	22–27a' / 10–14a''	1×2p 3×3d 1×1s 1×4s / 1×2p 3×3d 1×1s	1	0.01
0.9–1.0	7	23–26a' / 11–13a''	3×3d 1×4s / 3×3d	1	CAS

* 3d and 4s mean Ni 3d and Ni 4s, 2p means O 2p, and 1s means H 1s.

The $\text{Ni}_2\text{O}_2\text{H}_2^+$ product has 6 closed O 2p or O–H 2p-1s bonding orbitals and 6 open-shell 3d orbitals with altogether 8 electrons and one 4s orbital occupied with 1 electron. In contrast, the Ni_2O_2^+ reactant has essentially one open-shell O 2p orbital contributing to combined Ni–O orbitals and 4 open-shell Ni 3d orbitals with 4 electrons, while H_2 has 1 essentially doubly occupied 1s- σ orbital. Hence, going from the reactants to the products, the number of open-shell Ni 3d orbitals increases while the number of open-shell O 2p orbitals decreases. This redistribution of the electrons is reflected by the observed change of the nature of active orbitals within the section 0.38–0.40 of the calculated path. At point 0.38, the active space of 13 orbitals consists of the 6 2p orbitals from O (3 a', 3 a''), 4 3d orbitals from Ni (2 a', 2 a''), one 4s orbital from Ni (a'), and both 1s orbitals from H (a', a''). At point 0.40, the active space comprises 4 2p orbitals from O (2 a', 2 a''), 6 3d orbitals from Ni (3 a', 3 a''), and again one 4s orbital from Ni (a') and both 1s orbitals from H (a', a''). Therefore, to properly describe the electronic structure in this section, an active space containing 6 open-shell Ni 3d and 6 open-shell O 2p orbitals is used.

Occupation of the natural orbitals by CASSCF calculations for $\text{Ni}_2(\text{OH})_2^+$, $\text{NiONi}(\text{OH}_2)^+$, and $(\text{NiH})_2\text{O}_2^+$

The occupation of the natural orbitals of selected terms of $\text{Ni}_2(\text{OH})_2^+$ by CASSCF calculations is given in Table S2. According to their main contribution, the orbitals are assigned to the Ni 3d or 4s atomic orbitals. For the ${}^4\text{A}_g$ and ${}^2\text{B}_{1u}$ terms, the two a_g orbitals that have a total occupation of about two electrons are mixtures with about equal contributions from 3d and 4s orbitals, although classified in the Table as 3d or 4s. Taking as an example the ${}^6\text{A}_g$, ${}^4\text{B}_{1u}$, and ${}^2\text{A}_g$ terms, it is shown that the different terms of a given spin ladder have very similar occupations. The different spin ladders differ in principle by their 3d occupations.

The occupation of the natural orbitals of selected terms of $\text{NiONi}(\text{OH}_2)^+$ is given in Table S3. According to their main contribution, the orbitals are assigned to the 3d orbitals of the central Ni atom (Ni1) or to the 3d or 4s orbitals of the terminal Ni atom (Ni2). For Ni1, there are two singly occupied 3d orbitals, indicating a $3d^8$ configuration. For Ni2, there are either two singly occupied 3d and one 4s orbital or one singly occupied 3d orbital and an empty 4s orbital, indicating a $3d^8 4s^1$ or a $3d^9$ configuration.

Table S4 shows the occupation of the natural orbitals of the lowest-lying terms ${}^2\text{A}_2$ and ${}^2\text{B}_g$ of the *cis* and *trans* isomers of $(\text{NiH})_2\text{O}_2^+$. For the ${}^2\text{A}_2$ term, there are 4 orbitals that are essentially oxygen 2p orbitals each one occupied by about 2 electrons and 7 orbitals that are essentially nickel 3d orbitals one of them occupied by 1 electron the other by about 2 electrons. Furthermore, there are two orbitals that are about one to one mixtures of Ni 3d and O 2p orbitals, occupied by altogether 2.1 electrons. Hence, for these orbitals, about one electron can be assigned to nickel and one to oxygen. Finally, there are 5 orbitals with contributions from the hydrogen 1s orbitals, the oxygen 2p orbitals, and the nickel 3d orbitals. For the orbital with an occupation of 1.93, the main contribution comes from O 2p with contributions from H 1s. For the orbitals with occupations of 1.78 and 1.80, the main contribution comes from Ni 3d orbitals with contributions

Table S2: Occupation of natural orbitals of selected terms of $\text{Ni}_2(\text{OH})_2^+$ according to CASSCF calculations with 11, 9, or 5 active electrons at the MRCISD+Q structure of the ${}^6\text{B}_{1g}$ term (7s6p4d3f2g/5s4p3d2f/4s3p2d basis set).

Term	$\text{Ni}_2(\text{OH})_2^+$										
	Ni 3d										Ni 4s
	a_g	a_g	b_{3u}	b_{2u}	b_{1g}	b_{1u}	b_{1u}	b_{2g}	b_{3g}	a_u	a_g
${}^6\text{A}_g$	2	1.90	1.09	1.90	1.09	2	1.90	1.10	1.91	1.10	1.00
${}^4\text{B}_{1u}$	2	1.91	1.09	1.90	1.08	2	1.91	1.10	1.91	1.11	1.00
${}^2\text{A}_g$	2	1.91	1.09	1.90	1.07	2	1.91	1.10	1.91	1.12	1.00
${}^4\text{A}_g$	2	1.22	1.00	2	2	2	1.00	1.00	2	2	0.78
${}^2\text{B}_{1u}$	2	1.16	0.99	2	2	2	1.00	1.01	2	2	0.84
${}^6\text{B}_{1u}$	1.82	1.51	1.31	1.68	1.68	1.81	1.49	1.32	1.69	1.69	1.00
${}^6\text{B}_{3u}$	1.96	1.93	1.11	1.51	1.49	1.96	1.93	1.12	1.50	1.50	1.00
${}^6\text{B}_{2g}$	1.96	1.93	1.12	1.49	1.48	1.96	1.93	1.12	1.52	1.51	1.00
${}^6\text{B}_{2u}$	1.98	1.47	1.06	1.55	1.94	1.98	1.45	1.06	1.56	1.94	1.00
${}^6\text{B}_{3g}$	1.98	1.46	1.06	1.56	1.94	1.98	1.46	1.06	1.56	1.94	1.00
${}^6\text{B}_{1g}$	1.98	1.48	1.05	1.95	1.54	1.98	1.45	1.05	1.95	1.56	1.00
${}^6\text{A}_u$	1.98	1.46	1.05	1.95	1.55	1.98	1.47	1.05	1.95	1.56	1.00

Table S3: Occupation of the natural orbitals of selected terms of NiONi(OH₂)⁺ according to CASSCF calculations with 9, 7, or 5 active orbitals at the MRCISD+Q structure of the ⁴A₂ (3d⁹) term (7s6p4d3f2g/5s4p3d2f/4s3p2d basis set).

NiONiOH ₂ ⁺ Term	Ni1 3d					Ni2 3d					Ni2 4s
	a ₁	a ₁	b ₁	b ₂	a ₂	a ₁	a ₁	b ₁	b ₂	a ₂	a ₁
⁶ A ₁ (3d ⁸ 4s ¹)	2.00	1.93	1.07	1.07	1.93	2.00	1.00	2.00	2.00	1.00	1.00
⁶ A ₂ (3d ⁸ 4s ¹)	2.00	1.93	1.07	1.07	1.93	1.00	1.00	2.00	2.00	2.00	1.00
⁶ B ₁ (3d ⁸ 4s ¹)	2.00	1.93	1.07	1.07	1.93	2.00	1.12	1.88	1.12	1.88	1.00
⁶ B ₂ (3d ⁸ 4s ¹)	2.00	1.93	1.07	1.07	1.93	2.00	1.12	1.12	1.88	1.88	1.00
⁴ A ₁ (3d ⁹)	2.00	1.93	1.07	1.07	1.93	2.00	2.00	2.00	2.00	1.00	—
⁴ A ₂ (3d ⁹)	2.00	1.93	1.07	1.07	1.93	2.00	1.00	2.00	2.00	2.00	—
⁴ B ₁ (3d ⁹)	2.00	1.13	1.13	1.87	1.87	2.00	1.00	2.00	2.00	2.00	—
⁴ B ₂ (3d ⁹)	2.00	1.09	1.91	1.09	1.91	2.00	1.00	2.00	2.00	2.00	—

from H 1s and O 2p. The weakly occupied orbitals with occupations of 0.27 and 0.25 are more or less one to one mixtures of Ni 3d and H 1s orbitals. Unfortunately, the electrons cannot be assigned straightforwardly to the different atoms, in order to rationalise the electronic structure in a simple way. Nevertheless, since, for the b₂ orbitals with strong 3d-2p mixing, one electron can be assigned to the O 2p orbitals, and since among the other orbitals with considerable mixing there is one nearly doubly occupied orbital with the leading contribution from O 2p and there are further O 2p contributions in the other orbitals, one can assign 11 electrons to the O 2p orbitals. This gives an oxidation state of -1.5 for each of the O and shows that the O atoms cannot be considered as closed shell parts of the molecule. For the ²B_g term, the picture is practically the same.

Table S4: Occupation of natural orbitals of the lowest-lying terms of *cis* and *trans* (NiH)₂O₂⁺ (C_{2v} and C_{2h}) according to CASSCF calculations with 14 or 16 active orbitals at its MRCISD+Q structures (7s6p4d3f2g/5s4p3d2f/4s3p2d basis set).

<i>cis</i> (C _{2v})	O 2p				Ni 3d						O 2p/Ni 3d		Ni 3d/O 2p/H 1s					
	a ₁	b ₁	b ₂	a ₂	a ₁	a ₁	b ₁	b ₁	b ₂	a ₂	a ₂	b ₂	b ₂	a ₁	a ₁	a ₁	b ₁	b ₁
² A ₂	1.99	1.97	1.98	1.93	2	1.99	2	1.99	2	2	1.00	1.72	0.40	1.93	1.78	0.27	1.80	0.25
<i>trans</i> (C _{2h})	O 2p				Ni 3d						O 2p/Ni 3d		Ni 3d/O 2p/H 1s					
(C _{2h})	b _u	b _u	b _g	b _g	a _g	a _g	a _u	b _u	b _u	b _g	b _g	a _u	a _u	a _g	a _g	a _g	b _u	b _u
² B _g	2.00	1.97	1.99	1.90	2	1.99	2.00	2	1.99	2.00	1.00	1.73	0.40	1.93	1.80	0.26	1.78	0.25