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Association and insertion complexes of nickel with water and methanol studied using Kohn–Sham theory

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Summary. The complexes formed by simple association of the nickel atom with water and methanol, and those formed by insertion of nickel into O–H and O–C bonds, have been studied by the Linear Combination of Gaussian-type orbitals-density functional (LCGTO-DF) method. The binding energies calculated for the *association* complexes are 7 kcal/mol for both $Ni(H_2O)$ and $Ni(CH_3OH)$. These association complexes have equilibrium geometries characterized by a tetrahedral arrangement of bonds and lone pair around the oxygen atom. The *insertion* complexes HNiOH and $HNiOCH_3$ are more stable than the association complexes by 14 and 18 kcal/mol, respectively. The H_3CNiOH insertion complex is still more stable, by an additional 14 kcal/mol. In all five complexes, the lowest singlet and triplet states are nearly degenerate. Comparison of calculated frequencies with infrared spectra of matrix isolated species [MA Park (1988) PhD thesis, Rice University] indicates that only triplet states are seen in the experiment.

Key words: Kohn–Sham theory – Nickel – water – methanol

1 Introduction

Our qualitative understanding of the bonding of small molecules to surfaces and clusters derives largely from studies of relatively few and simple model systems. Complexes consisting of only one metal atom and one ligand molecule are particularly useful in that respect [1], in addition to being interesting in their own right. On the experimental side, there is an abundant literature on transition metal (TM) atom complexes isolated in inert matrix and characterized mostly by infrared (IR) and electronic spin resonance (ESR) spectroscopy. However, on the whole, data on small unsaturated complexes is sketchy: some of their basic properties are still unknown. For example, there is controversy about the geometry of CuCO, with theory predicting a bent structure [2, 3] and ESR experiments pointing to a linear structure [4, 5], and a similar situation holds for FeCO and CoCO [2, 6, 7]. In many cases – including nickel–water and nickel–methanol complexes – the spin multiplicity and geometric structure of the complex formed in matrix are not known. In that situation, it is desirable to have results from many different experimental and theoretical techniques applied to the same systems. Computation of harmonic frequencies and IR intensities seems especially worthwhile because it complements IR spectroscopy which is often used to characterize matrix isolated species.

Density functional theory (DFT) has become increasingly popular over the last few years, largely because of advances in methodology (exchange-correlation functionals, integration grids, basis sets, etc ...) [8–17]. The implementation of analytic energy derivatives [18], in particular, has removed a major obstacle to widespread applications of DFT in chemistry. Routine calculation of equilibrium geometries and harmonic vibrational frequencies (from the forces evaluated at geometries displaced from equilibrium) are possible with a number of computer codes. The accuracy of DFT-calculated geometries and frequencies is generally very good for organic molecules [8, 13, 14, 19] and saturated inorganic complexes [20, 21]. Unsaturated complexes of TM atoms are expected to be more difficult to describe by theory, but DFT calculations of the IR spectra of the $Pd(C_2H_4)$, $Ni(C_2H_4)$ and $Ni(C_2H_2)$ π-complexes show encouraging agreement with experiment [22–24]. Because IR spectroscopy is widely used to characterize unsaturated TM complexes, it seems important to further investigate the reliability of DFT in this respect, through detailed comparisons with experiment.

We undertook a theoretical study of monoligand complexes of first-row TM atoms which parallels a series of experiments on the kinetics of association of TM atoms with small ligands [25–27]. This study is based on a series of DFT Kohn–Sham calculations that were all done using the same set of approximations (the next section gives the details). DFT methods have two desirable features for trend studies of TM complexes: their computational cost is relatively low and their accuracy does not depend too strongly on spin state, number of valence electrons, number of electrons or holes in *d* shells, etc ... We chose a level of theory which is a compromise between the expected accuracy, the speed and ease of calculation, and the available literature documenting its performance. As we said, DFT methodology is evolving rapidly. We decided to keep a relatively simple standard method for compatibility with earlier results and to allow trend studies. The target properties of this theoretical study are the metal–ligand binding energy (BE), the relative stability of isomers, and the IR spectra (frequencies and intensities). We also seek to provide some rational for the calculated properties based on a simple molecular orbital picture. We have so far reported results of calculations on the first-row TM–CO series [2, 6, 28], NiC_2H_4 [23], NiC_2H_2 [24], and CuC_2H_2 [29]. As part of this continuing study, we present here results for the complexes of nickel with water and methanol. A more specific goal of the present work is to make a detailed comparison between DFT calculations and IR spectra reported by Park et al. [30, 31].

2 Computational method

All-electron Kohn–Sham calculations were performed using the linear combination of Gaussian-type orbitals density-functional (LCGTO-DF) [32] method implemented in the program deMon [33]. The self-consistent equations are solved within the local spin density (LSD) approximation using the exchange-correlation potential of Vosko et al. [34]. Gradient corrections to the exchange-correlation energy (Becke's correction to exchange [35] and Perdew's correction to correlation [36]) were added *non self-consistently* in the final energy evaluation.

Geometry optimization was carried out with a standard minimization method and the computed IR spectra were obtained by finite differences of analytical energy gradients and dipole moments. The treatment of density-gradient corrections to exchange-correlation being non self-consistent, the forces were calculated in the LSD approximation. The equilibrium geometries and harmonic frequencies reported here are LSD values, whereas the binding energies include non-self-consistent gradient corrections.

The orbital basis sets used are segmented contracted sets of Cartesian Gaussians (CG). They are: a $15s/9p/5d$ set contracted to (63321/5211/41) for the nickel atom, $11s/5p/1d$ sets contracted to (6311/311/1) for carbon and oxygen, and a $5s/1p$ set contracted to (311/1) for hydrogen. In terms of size, this orbital basis corresponds roughly to "basis F" of Blomberg et al. [37] which gave nearly converged MCSCF properties. We think that our basis set is adequate considering that Kohn–Sham calculations tend to be less sensitive to incompleteness in the orbital basis than are correlated *ab initio* calculations [6]. The charge density and exchange-correlation potential were fitted using two uncontracted auxiliary bases of CGs having the same pattern. On nickel, the auxiliary bases had the form (10, 5, 5) (ten *s*, five *p* and five *d* functions), on carbon and oxygen it had the form (8, 4, 4), and for hydrogen the bases were of the type (6, 2, 2). The grids used for handling the exchange-correlation terms of the potential and energy are superposition of atomic grids [38], each consisting of 32 radial shells of points. The atomic grids used for fitting have 26 angular points per radial shell, or 832 points per atom; those for integration have 50, 110, or 194 angular points per shell depending on the distance to the reference nucleus, for a total of 2968 points per atom (the "FINE" option in deMon) [33]. Each atom-centered angular grid is assigned a random orientation in order to improve the overall quality of the grid [39]. This has the drawback of artificially breaking the symmetry in some cases.

We will report all our binding energies relative to the ground state ($d^9s^1, {}^3D$) of the nickel atom. The lowest singlet state of the nickel atom is calculated to be 5 kcal/mol higher than the ground state and this number should be added in order to obtain the diabatic BE of singlet states.

A problem arose for the triplet state of $Ni(OH_2)$: it was not possible to attain SCF convergence with integer occupation numbers. In order to estimate the nickel–water BE of the triplet, both the nickel atom and the complex were treated using fractional occupation of the nickel *d* orbitals. The energy difference calculated in this way is 9.57 kcal/mol. In the case of triplet $Ni(CH_3OH)$, and also for the nickel atom, it was possible to attain convergence for both integer and fractional occupation of the *d* orbitals. For $Ni(CH_3OH)$, and for the nickel atom, the energy calculated with integer occupation is the lowest, by about 9.3 kcal/mol in both cases. Therefore, the two sets of calculations give very nearly equal energy differences, $\Delta E = 9.97$ and 9.86 kcal/mol (see Table 1). However, the forces calculated for triplet $Ni(CH_3OH)$ with integer occupation numbers are unstable with respect to small displacements and give unreliable frequencies. Harmonic frequencies and IR intensities in that case were obtained using fractional occupation of the nearly degenerate orbitals of $Ni(CH_3OH)$. The optimized geometries of triplet $Ni(CH_3OH)$ calculated with fractional and integer occupation differ by at most 0.029 Å on bond lengths (NiO bond) and 4.1° on angles (NiOCH dihedral angle). The occupation numbers were integers in all other cases.

Our best estimate of the energy to dissociate a complex into a ground state nickel atom and ground state water or methanol will be denoted as "BE" (binding energy). It is obtained by adding the difference in total energies (ΔE), the change in

Table 1. Total energy differences (ΔE), zero point energies (ZPE), estimated counterpoise correction to the BSSE (CC-BSSE), and estimated adiabatic energies for dissociation into ground state Ni and H_2O or CH_3OH (BE); all energies are in kcal/mol except where indicated

	ΔE	ZPE	CC-BSSE	BE
$Ni(OH_2)$ singlet	12.29	14.12	4.1	7
$Ni(OH_2)$ triplet	9.57[a]	14.17	2.9	6
HNiOH singlet	25.27	11.94	5.0	21
HNiOH triplet A[b]	22.81	11.11	4.7	20
HNiOH triplet B[c]	18.96	11.17	4.7	16
$Ni(OHCH_3)$ singlet	11.50	31.94	3.3	7
$Ni(OHCH_3)$ triplet	9.97 9.86[a]	31.93	3.2	6
$HNiOCH_3$ singlet	27.17	29.17	4.7	24
$HNiOCH_3$ triplet	26.69	28.48	4.7	25
$HONiCH_3$ singlet	45.66	29.08	8.2	39
$HONiCH_3$ triplet	42.33	28.71	8.2	37

	Energy (hartrees)	ZPE
Ni atom	− 1508.2524	
spherical Ni[d]	− 1508.2376	
H_2O	− 76.4359	13.03
CH_3OH	− 115.7335	31.10

[a] Calculated relative to a spherical nickel atom, see text

[b] Planar syn conformation

[c] Planar anti conformation

[d] The nickel atom was constrained to have a spherically symmetric density

zero-point energy (ZPE), and the counterpoise correction [40] for basis set superposition error (BSSE) (see Table 1). The energy lowering of fragment A due to the presence of the basis functions on fragment B at the singlet (triplet) complex equilibrium geometry will be denoted by S-A [B] (T-A[B]). The following counterpoise corrections (in kcal/mol) were calculated: S-Ni[OH_2] = 2.35, T-Ni[OH_2] = 1.91, S-Ni[$OHCH_3$] = 2.64, T-Ni($OHCH_3$] = 2.22, S-[Ni]OH_2 = 1.76, T-[Ni]OH_2 = 1.02, S-[Ni]$OHCH_3$ = 0.68, T-[Ni]$OHCH_3$ = 1.02, T-[H]Ni[OH] = 3.26, and T-[H_3C]Ni[OH] = 5.23. The remaining counterpoise corrections were *estimated* from these and should not be in error by more than a few tenths of a kcal/mol.

3 Results and discussion

We first make a few comments on the calculated properties of the free ligands. The geometries of water and methanol optimized in the LSD approximation can be compared to those given in the compilation of Dickson and Becke [14] who report results of fully numerical (essentially exact) LSD calculations and experimental

Table 2. Calculated harmonic frequencies and isotopic shifts of H_2O and CH_3OH, in cm^{-1}

	H_2O	HDO[a]	D_2O[a]	
OH anti. stretch	3844 (3756)[b]	− 4[c,d] (− 1)	1026 (968)	
OH sym. stretch	3713 (3657)	1035 (980)	1038 (986)	
OH_2 deform.	1524 (1595)	188 (193)	408 (417)	
	CH_3OH	CH_3OD[a]	CD_3OD[a]	$^{13}CH_3OH$[a]
a′ OH stretch	3743 (3666)	1017 (962)	1017 (961)	0 (0)
a′ CH_3 *d*-stretch	3050 (3005)	0 (− 2)[d]	791 (750)	10 (10)
a″ CH_3 *d*-stretch	2962 (2962)	0 (1)	764 (743)	11 (10)
a′ CH_3 *s*-stretch	2903 (2848)	0 (3)	817 (770)	3 (5)
a′ CH_3 *d*-deform.	1429 (1474)	3 (1)	403 (443)	2 (2)
a″ CH_3 *d*-deform.	1414 (1466)	0 (0)	394 (398)	12 (2)
a′ CH_3 umbrella	1407 (1452)	1 (0)	267 (319)	6 (6)
a′ OH bend	1293 (1334)	471 (469)	552 (558)	9 (8)
a″ CH_3 rock[e]	1123 (—)	1123 (1163)	871 (860)	1115
a′ CO stretch	1104 (1034)	5 (− 9)	117 (51)	20 (16)
a′ CH_3 rock	1018 (1076)	− 172[d] (− 151)	1 (13)	3 (7)
a″ torsion	311	65	86	0

[a] The isotopic shift is given instead of the frequency

[b] Experimental values are in parentheses, see Ref. [42, 13]

[c] Calculated relative to the average of the two OH stretches

[d] Negative numbers indicate that the frequency is higher in the heavier isotopomer

[e] Park et al. observed this mode for only two isotopomers. For this mode we give the frequencies, not the isotopic shifts

values. According to Dickson and Becke, errors inherent to the LSD approximation are usually less than 0.025 Å on bond lengths and 1° on angles. In most cases, bond lengths involving a hydrogen atom are overestimated and bond lengths not involving a hydrogen atom are underestimated. For water and methanol, the approximations used here (basis sets, grid, ...) introduce additional errors of up to 0.007 Å (R(OH) bond length in methanol) and 1.3° (HOH angle in water). These errors can either reinforce or partly cancel the LSD error. Although no systematic study was done on TM complexes, the errors associated with incomplete basis set and grid are expected to be larger in those systems [41].

The calculated harmonic frequencies of water and methanol are given in Table 2. The experimental values are for gas-phase water [42] and matrix isolated methanol [30]. The mean absolute difference between calculated *harmonic* and observed *fundamental* frequencies is about 70 cm^{-1} for water. For methanol, there is a clear trend in the differences between calculated harmonic and observed fundamental frequencies: the stretches are *overestimated*, by 50 cm^{-1} on average, and all other frequencies are *underestimated*, by 50 cm^{-1} on average. If the effect of anharmonicity was included, the calculated stretch frequencies would be very good and the bend frequencies would be rather poor. If the atypical CO stretch is excluded, the average relative error on isotopic shifts larger than 20 cm^{-1} is 6%. The CO stretch mixes with the *a′* CH_3 rocking and deformation modes to a different extent in different isotopomers. This mixing is difficult to reproduce accurately in the calculation. For this reason, the calculated isotopic shifts for free and complexed methanol are not accurate for frequencies in the 800–1100 cm^{-1} range. In general, this level of accuracy is typical for LSD calculations on small organic molecules: typical errors are 3–5% on frequencies [8, 13] and 10–20% on isotopic shifts [23, 24] except for the lowest frequency modes for which errors tend to be larger.

3a Nickel–water

There have been a number of theoretical studies of the nickel–water association complex. In one CI calculation, the ground state was predicted to be a singlet and to have a BE of 24 kcal/mol [43]. Subsequent *ab initio* studies with bigger basis sets gave the following estimates for the BE: 9 kcal/mol for both singlet and triplet states *relative to their asymptotes* with the MCSCF method [44]; values in the range from 19 to 3 kcal/mol for the singlet by MCSCF with different basis sets, with the best basis giving BE = 5 kcal/mol [37]; 5 kcal/mol for the triplet, obtained by the SDCI + Q method with a very large basis [45]; and a MCPF calculation giving a BE of 7 kcal/mol for the triplet ground state [27]. There is some uncertainty about the ground state multiplicity. A CI calculation by Bauschlicher [44] gave similar diabatic binding energies for the singlet and triplet, the latter thus being more stable by roughly 8 kcal/mol (the nickel atom's singlet-triplet separation). This seemed to rule out a singlet ground state. But in a recent MCPF study, the singlet energy calculated at the triplet equilibrium geometry is only 3.4 kcal/mol higher than that of the triplet [27]. This suggests that the singlet and triplet states may be almost equally stable.

On the experimental side, the kinetics of the reaction of nickel atoms with water suggests that the association complex is bound by less than 10 kcal/mol [27]. It also shows that a strongly bound insertion complex is formed with a very small barrier to reaction, if any. The absence of a substantial barrier to insertion is supported by a series of calculations performed using the MCPF, QCISD and CCSD (T) methods [27]. In another study, Park et al. observed IR bands of matrix isolated species which they assigned to HNiOH and its isotopomers but saw no evidence of the association complex $Ni(H_2O)$ [30, 31].

We find the singlet to be the ground state, with a BE of 7.1 kcal/mol. The BE calculated for the triplet state is slightly smaller, 5.5 kcal/mol. The singlet–triplet separation was also small, but the order reversed, in the most recent *ab initio* study [27]. It is possible that the present method is biased toward stabilizing the singlet considering that a similar calculation overestimates the BE of singlet NiCO by roughly 12 kcal/mol [2, 46]. In any case, our BE for $Ni(H_2O)$ is consistent with the upper bound deduced from the kinetics data of Mitchell et al. [27]. In agreement with them, we also find that the insertion complex HNiOH is more stable than $Ni(H_2O)$ and bound by at least 20 kcal/mol. The calculated BEs of the HNiOH insertion complex are 21 kcal/mol (singlet) and 20 kcal/mol (triplet). Park et al. suggested that two isomers of HNiOH were formed in their experiment and were responsible for the two sets of bands that they observed. We searched and found a second minimum on the triplet potential surface of HNiOH ("triplet B") at a dihedral angle close to 180° (anti conformation). This conformation is 4 kcal/mol less stable than the syn conformation of triplet HNiOH. However, the calculated frequencies of triplet B do not help explain the IR spectra of Park et al.

The geometry of the water molecule is only slightly perturbed in the association complex. As expected, the NiO bond length is shorter in the more strongly bound

Table 3. Optimized geometry of water and the nickel–water association complex

	H_2O	Ni–OH_2	
		Singlet	Triplet[a]
R (OH)[b]	0.976	0.995	0.986
	0.976	0.999[c]	0.986
∢(HOH)	105.6	106.0	107.9
R (NiO)	—	1.778	2.001
∢(NiOH)	—	106.5	110.6
	—	103.5	109.7
θ(NiOHH)	—	110.8	120.3

[a] Fractional occupation numbers were used
[b] Bond lengths in Å, angles in degrees. θ denotes a dihedral angle
[c] The slight asymmetry arises because we use a random orientation of grid points around each atom

Table 4. Optimized geometries of the nickel–water insertion complex

		H–Ni–OH	
	Singlet	Triplet A	Triplet B
R (HNi)[a]	1.423	1.483	1.482
R (NiO)	1.682	1.707	1.723
R (OH)	0.986	0.981	0.988
∢(HNiO)	98.6	131.4	122.0
∢(NiOH)	110.6	125.3	116.3
θ(HNiOH)	67.2	0.9	187.4

[a] Bond lengths in Å, angles in degrees; θ denotes a dihedral angle

singlet. The 4*s* and $3dz^2$ (the Ni–O axis is along *z*) orbitals of nickel are hybridized in the singlet state. The lowest energy (occupied) *sd* hybrid is perpendicular to the NiO bond and the highest energy (empty) *sd* hybrid is colinear with it. Thus, hybridization takes some charge density off the NiO axis, it reduces the repulsion between the oxygen lone pairs and the filled orbitals of nickel [43], and it allows a closer approach of the ligand. In contrast to this, there is very little *sd* hybridization in the triplet state. The $3dz^2$ populations [47] reflect this difference: 0.67 for the singlet and 0.99 for the triplet.

The NiOH unit is bent in each of the three structures of HNiOH (Table 4). Structures with a linear HNiO unit and bent or linear NiOH are roughly 6 kcal/mol less stable than those reported in Table 4 and relax to those geometries upon optimization. The oxygen atom has a coordination which is similar to the one it has in water and the bonding in HNiOH is essentially covalent. The NiOH angle in the singlet is smaller than any of those calculated by Siegbahn et al. for the insertion complexes of second-row TM atoms in water [48]. The angle in triplet HNiOH is similar to those calculated by Siegbahn et al. for the insertion complexes of Ru, Rh, and Pd. These authors, as well as Bauschlicher and co-workers [49],

Table 5. Calculated harmonic frequencies (cm^{-1}) and IR intensities (in parentheses, km/mol) of the nickel–water association complex

	H_2O	$Ni(OH_2)$ Singlet	$Ni(OH_2)$ Triplet
OH stretch	3844 (71)	3448 (17)	3662 (45)
OH stretch	3713 (7)	3354 (113)	3528 (250)
HOH bend	1524 (87)	1456 (47)	1503 (48)
NiO stretch	—	587 (40)	497 (5)
OH_2 rock	—	533 (16)	441 (81)
OH_2 wag	—	499 (253)	281 (111)

have pointed out that the MOH angle correlate with the ionic contribution to the M–OH bond. This is verified in our calculations. The Mulliken charges on the nickel atom are + 0.24, + 0.28, and + 0.35 for singlet, triplet B and triplet A, respectively, while the NiOH angles are 111°, 116° and 125°. The singlet and triplet equilibrium geometries differ in two respects: triplet HNiOH is planar while singlet HNiOH is not, and the HNiO angle is larger in the triplet.

Park et al. [30] observed a band at 1575.1 cm^{-1} which they assign to the association complex of dinickel with water, but saw no evidence of a nickel–water association complex. The change in the bending frequency of water upon association to Ni_2 which they measured, 18 cm^{-1}, is much closer to what is calculated for *triplet* $Ni(OH_2)$ (21 cm^{-1}) than for *singlet* $Ni(OH_2)$ (68 cm^{-1}; see Table 5). This indicates that a Ni_2 molecule and a triplet nickel atom bind to water in a similar way, through weak dipole-induced-dipole and dispersion interactions [45]. Although the nickel–water BE is small, there is a large shift in the calculated OH stretch frequencies, 380 cm^{-1} for singlet and 180 cm^{-1} for triplet. The large calculated intensities for these OH stretches and the big difference between singlet and triplet frequencies show that it would be easy to identify $Ni(OH_2)$ if it was formed. It is presumably not formed because insertion of nickel into the OH bond occurs readily.

Comparison of calculated and observed IR spectra clearly rules out singlet HNiOH as the species observed by Park et al. [30, 31]. The OH and NiH stretches of singlet HNiOH do not agree with experiment. Moreover, the calculated isotopic shifts in singlet DNiOD for the OH, NiH and NiO stretches are 988, 622 and 172 cm^{-1} compared to 972, 565 and 27 cm^{-1} experimentally. The calculated stretch frequencies and isotopic shifts suggest that the insertion complex seen in the experiment is "triplet A" (see Table 6). Agreement between experiment and calculation is good for the OH, NiH and NiO stretches. However, there are certain peculiarities in the observed IR spectra of HNiOH which are not easily explained.

First, Park et al. saw two bands corresponding to a NiH stretch, at 1901 and 1837 cm^{-1}. They suggested that this may be due to the presence of two isomers of HNiOH. But two things make this assignment uncertain: (i) the two bands are unusually large, their width is approximately 40 cm^{-1}, and (ii) the difference in their isotopic shifts in DNiOD, 565 and 513 cm^{-1}, is somewhat surprising. We searched other isomers but could not find one with a NiH frequency near 1837 cm^{-1}. The anti conformation ("triplet B") of HNiOH has a NiH stretch frequency similar to that of the syn conformation (see footnote to Table 6) and far from 1837 cm^{-1}. We can rule out the possibility that "triplet B" is the observed

Table 6. Calculated harmonic frequencies (cm^{-1}) and IR intensities (in parentheses, in km/mol) of the nickel–water insertion complex

	Singlet	Triplet A			
	HONiH	HONiH[a]	$H^{18}ONiH$[b]	DONiD[b]	$D^{18}ONiD$[b]
OH stretch	3629 (58)	3711 (151) [3699][c]	12.5 (148) [11.8]	1006.9 (91) [972.2]	1024.4 (87)
NiH stretch	2170 (12)	1947 (22) [1901][d] [1837]	0.1 (22) [2.7] [0.4]	558.5 (12) [564.8] [513.4]	558.6 (12)
NiOH bend	881 (110)	619 (78)	3.6 (79)	152 (42)	156 (41)
NiO stretch	753 (10)	764 (53) [707] [691]	33.2 (46) [26.5] [22.1]	8.0 (58) [26.7][e] [27.2]	40.4 (52) [52.0][e] [51.1]
HNiO bend	536 (34)	414 (101)	0.2 (101)	118.4 (51)	118.4 (51)
Torsion	381 (65)	317 (223)	3.1 (221)	70.8 (123)	74.7 (121)

[a] The frequencies and IR intensities for the isomer B (anti conformation) of triplet HNiOH, given in the same order as in the table, are: 3603 (84), 1927 (15), 655 (44), 762 (73), 450 (21), and 416 (20)

[b] The decrease in frequency relative to HONiH is given instead of the frequency itself

[c] Numbers in brackets are experimental values from Ref. [30]

[d] This and the 1837 cm^{-1} band are unusually large in the IR spectrum

[e] Two bands that were less than 3 cm^{-1} apart were actually observed by Park et al.; the value in the present table is the average of the two

species because its OH stretch frequency, 3603 cm^{-1}, is significantly smaller than the observed 3699 cm^{-1}. As for structures having linear HONi or ONiH units, they do not appear to be stable: geometry optimization runs started at such geometries lead to the bent structures of Table 4. On the other hand, we find a triplet excited state T_1 of a' symmetry roughly 2000 cm^{-1} (estimated from orbital energy differences) above the lowest triplet state T_0 which has a'' symmetry. There can be no vibronic coupling of T_0 and T_1 via the a' NiH stretch, but if a near resonance of $T_0 + \nu_2$ and $T_1 + \nu_6$ occurs the a'' torsion mode could couple T_0 and T_1 and give rise to two bands.

Three other features of the observed spectra of HNiOH can not be explained simply from our results: (i) the isotopic shifts on the NiO stretch frequency do not agree well with the calculated ones, (ii) the NiOH bend is apparently not seen experimentally although the calculated intensity is large, and (iii) the NiO stretch is much more intense in DNiOD than in HNiOH or $HNi^{18}OH$, contrary to calculations which give similar intensities for all isotopomers. We cannot offer a definitive explanation for these discrepancies but we would like to make a few comments.

First, recalling that stretch frequencies are overestimated and bend frequencies are underestimated for methanol, it is possible that our computational method gives large errors of *opposite* signs for the frequencies of the NiO stretch and NiOH bend. Our calculated 619 and 764 cm^{-1} frequencies could correspond to the observed bands at 691 and 707 cm^{-1}. That would not explain the observed isotopic shifts and the band at 1837 cm^{-1} however.

Second, the modes with the two lowest frequencies could be a source of complication. The HNiO bend (414 cm^{-1}) and the torsion around the NiO bond (317 cm^{-1}) have very large intensities (101 and 223 km/mol) and their first harmonics should fall in the 600–800 cm^{-1} range and have appreciable intensity. Either could mix with the fundamentals of the NiO stretch or NiOH bend and complicate the IR spectrum of some isotopomers in the 600–800 cm^{-1} range. That would make our simple harmonic analysis unsuitable.

Third, some of the bands could have been misassigned: they could belong to another species, such as $HNiOH(H_2O)$, instead of HNiOH. The stochiometry of the carriers of spectroscopic bands is usually inferred from the dependence of the band intensities on the concentration of the codeposited reactants. This kind of study can be difficult for molecules having a high propensity to form dimers, such as water. Moreover, in a similar series of experiments involving codeposition of nickel and ammonia, Ball et al. [50] observed NiH stretch bands at 1951 and 1881 cm^{-1} which they assigned to two isomers of $HNiNH_2(NH_3)$, in addition to the NiH stretch of $HNiNH_2$ (1918 cm^{-1}). In analogy with this, and consistent with our calculations, it is possible that the 1901 cm^{-1} band is the NiH stretch of HNiOH whereas the 1837 cm^{-1} band is due to an isomer of $HNiOH(H_2O)$ [51].

Finally, band shifts induced by the matrix and possible multiple trapping sites further complicate matters. Clearly, gas-phase spectroscopy of HNiOH would be desirable to remove some ambiguities. Besides, a quantitative analysis of the IR spectrum of HNiOH poses an extraordinary challenge to theory. It would require highly accurate electronic structure calculations, a proper treatment of anharmonicity and, possibly, of vibronic coupling.

3b Nickel–methanol

Complexes of nickel with methanol are analogous to those of nickel with water in many respects. The singlet and triplet states of the association complex have binding energies of 7 and 6 kcal/mol, respectively, equal to those of nickel–water, and the insertion of nickel into the OH bond leads to singlet and triplet complexes with binding energies of 25 kcal/mol. In $Ni(CH_3OH)$ the H, C, and Ni atoms and a lone pair of oxygen are in a roughly tetrahedral configuration around the oxygen, but with the NiOC angle somewhat larger than 109.5°. In the association complex, the methanol ligand is only slightly distorted from its free equilibrium geometry (see Table 7), as is water in $Ni(H_2O)$. Yet, there are appreciable shifts in the OH and CO stretch frequencies (see Table 8) which decrease by 6% and 10% due to bonding of O to Ni.

Park et al. did not observe the normal isotopomer of the nickel–methanol association complex but recorded IR spectra for $Ni(CH_3OD)$ and $Ni(CD_3OD)$. In Table 9, the observed and calculated frequencies for these isotopomers are listed. In making a comparison, one should remember that the calculated harmonic frequencies of methanol overestimate the stretch fundamentals by roughly 50 cm^{-1} and underestimate the bend fundamentals by about 50 cm^{-1}. With this in mind, it seems that the observed IR spectrum is due to the triplet state, not the singlet. The frequencies calculated for the triplet match fairly well those observed and the calculated intensities are generally consistent with the absences in the IR spectra. The calculated and observed isotopic frequency shifts from $Ni(CH_3OD)$ to $Ni(CD_3OD)$ agree well except for the CO stretch (calculated: 70 cm^{-1}, experiment: 37.3 cm^{-1}). If the assignments are correct, the calculated harmonic and observed fundamental frequencies of $Ni(CH_3OD)$ and $Ni(CD_3OD)$ typically agree within 2–5%.

Table 7. Optimized geometry of methanol and the nickel–methanol association complex

	CH_3OH	$Ni(CH_3OH)$		
		Singlet	Triplet[a]	Triplet[b]
R(OC)[c]	1.406	1.445	1.433	1.430
R(OH)	0.976	0.990	0.985	0.986
R(CH)[d]	1.113	1.109	1.107	1.108
	1.113	1.105	1.106	1.105
R(CH)	1.105	1.102	1.103	1.103
<(HOC)	109.2	109.9	109.6	110.8
<(HCH)	108.5	110.9	110.6	
	107.6	109.7	109.8	
	107.6	109.3[e]	109.0	
θ(HOCH)	− 62.5	− 62.7	− 59.7	− 63.2
	+ 61.1	+ 59.8	+ 63.4	+ 59.6
θ(HOCH)	+ 179.2	+ 178.1	+ 181.9	+ 178.3
R(NiO)		1.785	2.005	1.976
<(NiOC)		117.5	114.7	116.7
<(HONi)		105.2	105.7	107.1
θ($NiOCH_o$)[f]		120.2	118.7	122.8

[a] Fractional occupation of the nearly degenerated orbitals of nickel was used

[b] Integer occupation numbers were used

[c] Bond lengths in Å, angles in degrees. θ denotes a dihedral angle

[d] The CH bonds forming a dihedral angle of ± 60° with the OH bond

[e] Involving the two H atoms that make NiOCH dihedral angles of ± 60°

[f] H_o is the H atom bonded to oxygen

The NiH and NiO bond lengths and the dihedral angle HNiOC in the nickel–methanol insertion complexes are very close to those in the nickel–water complexes (see Tables 4 and 10). The HNiO and NiOC angles are somewhat larger in $HNiOCH_3$ than the corresponding angles in HNiOH for both singlet and triplet states.

The calculated NiH and NiO stretch frequencies (and, to a lesser extent, their isotopic shifts) suggest that, as for HNiOH, Park et al. observed the triplet state of the insertion complex. The calculated isotopic shifts for the isotopomers $H_3{}^{13}CONiH$, H_3CONiD and D_3CONiD in the singlet state – 3, 5 and 59 cm^{-1} for the NiO stretch and 0, 614 and 614 cm^{-1} for the NiH stretch – do not match the observed ones. For both singlet and triplet states, there are three modes with frequencies close to 1100 cm^{-1}. In the singlet, all three modes have appreciable intensity, but in the triplet only the highest frequency mode is intense (see Table 11). The many peaks seen by Park et al. in the 1100–1160 cm^{-1} range seem to agree better with the calculated intensities of the singlet. However, the calculated intensities for the triplet would be very different if the CO stretch and CH_3 deformations had similar frequencies and mixed. The LSD method may well give qualitatively wrong intensities for these three modes considering that it overestimates the CO stretch frequency and underestimates the CH_3 deformation and rock frequencies in methanol (Table 2). We believe that the observed IR spectrum is that of triplet $HNiOCH_3$. As is the case for HNiOH, there is a low-lying triplet excited state.

Table 8. Harmonic frequencies (cm^{-1}) and IR intensities (in parentheses, in km/mol) of methanol and the nickel–methanol association complex

	CH$_3$OH	Ni(CH$_3$OH)	
		Singlet	Triplet[a]
OH stretch	3743 (34)	3476 (74)	3569 (110)
CH stretch	3050 (14)	3102 (1)	3084 (2)
CH stretch	2962 (50)	3046 (12)	3043 (9)
CH stretch	2903 (72)	2948 (67)	2953 (33)
CH$_2$ scissors	1429 (7)	1418 (12)	1415 (10)
CH$_2$ scissors	1414 (5)	1383 (21)	1401 (20)
CH$_3$ umbrella	1407 (4)	1364 (6)	1375 (9)
HOC bend	1293 (19)	1231 (6)	1269 (9)
CH$_3$ deformation	1123 (0)	1101 (3)	1112 (1)
CO stretch	1104 (67)	965 (46)	1025 (30)
CH$_3$ deformation	1018 (74)	999 (12)	1017 (37)
NiOH bend[b]	311 (150)	441[c] (106)	502 (126)
NiO stretch		520 (11)	369 (5)
CO torsion		157 (2)	109 (1)
NiOC bend		191 (5)	95 (2)

[a] The frequencies of triplet Ni(CH$_3$OH) were calculated using fractional occupation or nearly degenerate orbitals

[b] The NiOH and NiOC bends correspond roughly to motion of the nickel atom in a plane perpendicular to the NiO bond axis

[c] Mixed with CH$_3$ "rock"

Table 9. Harmonic frequencies (cm^{-1}) and IR intensities (in parentheses, in km/mol) of the Ni(CH$_3$OD) and Ni(CD$_3$OD) isotopomers of the nickel–methanol association complex

	Ni(CH$_3$OD)			Ni(CD$_3$OD)		
	Calc. Singlet	Expt[a]	Calc. Triplet	Calc. Singlet	Expt[a]	Calc. Triplet
NiOC bend	190 (5)		96 (2)	173 (4)		88 (1)
CO torsion	156 (2)		109 (1)	118 (1)		77 (1)
NiO stretch	501 (3)		317 (52)	490 (2)		311 (17)
NiOD bend	335 (62)		427 (59)	330 (62)		415 (57)
DOC bend	790 (10)	850.7	821 (16)	721[b] (9)	768.7	739 (11)
CO stretch	963 (41)	975.3	1020 (51)	912 (27)	938.0	950 (19)
CH$_3$ deform.	1101 (3)		1111 (1)	857 (8)		864 (3)
CH$_3$ deform.	1150 (2)		1169 (1)	970[c] (12)	1017.0	1018[c] (20)
CH$_3$ umbrella	1364 (6)		1375 (9)	1052 (6)		1071 (11)
CH$_2$ scissors	1383 (20)	1450.7	1400 (18)	1002 (7)		1003 (14)
CH$_2$ scissors	1417 (12)		1413 (9)	1019 (3)		1018 (4)
OD stretch	2528 (45)	2591.9	2598 (61)	2528 (44)	2592.8	2598 (60)
CH stretch	2948 (65)	2831.2	2953 (32)	2116 (35)	2060.1[d]	2118 (21)
CH stretch	3046 (11)	2942.7[e]	3043 (9)	2260 (11)	2202.6	2260 (5)
CH stretch	3102 (1)		3084 (2)	2301 (1)		2289 (1)

[a] See Ref. [30, 31]

[b] With strong admixture of CD$_3$ deformation

[c] With strong admixture of DOC bend

[d] Actually, two bands are seen experimentally, at 2059.6 and 2060.6 cm^{-1}

[e] Actually, two bands are seen experimentally, at 2940.9 and 2944.5 cm^{-1}

Table 10. Calculated equilibrium geometry of the H_3CO–Ni–H insertion complex

	Singlet	Triplet
R(NiH)[a]	1.429	1.489
R(NiO)	1.684	1.704
R(OC)	1.397	1.383
R(CH1)	1.110	1.111
R(CH2)	1.110	1.114
R(CH3)	1.113	1.112
∠(HNiO)	104.3	134.6
∠(NiOC)	122.9	136.0
∠(H1CH2)	109.5	108.0
∠(H2CH3)	107.7	107.5
∠(H3CH1)	107.7	109.0
θ(HNiOC)	62.3	2.9
θ(NiOCH1)	40.6	− 22.4
θ(NiOCH2)	275.7	97.9
θ(NiOCH3)	158.8	216.1

[a] Bond lengths is Angstroms and angles in degrees. θ denotes a dihedral angle

A very rough estimate of its position, based on orbital energy differences, is 2400 cm^{-1} above the lowest triplet.

The other nickel–methanol insertion complex, $HONiCH_3$, also has an equilibrium geometry similar to that of HNiOH (see Table 12). The harmonic frequencies and IR intensities are reported in Table 13. Comparison to experiment is shown in Table 14 for the NiO and OH stretches. The change in frequencies with isotopomer does not help in deciding which of the singlet or triplet is seen experimentally. From the stretch frequencies, however, it seems more likely that the observed spectrum again corresponds to a triplet state.

4 Conclusion

The BEs calculated here with the LCGTO-DF method with gradient corrections to the exchange-correlation agree with recent findings by Mitchell et al.: (i) the nickel–water association complex is bound by 5 to 10 kcal/mol, and (ii) the insertion complex is bound by approximately 20 kcal/mol. We obtain almost exactly the same BEs for the nickel–methanol complexes. In addition, we find that the other insertion complex of nickel and methanol, $HONiCH_3$, is bound by about 38 kcal/mol. This does not necessarily mean that $HONiCH_3$ would be formed in reactions of nickel atoms with methanol since there could be a large barrier to reaction [52]. Indeed, $HONiCH_3$ was formed in matrix *only after irradiation* [30]. Locating the transition states is beyond the scope of the present study but would be necessary to discuss in detail the possible products of reaction of nickel with water and methanol. Such studies in the framework of DFT are just beginning [53–56] and may be useful in the future for understanding the reactivity of TM atoms.

Our calculations indicate that the lowest singlet and triplet states are nearly degenerate in all cases. However, comparison of calculated harmonic frequencies

Table 11. Calculated harmonic frequencies (in cm^{-1}) and IR intensities (in km/mol, in parentheses) and observed frequencies (in brackets) of isotopomers of H_3CONiH

	Singlet	Triplet			
	H_3CONiH	H_3CONiH	$H_3{}^{13}CONiH$	H_3CONiD	D_3CONiD
CO torsion	161 (9)	124 (6)	124 (6)	89 (10)	100 (9)
NiOC bend	219 (19)	184 (23)	183 (23)	163 (22)	155 (20)
NiO torsion	269 (16)	231 (73)	231 (74)	211 (36)	201 (34)
HNiO bend	541 (67)	480 (79)	479 (79)	374 (35)	368 (36)
NiO stretch	708 (18)	621 (15)	617 (15)	615 (20)	581 (17)
		[569.9]	[562.9]	[569.6]	[546.2]
		[567.0]	[560.5]	[567.0]	
CH_3 deform.[a]	1095 (20)	1069 (0)	1061 (0)	1069 (0)	836 (2)
CH_3 deform.	1103 (23)	1096 (1)	1087 (1)	1095 (1)	867 (4)
CO stretch[a]	1130 (24)	1187 (54)	1168 (54)	1187 (54)	1185 (58)
		[1158.8][b]	[1147.9]	[1158.5]	[1108.1]
		[1143.6]	[1134.2]	[1143.6]	[1095.6]
		[1139.2]	[1127.2]	[1139.5]	
		[1124.3]	[1109.8]	[1124.3]	
		[1121.2]	[1107.7]	[1121.2]	
CH_3 deform.	1364 (9)	1375 (10)	1373 (9)	1374 (9)	988 (9)
CH_3 deform.	1369 (2)	1380 (18)	1378 (20)	1380 (25)	994 (4)
		[1440.3]	[1436.0]	[1450.7]	
CH_3 deform.	1420 (39)	1392 (9)	1389 (8)	1392 (9)	1045 (1)
		[1458.6]	[1456.7]	[1458.6]	
NiH stretch	2144 (33)	1934 (35)	1934 (35)	1380 (13)	1380 (18)
		[1868.9]	[1868.9]	[1347.3]	[1347.3]
CH sym. stretch	2902 (41)	2893 (22)	2891 (22)	2893 (22)	2072 (15)
		[2825.4]	[2822.3]	[2825.4]	[2062.5]
					[2059.6]
CH a. stretch	2982 (14)	2970 (12)	2959 (12)	2970 (12)	2199 (7)
CH a. stretch	2994 (23)	2987 (11)	2976 (11)	2987 (11)	2215 (7)

[a] The CH_3 deformations and CO stretch are strongly mixed in the singlet but not in the triplet

[b] Park et al. [30] observed many bands in that region which probably correspond to the three frequencies we calculate for CO stretch and OCH bending modes, with further splittings due to the matrix. We cannot make a detailed assignment of all these bands. The most intense band of the group seen by Park et al. correspond to the highest frequency they report for each isotopomer

and intensities with IR spectra [30, 31] suggests that all species observed were in their triplet state. We think that the ground states all are triplets and that the computational method is slightly biased toward overestimating the stability of the singlet states. These singlet states are probably less than 5 kcal/mol above the triplet ground states.

Contrary to our previous work on $Ni(C_2H_4)$ and $Ni(C_2H_2)$, comparisons between theory and experiment for the complexes considered here are far from simple. The number of bands observed does not always match the number of modes with appreciable calculated intensity (≈ 10 km/mol or more), some observed bands cannot be assigned with confidence (e.g., the 1837 cm^{-1} band in Table 6), and in some instances the patterns in isotopic shifts differ greatly. This is only partly due to errors in the LCGTO-LSD computational method. We think that the most serious discrepancies are rooted in more fundamental limitations of

Table 12. Calculated equilibrium geometry of the H_3C–Ni–OH insertion complex

	Singlet	Triplet
R(NiO)	1.689[a]	1.713
R(NiC)	1.755	1.859
R(OH)	0.984	0.980
R(CH1)	1.105	1.114
R(CH2)	1.105	1.110
R(CH3)	1.152	1.105
∠(HONi)	110.0	124.3
∠(ONiC)	125.5	144.8
∠(NiCH1)	119.2	104.0
∠(NiCH2)	119.2	108.7
∠(NiCH3)	77.4	114.5
θ(HOCNi)	110.7	13.4
θ(ONiCH1)	74.6	131.0
θ(ONiCH2)	289.2	248.0
θ(ONiCH3)	181.4	11.7

[a] Bond lengths in Angstroms and angles in degrees. θ denotes a dihedral angles

Table 13. Calculated harmonic frequencies (cm^{-1}) and IR intensities (in parentheses, in km/mol) of H_3CNiOH

Mode	Singlet	Triplet
ONiC bend	98 (4)	150 (4)
NiC torsion	235 (2)	117 (3)
ONi torsion	376 (63)	298 (92)
NiC stretch	550 (35)	548 (61)
NiCH anti. bend[a]	642 (30)	496 (86)
NiO stretch	747 (5)	751 (56)
NiCH3 bend	761 (9)	683 (36)
HONi bend	844 (121)	590 (89)
CH_3 umbrella	1150 (42)	1072 (0)
CH_2 scissors	1210 (5)	1304 (7)
CH_2 scissors	1363 (14)	1339 (4)
CH3 stretch[b]	2597 (24)	3080 (2)
CH sym. stretch	3019 (6)	2915 (0)
CH anti. stretch	3096 (0)	3010 (0)
OH stretch	3651 (55)	3724 (153)

[a] Involves the two nearly equivalent H atoms with CH bond lengths of 1.114 and 1.110 Å

[b] H3 denotes the H atom with CH bond length of 1.105 Å

the approach we used. First, we calculate large intensities for some low-frequency modes (in particular for HNiOH) suggesting that relatively intense harmonics or combination bands may appear in the IR spectra. However, the simple harmonic analysis used here precludes quantitative predictions about these bands. Second,

Table 14. Calculated harmonic frequencies (cm^{-1}) and IR intensities (in km/mol, in parentheses) and observed frequencies (in brackets) of isotopomers of H_3CNiOH

	H_3CNiOH	$H_3{}^{13}CNiOH$	H_3CNiOD	D_3CNiOD
NiO stretch[a]				
singlet	844 (122)	844 (63)	814 (75)	810 (78)
triplet	751 (56)	751 (56)	743 (70)	738 (68)
	[715.0]	[716.2]	[696.9; 693.8]	[686.5; 682.9]
OH stretch				
singlet	3651 (55)	3651 (55)	2656 (34)	2656 (34)
triplet	3724 (153)	3724 (153)	2712 (92)	2712 (92)
	[3717.6]	[3717.8]	[2738.9; 2736.7]	[2738.7; 2736.5]

[a] There is a strong mixing of the NiO stretch and HONi bend. In H_3CNiOH and $H_3{}^{13}CNiOH$ the mode is predominantly HONi bend but in the two other isotopomers it is predominantly NiO stretch

there are sometimes two or more modes having similar frequencies and which can mix together in some isotopomers (e.g., the CO stretch and CH_3 deformations). When this occurs, isotopic shifts can be extremely difficult to compute accurately. Third, there are low-lying excited electronic states and transition to these states could occur, either directly or through vibronic coupling. Finally, multiple sites for a given species inside the matrix can give rise to many related bands with slightly different frequencies and complicate the interpretation. HNiOH seems to pose special difficulties and a detailed study of it could be very interesting. That would be a major undertaking, however, probably requiring gas-phase spectra, the highest possible level of electronic structure calculations, and an analysis of nuclear motion going beyond the harmonic and Born–Oppenheimer approximations.

Despite these difficulties, one can often reject a possible assignment when calculation and experiment do not match for one or two high frequencies (e.g., singlet HNiOH). The calculated stretch frequencies for methanol are accurate and systematically overestimate the observed fundamentals. If our assignments are correct, this carries on to the complexes: the level of agreement between calculated and experimental frequencies is no worse than for simple molecules, with typical errors on the order of 50 cm^{-1}. In general, the modes with largest calculated intensities, and frequency larger than 500 cm^{-1}, have a corresponding experimental band. However, the uncertainty in our interpretation of the experimental spectra does not allow us to assess with confidence the accuracy of the vibrational frequencies we calculate. More comparisons to IR spectra need to be made before we can assess the overall accuracy and reliability of the DFT method for vibrational frequencies of unsaturated TM complexes. We are currently working in that direction.

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