COMMUNICATIONS

NiH$_2$ has a singlet ground state

Joshua R. Barron, Amy R. Kelley, and Ruifeng Liu
Department of Chemistry, East Tennessee State University, Johnson City, Tennessee 37614-0695

Contrary to previous *ab initio* and semi-empirical studies, density functional theory and high level *ab initio* calculations predict that the ground state of NiH$_2$ is a bent singlet state. The linear triplet $^3\Delta_g$ state, predicted as the ground state by all previous calculations, is found a few kcal/mol higher. © *1998 American Institute of Physics.* [S0021-9606(98)01701-2]

The geometrical and electronic structures of nickel dihydride (NiH$_2$) have been the subject of several quantum mechanical investigations.[1–6] Among them the most detailed study reported so far is that of Blomberg and Siegbahn,[3] who investigated the reaction NiH$_2$→Ni+H$_2$ as a model for understanding the important reductive elimination and oxidative addition reactions catalyzed by nickel catalysts. The elimination reactions were observed to create H–H, C–H, and C–C bonds (in the latter cases, one or two hydrogens in NiH$_2$ are replaced by alkyl groups). The addition reaction was only observed to dissociate H–H and C–H bonds. By comparison of the properties of alkyl groups of those hydrogen atom, it was found that only the $^1A_1$ state of NiH$_2$ can, in principle, have a symmetry allowed reaction mechanism. The ground state of NiH$_2$ was found, however, to be a triplet $^3\Delta_g$ state by large scale contracted configuration interaction calculations.[3] For the triplet state the above reaction is symmetry forbidden. All *ab initio* and semi-empirical quantum mechanical studies[1–6] reported so far arrived at the same conclusion that the ground state of NiH$_2$ is a linear triplet $^3\Delta_g$ state.

A recent matrix infrared (IR) study[6] found, however, that both the symmetric and asymmetric Ni–H stretching vibrations of NiH$_2$ are IR active, indicating that the NiH$_2$ observed is nonlinear. Analysis of IR intensity data showed that the H–Ni–H bond angle is about 90°. Both the bond angle and observed IR frequencies agree very well with the predicted values of the $^1A_1$ state obtained from complete active space self-consistent field (CASSCF) calculations.[6] The same calculations predict that the $^1A_1$ state is about 7 kcal/mole higher than the linear $^3\Delta_g$ state. Thus there is no explanation why the bent $^1A_1$ state instead of the linear $^3\Delta_g$ state was observed.

In our recent quantum chemistry class at East Tennessee State University, calculating the structures, energies, and vibrational frequencies of both the lowest singlet and lowest triplet states of NiH$_2$ was assigned as a course project. The calculations were performed with GAUSSIAN94 program package[7] on an IBM RS6000 workstation. For hydrogen, the 6-311G basis set[8] was used. For Ni, the Wachters–Hay all electron basis set[9] with the scaling factors of Raghavachari and Trucks[10] was used. For convenience, the basis functions are termed 6-311G in the following discussions and tables.

These basic functions were augmented systematically by diffuse functions (indicated by ''+'' signs) and polarization functions (f functions on Ni and p functions on H). Several popular *ab initio* and density functional methods were used in the calculations. To our surprise, although Hartree-Fock (HF) and most HF-based *ab initio* methods predict the triplet state to be slightly lower than the singlet state, the density functional methods we used predict the singlet $^1A_1$ state as the ground state. The calculated structural parameters, total and relative energies of both the singlet and triplet states are presented in Table 1. The calculated IR frequencies of the singlet state are compared with the observed results in Table 2.

Table 1 shows that HF method predicts the $^3\Delta_g$ state to be 77–81 kcal/mol lower than the $^1A_1$ state. With the density functional methods using the B-LYP and B-PW91 functionals, we failed to make the self-consistent-field results (SCF) to converge when diffuse functions were used. Without the diffuse functions, B-LYP predicts the $^1A_1$ state to be about 8 kcal/mol more stable than the $^3\Delta_g$ state, and B-PW91 predicts the $^1A_1$ state about 7 kcal/mol more stable than the $^3\Delta_g$ state. With Becke's three-parameter hybrid DFT/HF method using both the LYP and PW91 correlation functionals, ordering of the two states depends on whether diffuse functions were used. Without diffuse functions, both B3LYP and B3PW91 predict that the $^3\Delta_g$ state is about 10 kcal/mol lower than the $^1A_1$ state. When diffuse functions were used, however, both B3LYP and B3PW91 predict the $^1A_1$ state as the ground state, with the $^3\Delta_g$ state a little less than 5 kcal/mol higher. The much more expensive QCISD calculations gave very similar results. When diffuse functions were not used, QCISD predicts the $^3\Delta_g$ state about 15 kcal/mol lower than the $^1A_1$ state, but when diffuse functions were used, the $^1A_1$ state is predicted to be 2 kcal/mol more stable than the $^3\Delta_g$ state.

Table 2 shows that the frequencies and deuterium isotope shifts calculated by both DFT and hybrid DFT/HF methods are in much better agreement with the observed results than the HF results. The agreement between the observed and calculated frequencies and isotope shifts confirms that the NiH$_2$ observed is in the $^1A_1$ state. It also shows that the HF method is incapable of giving a reasonable description of the subject molecule.

TABLE I. Structural parameters and energies of the $^1A_1$ and $^3\Delta_g$ states of NiH_2.

Method/basis set[a]	$^1A_1$			$^3\Delta_g$		
	E(hartree)	R_{NiH}(Å)	α_{HNiH}(°)	E(hartree)	R_{NiH}(Å)	ΔE_{S-T}[b]
HF						
6-311G	−1507.715825	1.530	118.3	−1507.839399	1.593	77.5
6-311G(f,p)	−1507.730498	1.536	120.1	−1507.856199	1.593	78.9
6-311++G(f,p)	−1507.761821	1.547	114.5	−1507.888173	1.620	79.3
6-311G($2f,2p$)	−1507.742043	1.552	121.4	−1507.870915	1.602	80.9
6-311++G($2f,2p$)	−1507.763973	1.550	114.6	−1507.890266	1.621	79.2
B-LYP						
6-311G	−1509.414323	1.440	93.2	−1509.401761	1.552	−7.9
6-311G(f,p)	−1509.424142	1.433	92.6	−1509.411854	1.548	−7.7
6-311G($2f,2p$)	−1509.438492	1.425	91.5	−1509.425078	1.543	−8.4
B-PW91						
6-311G	−1509.498637	1.431	90.1	−1509.488417	1.544	−6.4
6-311G(f,p)	−1509.509378	1.422	88.5	−1509.499060	1.540	−6.5
6-311G($2f,2p$)	−1509.524728	1.416	88.6	−1509.513281	1.535	−7.2
B3LYP						
6-311G	−1509.358758	1.435	98.1	−1509.372929	1.549	8.9
6-311G(f,p)	−1509.368567	1.431	98.2	−1509.383839	1.546	9.6
6-311++G(f,p)	−1509.434333	1.426	84.1	−1509.426643	1.559	−4.8
6-311G($2f,2p$)	−1509.381235	1.424	95.6	−1509.396718	1.546	9.7
6-311++G($2f,2p$)	−1509.434853	1.425	84.4	−1509.426977	1.559	−4.9
B3PW91						
6-311G	−1509.308022	1.429	96.0	−1509.323842	1.543	9.9
6-311G(f,p)	−1509.318482	1.424	95.8	−1509.335158	1.541	10.5
6-311++G(f,p)	−1509.385161	1.420	80.8	−1509.378613	1.555	−4.1
6-311G($2f,2p$)	−1509.331964	1.418	93.2	−1509.348790	1.540	10.6
6-311++G($2f,2p$)	−1509.385698	1.419	81.1	−1509.378974	1.555	−4.2
QCISD						
6-311G(f,p)	−1508.107766	1.440	90.3	−1508.132761	1.538	15.7
6-311++G(f,p)	−1508.189961	1.468	72.4	−1508.186254	1.561	−2.3
6-311G($2f,2p$)	−1508.174068	1.443	92.5	−1508.196857	1.542	14.3
6-311++G($2f,2p$)	−1508.236327	1.489	89.4	−1508.232237	1.565	−2.6

[a]The 6-311G basis for H and the Wachters–Hay all electron basis set (Ref. 9) for Ni.
[b]Singlet–triplet energy separation in kcal/mole.

In summary, density functional theory predicts correctly that the ground state of NiH_2 is the singlet $^1A_1$ state, the triplet $^3\Delta_g$ state is a few kcal/mol higher. Due to neglecting electron correlation, HF erroneously predicts the $^1A_1$ state about 80 kcal/mol higher than the $^3\Delta_g$ state. To overcome the shortcomings of the HF theory within the traditional post-HF approach, both a sophisticated method that recovers a large portion of electron correlation and a flexible basis set that includes diffuse functions are required. Probably due to errors introduced with the HF density, hybrid DFT/HF methods using a basis set without diffuse functions predict incor-

rectly a triplet ground state. When diffuse functions were added to the basis set, they predict correctly a $^1A_1$ ground state. On the other hand, even with the smallest basis set used in the present study, B-LYP and B-PW91 functionals predict the ground state correctly. More importantly, the singlet–triplet energy separation predicted by B-LYP and B-PW91 is insensitive to the basis functions used. These results indicate that DFT methods are more preferable for transition metal compounds than the HF and HF-based traditional *ab initio* methods.

TABLE II. Calculated[a] and observed[b] vibrational frequencies of the $^1A_1$ state of NiH_2.

Sym.	HF			B-LYP			B-PW91			B3LYP			B3PW91			obs.	
	ν	I_{IR}	$\Delta\nu$[c]	ν	I_{IR}	$\Delta\nu$	ν	I_{IR}	$\Delta\nu$	ν	I_{IR}	$\Delta\nu$	ν	I_{IR}	$\Delta\nu$	ν	$\Delta\nu$
a_1	1870	103.71	533	2066	16.31	585	2111	13.53	597	2104	34.35	596	2130	30.77	603	2007	562
b_2	1669	933.53	471	2058	39.58	586	2016	37.20	509	2081	103.58	593	2109	97.37	601	1969	543
a_1	683	146.57	194	630	2.94	180	602	0.47	172	686	6.25	196	661	2.34	189	771	169

[a]All calculations used the 6-311++G($2f,2p$) basis set. The frequencies are given in cm^{-1}, and IR intensities in km/mole.
[b]Observed frequencies are IR frequencies in argon matrix, Ref. 6.
[c]NiD_2 isotope shifts.

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