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A comparison between multireference CI and effective medium theories for diatomic FeN

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Summary. Internally contracted multireference CI calculations have been performed for the diatomic molecules FeN, CrN and CrO. For the latter two molecules the calculated dissociation energies are 3.18 eV (3.9 ± 0.2 eV) and 4.09 eV (4.5 ± 0.1 eV) respectively, where the corresponding experimental results are given in parentheses. It is argued that the correct value for CrN must lie in the lower end of the range given by experiment or perhaps slightly below. The best calculated result for FeN, for which no experimental result exists, is 1.69 eV. This value can be compared to an older CI value of 0.9 eV and a recent result of 5.25 eV obtained by an effective medium approach. Based on the results for all the three molecules treated here the correct dissociation energy of FeN can be estimated to be about 2.1 eV. The relevance of the present results for modelling chemical reactions in the regions around on-top positions of transition metal surfaces is discussed.

Key words: FeN – CrN – CrO – Configuration interaction

1. Introduction

The modelling of chemical reactions on transition metal surfaces is an important and very difficult task and it is not until recently that major progress has been made in this field. There have been two different lines of development. First, in the non-empirical approach, traditional quantum chemical methods based on *ab initio* techniques, such as SCF and CI methods, have been employed. When this is done, a cluster model of the surface has to be used, and the recent improvements in understanding this model in terms of cluster bond-preparation [1] has been very important for obtaining reasonable results. Normally in this approach, one-electron effective core potential (ECP) descriptions are used for most of the metal atoms in the cluster. The second type of method used to model reactions on surfaces is the corrected effective medium method [2], or the closely related embedded diatomics in molecules (EDIM) method [3]. More conventional local density methods [4] have not yet been used to study reactions on surfaces.

The H_2 dissociation reaction on Ni(100) has been studied in detail using both the approaches mentioned above [2, 3, 5–7]. For the regions around the hollow positions the results of the non-empirical method [7] and a carefully empirically parametrized (25 parameters) EDIM method [3] agree very well. It is expected that an empirical approach should work best for hollow positions since most available experimental information, such as activation energies, probably relate to this part of the potential surface. According to our experience [5–7], this is also the region of the potential surface which requires the least sophisticated computational treatment. In the region around the on-top positions, on the other hand, there is serious disagreement between the two approaches [2, 3, 5–7]. The non-empirical approach predicts a very small barrier, 1–2 kcal/mol at most, and a strongly bound molecular H_2 complex, 11 kcal/mol, whereas the EDIM method gives a substantial barrier, 9 kcal/mol, and only a weakly bound molecular complex, 1 kcal/mol. It is our experience that the computational effort required to describe chemisorption of an adsorbate X in on-top positions of a metal (M) surface closely parallels that of the corresponding diatomic MX molecule (or triatomic NiH_2, in this case). One reason on-top bonding is more difficult to describe is that the bond distances are generally much shorter at these points, which means that the interaction with the $3d$ orbitals will be stronger. Perhaps even more importantly, the overlap between the adsorbate orbitals and the delocalized (s, p band) surface orbitals with certain nodal structure is often small. The local $3d$ orbital of the on-top atom will, for example, be the only orbital with the correct nodal structure and sufficient overlap to break the H_2 bond in on-top positions. It was realized early, therefore, that when the interaction between adsorbates and surfaces around the on-top position is described in the non-empirical approach, the on-top position is described in the non-empirical approach, the on-top atom has to be modelled at the all-electron level [5, 8]. The surrounding atoms can to a good approximation be described by one-electron ECP atoms without creating any serious imbalance problems [8]. The $3d$ orbitals will, for similar reasons as given above, be relatively unimportant at hollow sites. To describe computationally the bonding when $3d$ orbitals are involved is quite difficult, and this is true using local density or effective medium approaches, as well as with *ab initio* techniques. To obtain a better understanding of how reliable these different approaches should be for regions around the on-top positions, it is therefore of great interest to perform direct comparisons. These comparisons can be made simply for the corresponding molecule where only one metal atom is involved, but comparisons have still not been done. The first possibility to test the effective medium method against the non-empirical method was only recently made possible by the detailed calculations on different diatomic molecules using the former method by Raeker and DePristo (RD) [9]. Of the molecules studied in that paper we have here selected FeN as the most representative case for a detailed comparison.

One reason we have chosen FeN for a comparison between the different methods is that there is a very big discrepancy between the published results. RD obtained a binding energy of 5.25 eV using the corrected effective medium (CEM) method [9], a result which they note is in line with the experimentally known large binding energies for CrN of 3.9 eV, for TiN of 4.9 eV and for VN of 4.9 eV [10]. Based on these results they therefore found it difficult to believe that our previously published multireference CI binding energy for FeN of only 0.9 eV should be correct [11]. At the time of the latter study, which was done in 1984, some compromises in the computational treatment had to be made. Most notably, the basis sets used were only of standard quality with, for example, no f functions on iron. Furthermore, the externally Contracted CI (CCI) method

[12] was used with an unusually high selection threshold for the reference states of 0.10, and the CCI method is known to be less reliable under such circumstances [12]. Based on previous experience [13], a discrepancy of 1.0–1.5 eV between a calculated and an experimental dissociation energy would not be unexpected. If, on the other hand, the CEM result of more than 5 eV is correct this could only mean that a serious error had been made in our previous calculation. Apart from trivial errors such as computer program or input errors, there could be a case of mistaken ground state, which is always a possibility for this type of system, where the wave-function is quite complicated. A straight failure of the present type of *ab initio* methods must be ruled out even though it is well known that these methods have so far yielded quite poor results for the case of Cr_2. Currently, the best multireference CI calculation for Cr_2 gives practically no binding [14] whereas the experimental dissociation energy is as large as 1.56 eV [15]. However, the basis sets used in [14] were quite limited with only a single f function. Since there are five d bonds in this hextuply bonded molecule, high angular functions are expected to contribute significantly, much more than is expected for the systems studied here. Cr_2 is therefore not a representative case in the present context.

In the present study the newly developed Internally Contracted CI (ICCI) method has been used [14]; ICCI is particularly suited for this application where a large number of reference states are needed. The basis sets used will also include f functions on iron. Since the binding energy of FeN is not known, comparative calculations will be made on the similar molecules CrN and CrO, for which experimental dissociation energies do exist [10]. Based on the combined results for these three systems a prediction of the binding energy of FeN can then be made, which should be reasonably accurate (within 0.3 eV).

Of these three molecules, CrO is the only one which has been studied by *ab initio* methods. Bauschlicher et al. [16] studied a series of transition metal oxides of which CrO was one, using multireference CI calculations with a rather limited reference space. Jasien and Stevens [17] calculated the spectroscopic constants of the $X^5\Pi$ state of CrO and low-lying states of CrO^+ using multireference CI methods and with an ECP description of the argon core of chromium. The binding energy for CrO was found to be 4.00 eV which is 11% smaller than the experimental value of 4.5 eV. This must be considered a rather satisfactory result for a transition metal compound. Recently the permanent electric dipole moment of CrO was determined in a joint theoretical and experimental paper [18]. The theoretical value obtained for the $X^5\Pi$ state, using large multireference CI iterative-natural-orbital and finite-field calculations, was in excellent agreement with the experimental value, 3.80 D compared to 3.88 D.

2. Computational details

Calculations have been performed for FeN, CrN and CrO. Basis sets of two different sizes were used, the smaller ones of standard quality and the larger ones with additional diffuse and polarizing functions. Dynamic correlation of all valence electrons was accounted for. Relativistic effects were obtained using first order perturbation theory including the mass-velocity and Darwin terms [19].

The metal basis sets were those given by Wachters, including the two suggested diffuse p functions multiplied by a factor of 1.5 [20]. The diffuse d functions given by Hay [21] were added to this primitive basis. The core orbitals were totally contracted using a generalized contraction scheme [22, 23]. The two outermost functions of each symmetry were left uncontracted. A set of three *f* exponents were added and in the standard basis sets these were contracted to one function leading to a 5*s*, 4*p*, 3*d*, 1*f* contracted basis set. In the extended basis the three *f* exponents were contracted to two functions leading to a 5*s*, 4*p*, 3*d*, 2*f* contracted basis set.

For nitrogen and oxygen the Huzinaga 9*s*, 5*p* set [24] was generally contracted to a 3*s*, 2*p* set. In the standard basis sets one *d* function, with exponent 1.0 for nitrogen and 1.33 for oxygen, respectively, was added leading to a 3*s*, 2*p*, 1*d* contraction. In the extended basis sets two *d* functions, with exponents 1.7 and 0.6 for both nitrogen and oxygen, were added together with one even-tempered diffuse *p* function leading to a 3*s*, 3*p*, 2*d* contraction.

For the generation of the zeroth-order wave-function the Complete Active Space SCF (CASSCF) method [25] was used. All valence electrons and all valence orbitals were active.

The dynamical correlation contributions to the binding were determined in multireference CI calculations selecting all configurations with a coefficient larger than 0.05 in the CASSCF wave-functions as reference states. Since this threshold leads to a large number of reference configurations for the present systems, the internally contracted CI method [14], which is particularly efficient for these situations, was used. To have a size-consistent description of the correlation energy, the Averaged Coupled Pair Functional energy expression [29] was used. The calculations are thus denoted IC-ACPF.

For FeN the bond distance was optimized using the standard basis set and for CrN the bond distance was optimized using a slightly smaller basis set, the standard basis without *f* functions on Cr. For CrO the experimental bond distance was used.

3. Results and discussion

The present comparative study starts with the FeN molecule. In our previous multireference CI study a binding energy of only 0.9 eV was obtained in a calculation using basis sets smaller than the present ones and a qualitative correlation treatment [11]. No experimental binding energy for this molecule is yet known, but the binding energies of CrN, TiN and VN are in the 3.9–4.9 eV range. The calculated value for FeN of 0.9 eV was therefore considered to be surprisingly low even at that time. To analyze the situation further a calculation was also performed for FeN^+, for which it is possible to form a full triple 3*d* bond in the $^1\Sigma^+$ state and for which the repulsion from the 4*s* electrons should be smaller than for neutral FeN. A quite accurate calculation on FeN^+, much more accurate than the one on FeN, gave only a maginally larger binding energy for this system of 1.0 eV [11]. Since the calculation on FeN^+ had *f* functions on iron, *d* functions on nitrogen and included all reference states with a coefficient larger than 0.05, the result for this molecule is not likely to change by much in an even more accurate treatment.

The value of the binding energy for FeN recently published by Raeker and DePristo (RD) led us to undertake another study of this system. Using the CEM method they obtained a large value of 5.25 eV. The results of the present calculations for FeN are given in table 1. The result for the $^2\Delta$ state, which was considered to be the ground state in our previous study, is 1.69 eV for the large

Table 1. Results for FeN, CrN and CrO, ground states. Populations and dipole moments are given at $R = 3.06\,a_0$ ($3.0\,a_0$ for FeN using the standard basis). Bond distances within parenthesis are taken from either experimental results or from optimization using a smaller basis set (see section 2)

	CASSCF		IC-ACPF		exp
	standard basis	large basis	standard basis	large basis	
Fe, $d^6s^2 \rightarrow d^7s^1$, eV	2.03	2.04	1.29	1.28	0.87
FeN, $^2\Delta$					
R_e, a_0	3.07	(3.06)	3.034	(3.06)	
D_e, eV	0.07	0.17	1.50	1.69	
q_N	−0.23	−0.34			
$3d_{Fe}$	6.39	6.36			
μ, Debye	−2.11	−2.31			
Cr, $d^5s^1 \rightarrow d^4s^2$, eV	1.07	1.07	0.97	0.97	1.00
CrN, $^4\Sigma^-$					
R_e, a_0	(3.06)	(3.06)	(3.06)	(3.06)	
D_e, eV	2.20	2.27	3.03	3.18	3.9 ± 0.2[a]
q_N	−0.28	−0.34			
$3d_{Cr}$	4.58	4.55			
μ, Debye	−2.07	−2.08			
CrO, $^5\Pi$					
R_e, a_0	(3.06)	(3.06)	(3.06)	(3.06)	3.06
D_e, eV	2.67	2.80[b]	3.88	4.09[b]	4.5 ± 0.1[a]
q_O	−0.42	−0.50			
$3d_{Cr}$	4.44	4.39			
μ, Debye	−2.78	−2.74			

[a] The experimental binding energies are D_0 values

[b] If instead D_e is calculated relative to Cr^+ and O^- and corrected by the experimental ionization energy and electron affinity 4.07 eV is obtained at the CASSCF level and 4.28 eV at the IC-ACPF level

basis set. This value is 0.8 eV larger than our previous value. Of this improvement the major part, probably about 0.6 eV, comes from the improved basis set and the rest from the improved correlation treatment. The main improvement in the basis set compared with the previous study is the addition of f functions. Even if the binding energy of FeN now has increased by 0.8 eV, which is an expected amount, the value of 1.7 eV is still very different from the value by RD of 5.25 eV.

One possible source of error in the present determination of the binding energy of FeN is that the $^2\Delta$ state may not be the ground state. The other five possible states of FeN were therefore investigated as well. The vertical excitation energies given in table 2 show that at the CASSCF level the $^2\Delta$ state is indeed the ground state. The excitation energy at this level to the $^4\Pi$ state, which is the lowest of the other states of 0.22 eV. Since this state is so close to the $^2\Delta$ state a geometry optimization for the $^4\Pi$ state was performed at the CASSCF level. The bond distance of the $^4\Pi$ state is found to be only slightly longer ($0.1\,a_0$) than that of the $^2\Delta$ state and the energy difference between the minima of the two potential curves is 0.18 eV, thus very close to the vertical excitation energy of 0.22 eV at $3.0\,a_0$ given in table 2. The excitation energies to the other states at the

Table 2. Vertical (at $R = 3.0\,a_0$) excitation energies and populations of FeN calculated at the CASSCF level using the standard basis

	ΔE, eV	q_N	$3d_{Fe}$	μ, Debye
$^2\Delta$	0.	−0.23	6.39	−2.11
$^4\Pi$	0.22[a]	−0.37	6.43	−2.18
$^2\Pi$	0.97	−0.33	6.46	−1.58
$^2\Sigma^+$	1.14[b]	−0.23	6.67	−1.28
$^4\Sigma^+$	1.40	−0.42	6.31	−2.22
$^4\Delta$	1.84	−0.28	6.33	−2.06

[a] IC-ACPF result is 0.10 eV
[b] IC-ACPF result is 0.98 eV

CASSCF level are 1.14 eV for the $^2\Sigma^+$ state, 0.97 eV for the $^2\Pi$ state, 1.84 eV for the $^4\Delta$ state and 1.40 eV for the $^4\Sigma^+$ state. Only two excited states were treated including dynamical correlation, the $^2\Sigma^+$ state and the $^4\Pi$ state. The $^2\Sigma^+$ state was selected for two reasons. First, it has the same type of wave-function as the $^4\Sigma^-$ ground state of CrN (see below) and second, this is the only state with significantly larger $3d$ population than the ground state, which could indicate that this state may be lowered more by correlation than the ground state. At the correlated level the excitation energy to the $^2\Sigma^+$ state is 0.98 eV compared to 1.14 eV at the CASSCF level. The $^4\Pi$ state was selected since it is rather close to the $^2\Delta$ state at the CASSCF level, being only 0.2 eV higher. At the correlated level the splitting decreases to 0.10 eV, but the $^2\Delta$ state is still the ground state in agreement with our previous study. It is possible that an even more accurate treatment might change the order of these two states but this would not modify the dissociation energy significantly.

In order to obtain more information about the accuracy of the computed dissociation energy, calculations were also performed for CrN and CrO, for which experimental values exist. The results of these calculations are given in table 1. We first note that for the $^5\Pi$ ground state of CrO the best calculated result for the binding energy is 4.09 eV compared to experimental values of 4.5 ± 0.1 eV [27] and 4.4 ± 0.3 eV [28]. In light of the experimental uncertainty, the calculated result is highly satisfactory. Since CrO is so ionic, the binding energy can also be calculated with respect to the ionic dissociation limit and can then be corrected by using the experimental electron affinity for oxygen and ionization potential for chromium. If this procedure is used the binding energy becomes 4.28 eV, which is in even better agreement with experiment. Furthermore, an effect of up to a few tenths of an eV from correlating also the chromium $3s$ and $3p$ electrons cannot be ruled out – such effects have been observed previously. For Sc_2, for example, the binding energy is increased by 0.1 eV due to $3s$, $3p$ correlation [29].

The results for the binding energy of the $^4\Sigma^-$ state of CrN in table 1 is also in at least reasonable agreement with experiments. The best calculated value is 3.18 eV and the experimental value 3.9 ± 0.2 eV [30]. However, the theoretical result indicates that the true value must lie in the lower end of the range given by the error bars for the experimental result or perhaps a little lower. First, an error in the calculated value for CrN of 0.7 eV is substantially larger than the error of 0.2–0.5 eV for CrO. Judging from the quality of the calculations, a larger error would actually be expected for CrO. In the IC-ACPF calculation for CrN no large coefficients appear except for the configurations which were already selected as reference states. This was not the case for CrO, for which a few additional configurations appeared with coefficients in the range 0.05–0.10. Secondly, the bond distance of CrN was optimized but not the one for CrO, which was taken from experiment. Finally, CrO is much more ionic than CrN which is expected to lead to a larger error due to larger problems in describing the electron affinity for oxygen compared with nitrogen, and which also might lead to a larger $3s$, $3p$ correlation effect for CrO. Taken together, it is difficult to see that the actual binding energy in CrN should be much larger than 3.6 eV. It should be noted that the estimated uncertainty in the experimental result, 0.2 eV [30], is probably a lower limit, taking into account that there are several unknown factors involved in the experimental determination. The experiment is an effusion-mass spectrometric study and an error of a few tenths of an eV is easily obtained in this type of experiment, in particular when the spectrum of the molecule is not known, as is the case for CrN. For example, it was shown in a study on Pd_2 [31], using the same experimental technique together with quantum chemical calculations of the molecular spectrum, that the deduced binding energy changed by 0.2 eV just by taking the spin-orbit effects on the spectrum into account.

Based on the errors in the computed binding energies of CrN and CrO, an error of 0.3–0.4 eV can thus be expected for the calculated binding energy of FeN. This error estimate leads to a predicted value of about 2.1 eV for this binding energy. The error in the value calculated by RD using the CEM method should thus be about 3.1 eV, whereas the error in our previously computed value should be about 1.2 eV. For the surface chemisorption problem, the conclusion we draw is that none of these latter treatments has a high enough accuracy to be trusted in the regions around on-top positions for this particular case. It is, for example, clear from the calculations on FeN that f functions are definitely required to describe the on-top iron atom. It should be added that nitrogen chemisorption at on-top positions of iron surfaces is an unusually difficult surface problem. The chemisorption problem discussed in the introduction with an on-top dissociation of a hydrogen molecule on nickel should be much easier. In fact, earlier calculations on systems similar to NiH_2 ($NiHCH_3$ and $Ni(CH_3)_2$ [32]) have indicated that even a moderate correlation treatment, using standard basis sets without f functions, is capable of producing a reasonably accurate binding energy. From this point of view there is thus no reason to distrust the qualitative correctness of the low barrier and the strong molecular chemisorption of H_2 in on-top positions of Ni(100) as obtained using the non-empirical approach [6]. From the same viewpoint, the EDIM results for the same problem [3] must be viewed with greater scepticism. An accurate treatment of the local area in chemisorption problems is, however, only one prerequisite for obtaining a reliable final answer. The accuracy of the surface model is another equally important aspect, for which the present comparative calculations cannot add anything.

Since the present calculations on CrO, CrN and FeN are the most accurate performed to this date for these molecules, a few comments on the electronic structure should be added. The $^4\Sigma^-$ ground state of CrN, with a binding energy of 3.2 eV, has the electronic structure which is easiest to describe. The ^7S ($3d^5 4s^1$) ground state of the chromium atoms forms a triple bond to nitrogen using one d_σ and two d_π electrons. The remaining valence electrons on chromium, the $4s$ electron and the two $3d_\delta$ electrons are coupled to $^4\Sigma^-$. The $4s$ electron is *sp* hybridized away from nitrogen and the three covalent bonds are all slightly distorted towards nitrogen, yielding a charge transfer of about 0.3 electrons from chromium to nitrogen and a corresponding decrease of the $3d$ population on chromium. Most similar to this state is the $^2\Sigma^+$ state of FeN, with a binding energy of only 0.7 eV, the main difference being that FeN has two more $3d_\delta$ electrons than CrN. The charge transfer is slightly smaller in FeN, about 0.2 electrons compared to 0.3 electrons for CrN, which is due to the larger $3d^{n+1}4s^1$ to $3d^n4s^1$ ionization energy of Fe, 8.8 eV compared with 8.3 eV for Cr. One reason the binding energy for FeN is smaller than for CrN is that the $^2\Sigma^+$ state of FeN does not correlate with the ^5D ground state of Fe, but rather with the first excited state, ^5F. Relative to this excited state the binding energy is 2.0 eV, which is closer to but still significantly smaller than the value of 3.2 eV for CrN. The other main reason for the smaller binding energy of FeN compared to CrN must be the additional repulsion from the extra *d* electrons on iron.

The $^2\Delta$ ground state of FeN, which correlates with the ground state of the Fe atom, also has a triple bond, but in this case the σ bond is formed by a $4s$ electron on iron rather than a $3d_\sigma$ electron as was the case for the wave-functions discussed in the preceding paragraph. The remaining two σ electrons on iron form two sd_σ-hybrids, with 1.85 electrons in the hybrid perpendicular to the molecular axis and 0.15 electrons in the one pointing along the molecular axis. The main charge transfer from iron to nitrogen occurs in this case in the σ bond, which has about 0.5 electrons on Fe and 1.5 electrons on N. This state of FeN has a binding energy of only 1.7 eV, compared with 3.2 eV for the ground state of CrN. One important reason for this difference is that the $^2\Delta$ state of FeN has a mixed *s*- and *d*-bonding, while CrN has a pure *d*-bonding, which in turn can be explained by the fact that iron has more $4s$ electrons in its ground state ($3d^64s^2$) than chromium ($3d^54s^1$). Since for the first row transition metals the $3d$ and $4s$ orbitals have rather different density maxima, the bond-distance cannot be optimal for both types of bonding at the same time, which should lead to a lower binding energy for the mixed *sd*-bonding compared to the pure *d*-bonding. Further, the repulsion from the extra $3d$ electrons on iron compared to chromium, as discussed above, should have an effect on the binding energy of all states of FeN. Finally, the $^4\Pi$ state of FeN, which is found to be close to the $^2\Delta$ state, has a pure *d*-bonding, and in contrast to the $^2\Sigma^+$ state discussed above it correlates with the ground state of Fe. However, for this state there is one electron in the antibonding 2π orbital, which reduces the strength of the π bond, making this state slightly less bound than the $^2\Delta$ state.

The $^5\Pi$ ground state of CrO is formed in the same way as the $^4\Sigma^-$ state of CrN, but there is an extra electron added in the 2π orbital. The bonds are more ionic in CrO compared to CrN, particularly the σ bond, since oxygen has a much higher electron affinity than nitrogen, 1.42 eV compared with zero.

4. Conclusions

To obtain accurate dissociation energies of neutral transition metal diatomic molecules is not trivial, neither by calculations nor by experiments. In effusion-mass spectrometric experiments the analysis becomes uncertain when the low-lying excited states are unknown. Another source of error in the experimental analysis is uncertainties in the ionization cross sections [33, 34]. In *ab initio* calculations on these systems large basis sets and a high level of correlation treatment are required. Therefore, dissociation energies for these systems are seldom known to high accuracy. The situation for the three molecules studied here, CrO, CrN and FeN are rather different from each other. For CrO, the experimental dissociation energy is 4.5 eV compared with the best calculated result of 4.28 eV (obtained by going to the ionic dissociation limit). This discrepancy between experiment and theory of 5% is not alarming, in particular since the calculated result can be expected to be in error by a few tenths of an eV due to missing core correlation effects. For CrN the situation seems to be less satisfactory. The discrepancy between the best calculated value of 3.18 eV and the experimental value of 3.9 eV for CrN is 18%. Based on the absence of large coefficients in the final ACPF wave-function and the type of bonding, a much larger error in the calculated value for CrN than for CrO appears unlikely. On the contrary, the computational indications point towards a smaller error for CrN. Therefore, we expect that the correct dissociation energy for CrN should be at most 3.6 eV. However, this value is actually just below the lower limit of the experimental range if the uncertainty in the measurement, estimated to 0.2 eV is taken into account.

The situation for the dissociation energy of FeN, which has been the main topic of this paper, has been even more unclear than for CrN and CrO since no experimental value exists for FeN. In our previous study a surprisingly small value of 0.9 eV was obtained for the dissociation energy, but in the present more accurate study the value increased to 1.69 eV. This value is still much smaller than the value of 5.25 eV obtained using an effective medium approach. Based on the comparisons between calculations and experiments for CrN and CrO a correct value larger than 2.1 eV would be surprising and the effective medium value should thus be a rather large overestimate. Overestimates of dissociation energies when local density approaches are used are quite common. In a recent analysis of the dissociation energy of Pd_2CO we conclude that the dissociation energy calculated by local density methods was overestimated by nearly 80% [35, 36]. Also, in model calculations of the carbon chemisorption energy on Ni(100) an overestimate of 54% compared with the best experimental value was obtained [37]. It seems as if these overestimates are particularly large when the bonding involves large *d* contributions. In contrast, this type of method, including such as the effective medium method, perform remarkably well in situations where *s*, *p* bonding is expected to dominate [2, 3, 9]. For adsorbates on transition metal surfaces this is the most common type of bonding and occurs, for example, for hydrogen at most positions on the surface except at on-top positions.

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