

*Regular article***Computational studies of bond dissociation energies, ionization potentials, and heat of formation for NH and NH⁺. Are hybrid density functional theory methods as accurate as quadratic complete basis set and Gaussian-2 ab initio methods?**

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Abstract. Ionization potentials, bond dissociation energies, and heat of formation for NH and NH⁺ molecular species as well as for their elements were computed with highly reliable quadratic complete basis set and Gaussian-2 ab initio methods. The results are compared with experimental results and the assurance of these ab initio approaches is assessed. The same studies were also performed with three hybrid density functional methods (B3LYP, B3P86, and B3PW91) in combination with variously sized basis sets. The computational results are discussed in light of density functional theory reliability for exploring the potential energy of small polar molecular systems.

Key words: Bond dissociation energies – Ionization potentials – Hybrid density functional theory

(BDEs) in NH and NH⁺ molecular species [6]. Their results are supposed to be much closer to the expected values than results of previous computational studies obtained at MP4, CBSQ, and CASSCF ab initio levels of theory [7, 8].

These results have stimulated a series of ab initio calculations targeted to obtain highly accurate BDEs as well as the heat of formation ($\Delta H_{f,0}$) for NH and NH⁺ [8–11]. In our opinion, there is sufficient experimental data as well computational data, on these two molecular systems to allow performance of high-level ab initio and hybrid density functional theory (DFT) computational studies. Previously, we have demonstrated that some DFT methods are capable of accurately computing geometries [12–16], activation energies [17–19], BDEs [20–23], and ionization potentials (IPs) [24–26] for small polar molecules. It is therefore of interest to extend our computational studies to molecular systems of general interest to the atmospheric and combustion chemist.

1 Introduction

These days there is considerable interest in the computational study of simple diatomic molecules that play a role in combustion and atmospheric chemistry. Two of them are NH and NH⁺. It is believed that these molecular species are involved in the combustion of nitroamine propellants that are widely used as fuel in astronautic aeronautics [1, 2]. Furthermore, NH⁺ is considered to be the first step in the formation of ammonia in interstellar molecular clouds [3]. The most detailed information about these two molecular species is available from scattering experiments of the ion-molecule reaction $N^+ + D_2 \rightarrow ND^+ + D$ [4]. This experimental data was used by Tarroni and coworkers [5] to accurately evaluate the bond dissociation energies

2 Computational methods

All computational studies were performed with the Gaussian 94 computational package [27]. For computation of very accurate energies Gaussian-2 (G2) [28] and the quadratic complete basis set (CBSQ) [29, 30] were used. There are three hybrid density functional methods that are a combination of Becke's three parameters exchange functional (B3) [31] with three different exchange functionals: (LYP) [32], (P86) [33], and PW91 [34]. These combinations make the B3LYP, B3P86, and B3PW91 hybrid DFT methods. In conjunction with these hybrid DFT methods 6-31+G(*d*), 6-311+G(2*d*,2*p*), and 6-311+G(3*df*,3*pd*) Gaussian-type basis sets were employed [35]. These basis sets have been used by us to study many different chemical systems with DFT methods and have proven to produce reliable values. All experimental data used in this study were obtained from Ref. [5]. The $\Delta H_{f,0}$ for all molecules was computed directly from the total energies of elements from which they were built. For instance, the $\Delta H_{f,0}$ of H⁺ is its total energy, while the $\Delta H_{f,0}$ for the H atom is a half of the total energy difference between two hydrogen atoms and one hydrogen molecule. Of course the $\Delta H_{f,0}$ for both H₂ and N₂ is by definition equal to zero.

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3 Results and discussion

The complete basis set ab initio method is extraordinary accurate for computation of BDEs and the $\Delta H_{f,0}$ for some small molecular systems [36, 38]. Knowing that there is recent data for energetic properties of NH and NH^+ as well as atoms and ions associated with these molecular species obtained through experimental and high-level ab initio studies [5], these molecular systems are a perfect choice for the evaluation of the accuracy of CBSQ ab initio and hybrid DFT methods. Furthermore, some of the energetics values are not accurate; so we are also seeking more accurate values for the $\Delta H_{f,0}$ of these molecular species.

Let us first examine the energetics with the highly accurate G2 and CBSQ ab initio methods. The results are presented in Table 1. As we expect based on our previous studies of small polar chemical systems, CBSQ generates highly accurate IPs, BDEs, and $\Delta H_{f,0}$ values. The largest inconsistency between computed and experimental values for the $\Delta H_{f,0}$ of N^+ is 0.1 eV. All other values are almost identical to the experimental values (Table 1). It is therefore safe to state that the CBSQ ab initio method appears to be a highly accurate approach for the computation of energetics of small polar and small-charged molecular systems such as NH and NH^+ (Table 1).

The energies computed with the G2 ab initio method (Table 1) deviate slightly more from the experimental values than those computed with CBSQ, but in general the computed energies are of almost the same *quality*. For instance, the NH^+ homolytic BDE computed with G2 is 4.442 eV, this is closer to the experimental value of 4.477 eV than 4.415 eV computed with CBSQ (Table 1). On the other hand, for the computation of the heterolytic $\text{NH} + \text{BDE}$ the situation is the opposite. The G2 estimated energy is 3.571 eV while the CBSQ estimated energy of 3.524 eV is much closer to the experimental value of 3.5 eV (Table 1). It is fair to say that both of these computational approaches should produce reliable energetics for small polar chemical systems but CBSQ

might produce energies that are in slightly better agreement with the experimental results.

There are many computational studies in which we have demonstrated the accuracy of density functional methods in exploring the potential energy surface for a wide variety of molecular systems. One that is in exceptional agreement with high-level ab initio studies is for Al_2H_2 isomers [38]. A particularly successful performance was obtained with hybrid DFT methods. To determine their accuracy for small chemical systems with multi-spin electron configuration, we have performed computational studies with three widely used hybrid DFT methods (B3LYP, B3P86, and B3PW91) on NH and NH^+ as well as related atoms and molecules. The computational results with B3LYP are presented in Table 1. Three sizes of basis set, 6-31+G(*d,p*), 6-311+G(2*d,2p*), and 6-311+G(3*df,3pd*), were employed, aimed at exploring the influence of basis-set size on the accuracy of computed results. To our surprise computed values closest to the experimental data were obtained with the 6-31+G(*d,p*) basis set (Table 2). Regardless of the size of the basis set used in these studies many values are slightly higher than the experimental energies obtained. The highest deviation obtained is approximately 0.3 eV for the IP of NH (Table 2). One can argue that even closer agreement can be obtained if a scaling factor, which is a function of the basis set, is applied. This is applicable for IPs, but not for some BDEs and $\Delta H_{f,0}$ values that are already in excellent agreement with the experimental data. For instance, the B3LYP/6-31+G(*d,p*) computed BDEs for NH and NH^+ are 3.442 and 3.513 eV, respectively. These values are in excellent agreement with the experimental values of 3.419 and 3.5 eV, respectively. Similarly, high agreement between computed and experimental energies is obtained for the $\Delta H_{f,0}$ of H^+ , N^+ , and NH^+ . Unfortunately, the $\Delta H_{f,0}$ for NH is 0.25 eV lower than the experimental value. The energy difference between the doublet and the excited quartet electronic state is estimated to be 0.162 eV (Table 2) which is in relatively good agreement with 0.066 eV computed with CBSQ (Table 1) or 0.071 eV

Table 1. Ionization potential (IP), bond dissociation energies (BDEs), heat of formation ($\Delta H_{f,0}$), and energy difference between quadratic and doublet NH^+ (DE) in eV computed with Gaussian-2 (G2) and quadratic complete basis set (CBSQ) ab initio methods

	G2	G2(0 K)	CBSQ	CBSQ(0 K)	Exp.
IP(H)	13.542	13.606	13.537	13.600	13.598 ± 0.005
IP(N)	14.476	14.476	14.492	14.492	14.534 ± 0.005
IP(NH)	13.415	13.415	13.446	13.446	13.476 ± 0.002
BDE(NH)	3.419	3.380	3.408	3.369	3.419 ± 0.010
BDE(NH^+) ^a	4.480	4.442	4.454	4.415	4.477 ± 0.008
BDE(NH^+) ^b	3.546	3.571	3.498	3.524	3.500 ± 0.009
$\Delta H_{f,0}(\text{H})$	2.283	2.264	2.284	2.265	2.239 ± 0.001
$\Delta H_{f,0}(\text{H}^+)$	15.825	15.870	15.821	15.866	15.837 ± 0.005
$\Delta H_{f,0}(\text{N})$	4.873	4.853	4.855	4.836	4.879 ± 0.005
$\Delta H_{f,0}(\text{N}^+)$	19.349	19.329	19.347	19.328	19.413 ± 0.005
$\Delta H_{f,0}(\text{NH})$	3.737	3.737	3.731	3.731	3.699 ± 0.006
$\Delta H_{f,0}(\text{NH}^+)$	17.152	17.152	17.177	17.177	17.175 ± 0.006
DE	0.101	0.100	0.066	0.066	0.071

^a BDE computed as the energy difference between NH^+ and $\text{N}^+ + \text{H}$

^b BDE computed as the energy difference between NH^+ and $\text{N} + \text{H}^+$; $\Delta H_{f,0}(\text{H}^+) = \Delta H_{f,0}(\text{H}) + \text{IP}(\text{H})$; $\Delta H_{f,0}(\text{N}^+) = \Delta H_{f,0}(\text{N}) + \text{IP}(\text{N})$; $\Delta H_{f,0}(\text{NH}^+) = \Delta H_{f,0}(\text{NH}) + \text{IP}(\text{NH})$

Table 2. IP, BDEs, $\Delta H_{f,0}$, and DE in eV computed with the B3LYP method

	A	B	C	D	E	Exp.
IP(H)	13.613	13.613	13.664	13.664	13.664	13.598 \pm 0.005
IP(N)	14.718	14.718	14.676	14.676	14.675	14.534 \pm 0.005
IP(NH)	13.794	13.777	13.789	13.771	13.789	13.476 \pm 0.002
BDE(NH)	3.454	3.442	3.512	3.502	3.543	3.419 \pm 0.010
BDE(NH ⁺) ^a	4.803	4.617	4.781	4.596	4.801	4.477 \pm 0.008
BDE(NH ⁺) ^b	3.699	3.513	3.769	3.584	3.791	3.500 \pm 0.009
$\Delta H_{f,0}$ (H)	2.422	2.283	2.390	2.254	2.239	2.239 \pm 0.001
$\Delta H_{f,0}$ (H ⁺)	16.035	15.896	16.054	15.918	15.903	15.837 \pm 0.005
$\Delta H_{f,0}$ (N)	4.820	4.744	4.926	4.850	4.979	4.879 \pm 0.005
$\Delta H_{f,0}$ (N ⁺)	19.538	19.462	19.602	19.526	19.654	19.413 \pm 0.005
$\Delta H_{f,0}$ (NH)	3.455	3.442	3.512	3.500	3.543	3.699 \pm 0.006
$\Delta H_{f,0}$ (NH ⁺)	17.249	17.219	17.301	17.271	17.332	17.175 \pm 0.006
DE	0.190	0.162	0.212	0.182	0.212	0.071

^a BDE computed as the energy difference between NH⁺ and N⁺ + H

^b BDE computed as the energy difference between NH⁺ and N+H⁺; A = 6-31+G(*d,p*) basis set; B = 6-31+G(*d,p*) basis set and zero-point energy correction; C = 6-311+G(2*d,2p*) basis set; D = 6-311+G(2*d,2p*) basis set and zero point energy correction; E = 6-311+G(3*df,3pd*) basis set; $\Delta H_{f,0}$ (H⁺) = $\Delta H_{f,0}$ (H)+IP(H); $\Delta H_{f,0}$ (N⁺) = $\Delta H_{f,0}$ (N)+IP(N); $\Delta H_{f,0}$ (NH⁺) = $\Delta H_{f,0}$ (NH)+IP(NH)

Table 3. IP, BDEs, $\Delta H_{f,0}$, and DE in eV computed with the B3P86 method

	A	B	C	D	E	Exp.
IP(H)	14.063	14.063	14.108	14.110	14.110	13.598 \pm 0.005
IP(N)	15.346	15.346	15.302	15.302	15.300	14.534 \pm 0.005
IP(NH)	14.318	14.302	14.314	14.295	14.314	13.476 \pm 0.002
BDE(NH)	3.485	3.475	3.534	3.526	3.565	3.419 \pm 0.010
BDE(NH ⁺) ^a	4.915	4.728	4.900	4.714	4.920	4.477 \pm 0.008
BDE(NH ⁺) ^b	3.633	3.445	3.708	3.517	3.739	3.500 \pm 0.009
$\Delta H_{f,0}$ (H)	2.456	2.318	2.429	2.292	2.429	2.239 \pm 0.001
$\Delta H_{f,0}$ (H ⁺)	16.519	16.381	16.537	16.402	16.539	15.837 \pm 0.005
$\Delta H_{f,0}$ (N)	4.916	4.840	5.018	4.942	5.070	4.879 \pm 0.005
$\Delta H_{f,0}$ (N ⁺)	20.262	20.186	20.320	20.244	20.370	19.413 \pm 0.005
$\Delta H_{f,0}$ (NH)	3.485	3.475	3.534	3.526	3.483	3.699 \pm 0.006
$\Delta H_{f,0}$ (NH ⁺)	17.803	17.777	17.848	17.821	17.797	17.175 \pm 0.006
DE	0.013	-0.010	0.033	0.010	0.010	0.071

^a BDE computed as the energy difference between NH⁺ and N⁺ + H

^b BDE computed as the energy difference between NH⁺ and N+H⁺; A = 6-31+G(*d,p*) basis set; B = 6-31+G(*d,p*) basis set and zero point energy correction; C = 6-311+G(2*d,2p*) basis set; D = 6-311+G(2*d,2p*) basis set and zero-point energy correction; E = 6-311+G(3*df,3pd*) basis set; $\Delta H_{f,0}$ (H⁺) = $\Delta H_{f,0}$ (H) + IP(H); $\Delta H_{f,0}$ (N⁺) = $\Delta H_{f,0}$ (N)+IP(N); $\Delta H_{f,0}$ (NH⁺) = $\Delta H_{f,0}$ (NH)+IP(NH)

Table 4. IP, BDEs, $\Delta H_{f,0}$, and DE in eV computed with the B3PW91 method

	A	B	C	D	E	Exp.
IP(H)	13.665	13.665	13.714	13.714	13.714	13.598 \pm 0.005
IP(N)	14.830	14.830	14.787	14.787	14.786	14.534 \pm 0.005
IP(NH)	13.794	13.777	13.789	13.771	13.789	13.476 \pm 0.002
BDE(NH)	3.691	3.487	3.712	3.508	3.734	3.419 \pm 0.010
BDE(NH ⁺) ^a	4.727	4.540	4.710	4.523	4.730	4.477 \pm 0.008
BDE(NH ⁺) ^b	3.563	3.375	3.637	3.451	3.659	3.500 \pm 0.009
$\Delta H_{f,0}$ (H)	2.356	2.218	2.327	2.190	2.327	2.239 \pm 0.001
$\Delta H_{f,0}$ (H ⁺)	16.021	15.883	16.041	15.904	16.041	15.837 \pm 0.005
$\Delta H_{f,0}$ (N)	4.743	4.666	4.844	4.768	4.895	4.879 \pm 0.005
$\Delta H_{f,0}$ (N ⁺)	19.573	19.496	19.631	19.555	19.681	19.413 \pm 0.005
$\Delta H_{f,0}$ (NH)	3.408	3.397	3.458	3.450	3.487	3.699 \pm 0.006
$\Delta H_{f,0}$ (NH ⁺) \	17.202	17.174	17.247	17.221	17.276	17.175 \pm 0.006
DE	-0.097	-0.119	-0.077	-0.100	-0.075	0.071

^a BDE computed as the energy difference between NH⁺ and N⁺ + H

^b BDE computed as the energy difference between NH⁺ and N+H⁺; A = 6-31+G(*d,p*) basis set; B = with 6-31+G(*d,p*) basis set and zero-point energy correction; C = 6-311+G(2*d,2p*) basis set; D = 6-311+G(2*d,2p*) basis set and zero-point energy correction; E = 6-311+G(3*df,3pd*) basis set; $\Delta H_{f,0}$ (H⁺) = $\Delta H_{f,0}$ (H) + IP(H); $\Delta H_{f,0}$ (N⁺) = $\Delta H_{f,0}$ (N)+IP(N); $\Delta H_{f,0}$ (NH⁺) = $\Delta H_{f,0}$ (NH)+IP(NH)

obtained by Tarroni and coworkers [5]. Considering all the presented energies computed with the B3LYP/6-31+G(*d,p*) model, it is fair to say that this method should produce energies well in agreement with the experimental values.

The second hybrid DFT method B3P86 computes energies that deviate from the experimental results substantially more (Table 3). The majority of the computed energies are higher than the experimental values, although the $\Delta H_{f,0}$ for NH is more than 0.2 eV lower than the experimental value. Maximum deviation is observed for the NH IP. The computed value is more than 0.8 eV higher than the experimental value (Table 3). Although few of the computed energies are in close agreement with the experimental values such as the $\Delta H_{f,0}$ for N and the BDE for NH, overall this method performed poorly when compared to B3LYP.

The third hybrid DFT method tested was B3PW91. The computed energies (Table 4) are in much better agreement with the experimental values than ones obtained with the B3P86 method. In fact, the deviation from the experimental values is almost as small as for B3LYP computed energies (Table 2). Maximum deviation is again obtained for the IP of NH; it is 0.4 eV higher than the experimental value. Another interesting point is that B3PW91 finds the quartet electronic state for NH^+ to be lower in energy than the doublet electronic state of NH^+ (Table 4). The same results were obtained with B3P86 with a relatively small basis set such as 6-31+G(*d,p*). This was not true when the computational study was performed with a larger basis set. On the other hand, for B3PW91 this seems to be the effect of the method because the size of the basis set does not change the stability order. At present we do not have a plausible explanation for this result.

5 Conclusion

From the computational studies presented here one can conclude that the CBSQ is a highly reliable ab initio method for computing energies of small polar molecular systems. In many cases the computed energies of NH and NH^+ systems are almost identical to the experimental results. The G2 ab initio method is almost as reliable. The energies do not differ from the experimental data by more than 0.1 eV.

From the three DFT methods, the most reliable was B3LYP. The highest agreement was obtained with the 6-31+G(*d,p*) basis set which has a rather modest size. The majority of the computed energies are slightly higher than the experimental values but in the margin of 0.3 eV. The major deviation is for $\Delta H_{f,0}$ and IP of NH. Therefore, we recommend the use of CBSQ, G2, and B3LYP computational methods for evaluating energies of small polar molecular system. The deviation of B3P86 energies is too high and should be avoided as the method of choice for computing the energetics of these and similar molecular systems.

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