THE JOURNAL OF CHEMICAL PHYSICS **125**, 184514 (2006)

On theoretical predictions of noble-gas hydrides

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(Received 21 September 2006; accepted 5 October 2006; published online 14 November 2006)

We discuss the present status and reliability of theoretical predictions of noble-gas hydride molecules. It is shown that the single-reference MP2 calculations can produce a rather inaccurate energy diagram for the formation of noble-gas hydrides, and this may mislead the theoretical predictions. We suggest that the computational dissociation energy of the HY precursors should always be compared with the experimental values as a checkpoint for the computational accuracy. The computational inaccuracy probably explains why some compounds that are stable with the single-reference MP2 method ($HArC_4H$, $HArC_3N$, and HArCN) did not appear in matrix-isolation experiments, whereas the corresponding compounds with Kr and Xe are known. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2378624]

Noble-gas (Ng) hydride molecules have recently attracted substantial theoretical and experimental attention.[1] Twenty two molecules of this HNgY family have been reported experimentally to date including the first ground-state neutral chemical compound containing argon, HArF.[2–4] Most of the decisive experiments in this research field have been done in noble-gas matrices using IR absorption spectroscopy.[1] The synthesis consists of photodissociation of HY precursor in a Ng matrix and thermal mobilization of atoms (hydrogen in most cases).[5,6] The formation of HNgY molecules presumably occurs via the thermally activated H+Ng+Y reaction of the neutral fragments.[7] Thus, it is crucial for this method that HNgY is somewhat lower in energy than the H+Ng+Y reagents. This energy difference has been attributed as the first indication for a stable HNgY molecule and careful analysis of this energy diagram is of primary importance for the practical predictions of HNgY molecules. Here we present a short discussion of the present status and reliability of such theoretical predictions. This is important because the expansion of the HNgY family is challenging, especially for the lighter noble-gas atoms.

Many of the energetic and spectral calculations on HNgY molecules have been done with the single-reference MP2 method.[1] This method is a practical compromise over computational time and accuracy. More sophisticated computational approaches are rather complicated and time consuming for the noble-gas hydrides.[4] A few attempts to apply the density functional theory (DFT) method has emerged.[8] It is shown that the DFT and MP2 calculations yield spectral results close to each other for heavier noble-gas molecules in their equilibrium structure. On the other hand, the use of DFT has faced some criticism with respect to the lighter noble-gas species.[8] Moreover, calculations of the more weakly bound noble-gas hydrides should use large basis sets and state-of-the-art electron correlation methods to describe the molecular properties and to reproduce the experimental findings.[9]

Despite the fact that many of the theoretical predictions were experimentally realized, the widely applied MP2 method could in general be rather inaccurate with respect to the relative energies of the HNgY molecule and the H+Ng+Y reagents. Indeed, high-level *ab initio* methods are required to treat accurately open-shell species (such as C_3N and C_4H) appearing after dissociation of noble-gas hydrides.[10] In particular, the dissociation energy of HY precursors is usually overestimated with the MP2 method. This trend is demonstrated in Table I for a number of selected species. In some cases (H_2O, HF, and H_2C_2), the agreement with the experimental data is acceptable. However, the relative success is not general, and the computational H–C bond energy of H_2C_{2n} artificially increases quickly with n,[11–13] and the computational error exceeds 2 eV for H_2C_6. The increase of the electron correlation level and basis set representation in a balanced manner can improve the computed energy estimates, as it was shown for HF;[4] however, such extensive CCSD(T) calculations are less tempting for large H_2C_{2n}-type systems.

On the other hand, the DFT method often gives better estimates for the HY bond energy than the MP2 method, thus offering an attractive alternative to study large HNgY species. Even though there are no systematic studies on HNgY molecules employing various DFT functionals, the B3LYP functional used here appears to compete with MP2 for equilibrium structure properties and outdo MP2 when estimating the dissociation energy diagrams. This trend is most likely due to its better applicability when treating radicals and/or delocalized electron distributions, whereas the MP2 method is rather poor in these cases. For instance, the MP2 method overestimates the HC_3N dissociation energy by ~1.4 eV, whereas the B3LYP method gives a quite smaller mismatch of ~0.5 eV when compared with the experimental value. The corresponding MP2 error for HCN is ~1.2 eV and the result is better with the B3LYP method (error ~0.6 eV), even though the CCSD(T) value is somewhat more correct (error ~0.4 eV).[14] The B3LYP results for H_2C_4 and H_2C_6 are also quite good.

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TABLE I. Computational and experimental H–Y bond energies.

Molecule	D_0 (Theor., eV)	D_0 (Expt., eV)	Difference (eV)
HF	MP2: 6.13[a]	5.86[b]	0.27
	CCSD(T): 6.52[a]		0.66
	CCSD(T): 5.87[c]		0.01
H_2O	MP2: 5.43[e]	5.12[b]	0.31
	CCSD(T): 5.26[d]		0.14
HCN	MP2: 6.4[e]	5.2[b]	1.2
	CCSD(T): 5.6[f]		0.4
	B3LYP: 5.8[e]		0.6
H_2C_2	MP2: 5.96[g]	5.7[h]	0.26
	B3LYP: 6.08[e]		0.38
H_2C_4	MP2: 7.0[i]	5.6[h]	1.4
	B3LYP: 5.82[e]		0.22
H_2C_6	MP2: 7.66[i]	5.5[j]	2.16
	B3LYP: 5.62[e]		0.12
HC_3N	MP2: 7.1[k]	5.6[j]	1.5
	B3LYP: 6.17[e]		0.47

[a] From Ref. 21 using the 6-311++G(2*d*,2*p*) basis set. The same basis set is used in the computations of this table except Ref. 4.

[b] From Ref. 22.

[c] From Ref. 4 using the aug-cc-pVQZ basis set.

[d] From Ref. 23.

[e] The present work (Ref. 24). The calculations were done at the B3LYP/6-311++G(2*d*,2*p*) level of theory.

[f] From Ref. 14.

[g] From Ref. 11.

[h] From Ref. 25.

[i] From Ref. 13.

[j] Estimate.

[k] From Ref. 19.

Next we analyze the reliability of the theoretical energy diagram for the HNgY molecules. A clear complication of this analysis is the unknown computational error for the HNgY energy. As a measure of the energetic stability of HNgY with respect to the energy of the H+Ng+Y reagents, we use the fact of their formation in matrix-isolation experiments. We assume here that the possible barriers of the H+Ng+Y reaction are not of major importance, which is supported by the low-temperature formation of these molecules in Ne and Ar matrices.[15–17] Table II presents selected examples of observed and predicted HNgY molecules. In some cases such as $HArC_4H$, HArCN, and $HArC_3N$, the computationally (MP2) stable species did not form in the matrix-isolation experiments, even though extensive experimental work has been done.[12,18,19] In all these cases, the computational overestimate of the HY dissociation energy by the single-reference MP2 method is *larger* than the stability of HNgY with respect to the H+Ng+Y energy. This leads us to an empirical hypothesis that these HNgY molecules are, in fact, *higher* in energy than the corresponding H+Ng+Y fragments. In other cases (HKrF, HXeOH, HXeCN, etc.), the computationally stable molecules have been found experimentally. In contrast to the MP2 predictions, the B3LYP method suggests that $HArC_4H$, HArCN, and probably $HArC_3N$ should be higher in energy than the H+Ng+Y

TABLE II. Data on selected HNgY molecules. The dissociation energies $E(H+Ng+Y)-E(HNgY)$ are in eV. The D_0 overestimate from Table I (eV) is in brackets. The harmonic computational data for the H–Ng stretching frequencies are presented. The experimental H–Ng stretching frequency is in cm^{-1} in parentheses in the "Comment" column for the experimentally observed species. For the exact levels of theory, see the references.

Molecule	$E(H+Ng+Y)-E(HNgY)$	ν(H–Ng) (cm^{-1})	Comment
HArF	MP2: 0.07[a] [0.27]	2149[a]	Observed[c]
	CCSD(T) 0.51[a] [0.66]	1793[a]	(1970) (2016)
	CCSD(T) 0.15[b] [0.01]	2053[b]	
HKrF	MP2: 0.95[a] [0.27]	2316[a]	Observed[d]
	CCSD(T) 1.37[a] [0.66]	2174[a]	(1925) (1952)
HKrCCH	MP2: 0.7[e] [0.26]	1575[e]	Observed[e]
	B3LYP: 0.41[f] [0.38]	1592[f]	(1242)
HXeCCH	MP2: 1.46[g] [0.26]	1736[g]	Observed[h]
	B3LYP: 1.74[f] [0.38]	1721[f]	(1486)
$HArC_4H$	MP2: 0.45[i] [1.4]	1136[i]	Not observed[j]
	B3LYP: −0.49[f] [0.22]	1616[f]	
$HKrC_4H$	MP2: 1.3[j] [1.4]	1517[j]	Observed[j]
	B3LYP: 0.24[f] [0.22]	1670[f]	(1317)
$HXeC_4H$	MP2: 2.5[j] [1.4]	1759[j]	Observed[j]
	B3LYP: 1.56[f] [0.22]	1751[f]	(1545)
HArCN	MP2: 0.1[f] [1.2]	1680[f]	Not observed[f]
	B3LYP: −0.1[f] [0.6]	1667[f]	
HKrCN	MP2: 1.15[k] [1.2]	2011[k]	Observed[k]
	CCSD(T): 0.53[k] [0.4]	1781[k]	(1497)
	B3LYP: 0.60[f] [0.6]	1759[f]	
HXeCN	MP2: 2.15[k] [1.2]	1820[k]	Observed[k]
			(1624)
HXeOH	MP2: 0.7[f] [0.31]	1823[l]	Observed[l]
	CCSD(T): 0.6[l] [0.14]	1678[l]	(1578)
$HArC_6H$	MP2: 1.14[i] [2.15]	1227[i]	Improbable[f]
	B3LYP: −0.65[f] [0.12]	1646[f]	
$HArC_3N$	MP2: 0.68[m] [1.5]	1555[m]	Not observed[m]
	B3LYP: 0.05[f] [0.47]	1724[f]	
$HKrC_3N$	MP2: 1.51[m] [1.5]	1692[m]	Observed[m]
	B3LYP: 0.77[f] [0.47]	1784[f]	(1492)
$HXeC_3N$	MP2: 2.80[m] [1.5]	1777[m]	Observed[m]
	B3LYP: 2.05[f] [0.47]	1803[f]	(1625)

[a] From Ref. 21.

[b] From Ref. 4.

[c] From Refs. 2 and 3.

[d] From Ref. 20.

[e] From Ref. 26.

[f] This work (Ref. 24). The calculations were done at the MP2/6-311++G(2*d*,2*p*) and B3LYP/6-311++G(2*d*,2*p*) levels of theory.

[g] From Ref. 11.

[h] From Refs. 27 and 28.

[i] From Ref. 13.

[j] From Ref. 12.

[k] From Ref. 14.

[l] From Ref. 23.

[m] From Ref. 19.

fragments, which agrees with the experimental evidence. Based on this consideration, we do not expect that the computationally predicted $HArC_6H$ molecule (Ref. 13) can be prepared with the conventional matrix-isolation method. We suggest that the prediction of noble-gas hydrides in problematic cases should involve a complementary study with the DFT method if high-level *ab initio* approaches cannot be used. Without doubt, the high-level *ab initio* studies can produce the most reliable information on the molecular properties. In any case, the computational dissociation energy of HY precursors should always be compared with the experimental values as an important checkpoint for the computational accuracy (see Table I).

The infrared absorption spectrum is an excellent tool for identification of the HNgY molecules.[1] Table II demonstrates that the *ab initio* predictions of the characteristic H–Ng stretching frequency can be somewhat closer to the experimental values than the B3LYP values. However, the vibrational spectra provided by these methods are quite similar for the most stable species as pointed out previously.[8] It seems that the computation of vibrational spectra is not the major complication in practical work with the HNgY molecules. These molecules can be reliably identified based on their intense H–Ng stretching absorption even though some specific problems can arise from matrix-site structure[3,20] and isomerization.[19]

In conclusion, the single-reference MP2 calculations can produce a rather inaccurate energy diagram for the formation of noble-gas hydrides, and this may mislead the theoretical predictions. This is especially important for the present search for additional Ar compounds and possible He and Ne compounds. The computational inaccuracy explains why some compounds that were stable with the single-reference MP2 method do not appear in matrix-isolation experiments [$HArC_4H$ (Ref. 13), $HArC_3N$ (Ref. 19), and HArCN (this work)], whereas the corresponding compounds with Kr and Xe are known. The $HArC_6H$ molecule predicted by Sheng and Gerber[13] is also improbable by the conventional preparation method. Among these, $HArC_3N$ has been the most probable candidate for the experimental observation of the second Ar molecule. The energetic stabilization of $HNgC_{2n}H$ molecules for larger n suggested in Ref. 12 is also questionable. The justification of these conclusions needs extensive theoretical work based on high-level multireference *ab initio* computational methods, which clearly exceeds the framework of the present discussion. Up to date, the calculations dealing with the energetic properties of HNgY molecules have relied on rather economical approaches, but clearly more thorough theoretical treatments should be employed if new, especially weakly bound and large, noble-gas species are to be investigated.

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