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On the stability of noble gas molecules

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Abstract

We have tested the MP2 and CCSD(T) theory with various basis sets on the reaction energies and barrier heights of the two dissociation channels for the noble gas (Ng) molecules of the type XNgY: (a) XNgY → X + Ng + Y, and (b) XNgY → Ng + XY. We demonstrated that the MP2 method systematically overestimates the bond energies of XNgY molecules. We also obtained the theoretical half-lives of HArF and HCCArF as a function of temperature and energy barriers by calculating the unimolecular thermal rate constants of the two dissociation channels.
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1. Introduction

The interest in studying the noble gas molecules seem to have been revived after the discovery that the noble gas can act as ligands to transition metals and the discovery of the first neutral argon-containing molecule [1–5]. Most of the noble gas molecules studied to date are meta-stable species, and were observed only at cryogenic conditions in noble gas matrixes [2,6]. Theoretical calculation plays a very important role in studying simple noble gas molecules because the fingerprint IR peaks can be readily calculated and compared with experimental data. Furthermore, the stability of the observed noble gas molecules can be justified by high-level electronic structure calculation. More importantly, new stable noble gas molecules can be predicted theoretically, and thus the computational work can guide future synthesis effort. Recently, a few new noble gas molecules or ions have been predicted to be meta-stable, and some of them have been confirmed experimentally [7–16].

In this Letter we wish to address the issues regarding (1) the appropriate theoretical methods and (2) the energetic criteria for predicting the stability of noble gas molecules. For the first issue, we tested the MP2 theory against the

CCSD(T) theory with various basis sets on the reaction energetics of the two dissociation channels (a) XNgY → X + Ng + Y, and (b) XNgY → Ng + XY for five recently studied neutral noble gas molecules [3,4,7,8,10,14] where X and Y are atoms or functional groups, and Ng is the noble gas atom Ar or Kr. We wish to demonstrate that while the MP2 method is quite successful for studying channel (b), it systematically overestimates the bond energies of XNgY molecules, and it is thus unreliable for studying channel (a). For the second issue, we obtained the theoretical half-lives of HArF and HCCArF as a function of temperature and energy barriers by calculating the unimolecular thermal rate constants of the two dissociation channels. The HArF and HCCArF were chosen to model systems in which the tunneling effects are and are not important, respectively. Since channel (b) is highly exoergic, the XNgY molecules can only be meta-stable at best. From the experimental point of view the stability of these XNgY molecules in the noble gas matrixes is not only determined by the unimolecular dissociation rates, but also on the cage effects and the presence of other reactive species in the matrixes [3,4,17,18]. It has been speculated that some of the noble gas molecules can also exist in the gas phase [6,17] where many more interesting chemical studies can be carried out. Here we wish to quantitatively define the 'meta-stability' of the XNgY molecules in the gas phase in terms of the energy barriers and temperature.

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2. Method

The geometries of HArF, OBArF, HCCArF, HC$_4$ArH, HKrCCH, their dissociation products by the two channels, and the transition states for channel (b) were calculated at MP2 theory with the aug-cc-pVDZ basis set. The geometries for HArF, OBArF, HCCArF, and HKrCCH were also calculated at CCSD(T)/aug-cc-pVDZ, MP2/aug-cc-pVTZ and CCSD(T)/aug-cc-pVTZ levels, and are consistent with available results from earlier studies [8,17,19]. Single-point energy calculation at CCSD(T) theory with aug-cc-pVDZ and aug-cc-pVTZ basis sets were performed on the geometries calculated only at lower-level theory. Additionally, for HArF and OBArF the geometries was calculated at MP2/aug-cc-pVQZ level, and single-point energy calculation at CCSD(T)/aug-cc-pVQZ level was performed on CCSD(T)/aug-cc-pVTZ geometries.

We made dual-level transition state theory calculation [20,21] on the unimolecular rate constants of the HArF and HCCArF through the two dissociation channels. The tunneling effects were considered for the former system by the small-curvature tunneling (SCT) method [22] since it involves significant hydrogen motions. The classical barrier heights were input as parameters. The energies of reactions were obtained from the CCSD(T)/aug-cc-pVQZ calculation. The transition states and the reaction paths (for the HArF system) were calculated using MPW1PW91/aug-cc-pVTZ and MP2/aug-cc-pVTZ [19,23] methods for channels (a) and (b), respectively. The MPW1PW91 functional was chosen because it was found to predict very reasonable reaction energetics and stationary point geometries. It is understood that the calculated reaction path for channel (a) is subjected to more uncertainty as mentioned earlier. However, the DFT methods suffer less from the spin-contamination, and the barrier heights, which are the most sensitive data in the rate constant calculation, are input as parameters. Thus we believe we can estimate the rate constants very close to the correct order of magnitude.

3. Results and discussion

Table 1 lists the calculated energies of reactions and barrier heights for the two dissociation channels. The energies of reactions for HArF agree very well with the previous study by Runeberg et al. [17]. As shown in the table, the calculated energies are very different by the MP2 and CCSD(T) theory for channel (a). The MP2 theory predicts significantly higher X–Ng and Ng–Y bond energies than the CCSD(T) theory; and the differences are more significant in larger systems. For example, with the aug-cc-pVTZ basis set the differences are 4 and 9 kcal/mol for HArF and OBArF, respectively, and are 21, 15, and 13 kcal/mol for HCCArF, HArC$_4$H, and HKrCCH, respectively. Since the energy of reaction of channel (a) is often used to judge the stability of the XNgY molecules, the results obtained by the MP2 theory should be taken with caution [7,15].

Table 1
Calculated energies[a] of reactions and barrier heights (kcal/mol)

	XNgY → X + Ng + Y	XNgY → Ng + XY	
	Erxn	Barrier	Erxn
HArF			
Aug-cc-pVDZ	2.1 (0.7)	23.1 (21.8)	−136.5 (−137.8)
Aug-cc-pVTZ	5.4 (9.7)	23.7 (23.0)	−133.9 (−134.0)
Aug-cc-pVQZ	7.4[b](12.5)	24.4[b](23.9)	−133.5[b](−133.0)
OBArF			
Aug-cc-pVDZ	−6.6 (0.8)	18.2 (17.0)	−156.0 (−157.0)
Aug-cc-pVTZ	0.8 (9.8)	18.3 (17.5)	−158.8 (−158.1)
Aug-cc-pVQZ	3.0[b](12.8)	18.7[b](18.1)	−158.6[b](−157.1)
HCCArF			
Aug-cc-pVDZ	−4.8 (15.2)	35.3[c](33.8)	−127.2 (−127.3)
Aug-cc-pVTZ	3.4 (24.4)	33.8[c](33.7)	−126.6 (−124.8)
HArC$_4$H			
Aug-cc-pVDZ	−8.9[c](3.8)	25.4[c](23.2)	−148.0[c](−151.6)
Aug-cc-pVTZ	−5.9[c](9.4)[c]	26.4[c](25.1)[c]	−146.9[c](−148.7)[c]
HKrCCH			
Aug-cc-pVDZ	3.6 (12.8)	38.6 (37.4)	−130.2 (−133.2)
Aug-cc-pVTZ	9.7 (22.3)	39.3[d](41.7)	−129.0 (−127.5)

[a] CCSD(T) and MP2 (in parentheses) energies (Born–Oppenheimer energies, not including vibrational zero-point energies).
[b] Single-point energy at CCSD(T)/aug-cc-pVTZ structure.
[c] Single-point energy at MP2/aug-cc-pVDZ structure.
[d] Single-point energy at CCSD(T)/aug-cc-pVDZ structure.

That is, the MP2 theory seems to significantly overestimate the bond energies in larger systems. For example, HArC$_4$H was recently predicted to be stable at MP2 = full/6-311++G(2d,2p) level with an energy of reaction of 10.4 kcal/mol for channel (a) [7]. However, the current result shows that at CCSD(T)/aug-cc-pVTZ level the energy of reaction is −5.9 kcal/mol. This does not rule out the possibility of its experimental identification in the argon matrix, however, HArC$_4$H is apparently much less stable than previously thought.

Of course, kinetic stability is determined by the energy barrier instead of the energy of reaction which is only the lower limit for the barrier height of an endoergic reaction. The barrier heights for channel (a) are very difficult to determine due to the multi-configurational characters of the structures on the reaction path [23,24]. Single-configurational methods may also suffer from significant spin contamination. Full-valence active space multi-configurational calculation with large basis sets for systems with three or more heavy atoms is currently impractical. Furthermore, methods incorporating high-level dynamic correlation seem necessary to obtain accurate energies. There have been some efforts to calculate the barrier heights for channel (a) [8,10,23,24], however, these values might still be subjected to large uncertainties. Thus we decided not to use the barrier heights of channel (a) in our test. Table 1 also shows that the sizes of the basis sets may have important effects on the energies of channel (a), especially for systems containing fluorine. For example, in HCCArF system, the CCSD(T) energy of reaction is raised by 8 kcal/mol, from

aug-cc-pVDZ to aug-cc-pVTZ basis sets. From the CCSD(T)/aug-cc-pVQZ calculation on HArF and OBArF systems the basis-set convergence on the relative energies by CCSD(T)/aug-cc-pVTZ is probably on the order of 2 kcal/mol for channel (a). Table 1 also shows that all the energies for channel (b) are well predicted by the MP2 method, and the sizes of the basis sets have smaller effects.

The discussion above demonstrated that higher-level electron correlation and large basis sets are needed to predict the meta-stability of the noble gas containing molecules XNgY. However, what are the quantitative criteria for the meta-stability? More specifically, what are the minimum barrier heights for the noble gas containing molecule to be meta-stable in the gas phase? The calculated half-lives, $t_{1/2} = \ln 2/k(T)$, where $k(T)$ is the calculated rate constant at temperature T, are plotted as a function of barrier heights and temperature in Figs. 1 and 2 for HArF and HCCArF systems, respectively. For example, Fig. 1 shows that for an HNgY system, in order to have a half-life of $\sim 10^2$ seconds for spectroscopic study in the gas phase at 100, 200, and 300 K, channel (a) must have barriers of 13, 19, and 26 kcal/mol, respectively; and channel (b) must have barriers of 8, 16, and 23 kcal/mol, respectively. Similarly, Fig. 2 shows that for an XNgY system (X, Y are not hydrogen), channel (a) must have barriers of 9, 17, and 25 kcal/mol, respectively, and channel (b) must have barriers of 6, 13, and 21 kcal/mol, respectively. This is compared to the estimated barrier heights of HArF: 12–16 kcal/mol for channels (a) and ~ 24 kcal/mol for channel (b) [19,23]. From the above discussion, HArF is predicted to be stable
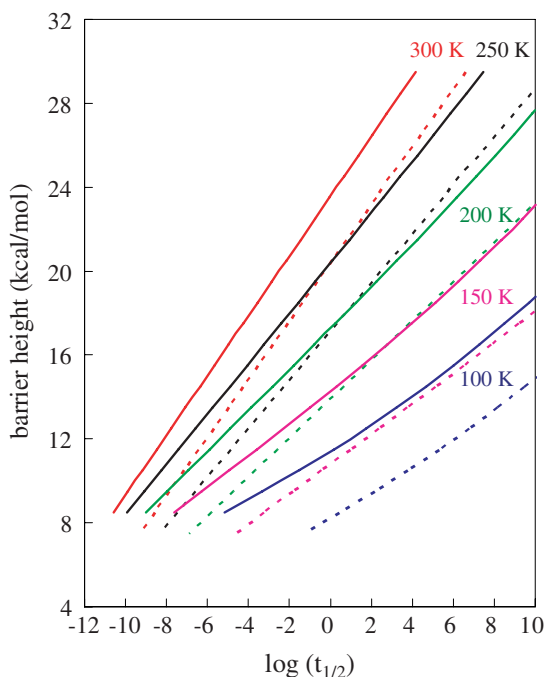
in the gas phase up to ~ 100 K. Similarly, the barrier heights of HKrF were estimated 26–30 kcal/mol for channels (a) and ~ 32 kcal/mol for channel (b), and it is predicted to be stable in the gas phase up to ~ 300 K.

It is noted that since these noble gas molecules mentioned above are only meta-stable at best, they will be destroyed easily by reactive species in the matrix or in the gas phase. However, this effect is difficult to quantify since it depends on the nature and concentration of the reactive species. Thus, the above discussion applies only to environment where no other reactive species are present.
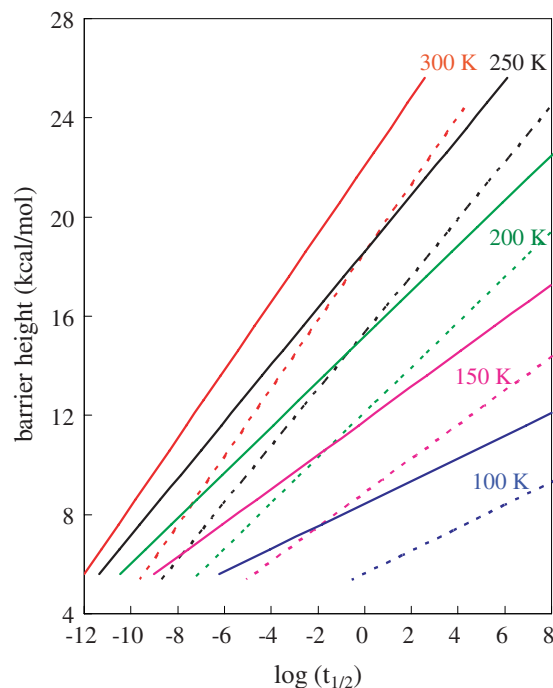
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Fig. 2. The calculated half-lives as a function of barrier heights and temperature for $HCCArF \rightarrow HCC + Ar + F$ (solid lines) and $HCCArF \rightarrow Ar + HCCF$ (dashed lines).

Fig. 1. The calculated half-lives as a function of barrier heights and temperature for $HArF \rightarrow H + Ar + F$ (solid lines) and $HArF \rightarrow Ar + HF$ (dashed lines).

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