After the Electronic Field: Structure, Bonding, and the First Hyperpolarizability of HArF


In this work, we add different strength of external electric field ($E_{\text{ext}}$) along molecule axis (Z-axis) to investigate the electric field induced effect on HArF structure. The H-Ar bond is the shortest at $E_{\text{ext}} = -189 \times 10^{-4}$ and the Ar-F bond show shortest value at $E_{\text{ext}} = -185 \times 10^{-4}$ au. Furthermore, the wiberg bond index analyses show that with the variation of HArF structure, the covalent bond H-Ar shows downtrend (ranging from 0.79 to 0.69) and ionic bond Ar-F shows uptrend (ranging from 0.04 to 0.17). Interestingly, the natural bond orbital analyses show that the charges of F atom range from -0.961 to -0.771 and the charges of H atoms range from 0.402 to 0.246. Due to weakened charge transfer, the first hyperpolarizability ($\beta_{\text{tot}}$) can be modulated from 4078 to 1087 au. On the other hand, make our results more useful to experimentalists, the frequency-dependent first hyperpolarizabilities were investigated by the coupled perturbed Hartree-Fork method. We hope that this work may offer a new idea for application of noble-gas hydrides. © 2013 Wiley Periodicals, Inc.

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Introduction

The past decades have witnessed progress in the design and synthesis of neutral ground-state species containing chemically bound noble-gas (Ng) atoms.[1–11] Among these investigations, scientists show great interest in noble-gas hydrides, HNgY, where Ng accounts for noble-gas and Y corresponds to an electronegative atom or group. These interesting HNgY molecules can be viewed as containing Ng-Y ionic bonds and covalent H–Ng bonds. They can be noted as in the form (H-Ng)+Y− where (H-Ng)+ is mainly covalent, while the interaction between (H-Ng)+ and Y− is prevalently ionic.[3] Because of positive charges on Ng and H, and large negative charge on Y, the stabilization of HNgY can be rationalized in terms of the strong coulomb attraction between (H-Ng)+ and Y−.[6] In addition, these molecules are fascinating for their relatively weak bondings and large dipole moments, which lead to strongly enhanced effects of the environment, complexation and reactions.[3]

The most typical HNgY molecule is HArF which arouses increasing attention among scientists in many fields. For example, Khrachtchev and coworkers[12] reported that the photolysis of hydrogen fluoride in a solid argon matrix leads to the formation of HArF which is the first chemically bonded neutral argon compound. And then, McDowell and coworkers[13] demonstrated computationally that HArF–CO and HArF–N2 show an interesting blue-shift of the H–Ar stretching frequency. This blue-shift is unusual as hydrogen bonding normally causing a red-shift of the covalent H–Ar vibrational stretching frequency. Furthermore, noble-gas hydrides are important candidates for the nonlinear optical (NLO) materials.[14–17] For example, the first hyperpolarizability of HArF has already been investigated by Avramopoulos.[16] According to their investigation, HArF has a very large first hyperpolarizability along the dipole direction (z axis) due to the difference in the electronic structure between the ground and the first excited state. Deserving attention, electron transfer from the closed-shell Ar atom to electronegative F in HArF molecule has been demonstrated. There is any effective methods to modulate the interesting electron transfer?

On the other hand, the external electric field effect is widely applied to modulate and control the electronic properties of materials, such as, organic conductors[18], hydrogen bonding complexes,[19] nanotubes,[20,21] and graphene.[22–24] It is worth mentioning that electric field is tunable and might provide different degrees of stimuli for charge transfer. Inspired by the above discussions, external electric field ($E_{\text{ext}}$) is applied in HArF molecule in this work. Our results show that the $E_{\text{ext}}$ dramatically influences the bond lengths (H–Ar and Ar–F) in HArF. Furthermore, the natural bond orbital (NBO) and the detailed fragment contributions analyses to the highest occupied molecular orbital (HOMO) show that there exists obvious charge transfer in HArF. As a result of this interesting charge transfer,
the first hyperpolarizability ($\beta_{\text{tot}}$) ranges from 4078 to 1087 au, in which the effect of electric field like $\beta_{\text{tot}}$ regulator that can module the $\beta_{\text{tot}}$ values by controlling HArF structures. It is our hope that our work may provide a new idea for application of noble-gas hydrides.

Methods

The optimized geometric structures of HArF with all real frequencies in external electric field (from $-276 \times 10^{-4}$ to $257 \times 10^{-4}$ au) were obtained at MP2/aug-cc-pVTZ level. In Supporting Information (Supporting Information Table S1), we can find that the bond lengths obtained at MP2/aug-cc-pVTZ level are very similar to the result obtained at QCISD/aug-cc-pVQZ level. The NBO[25,26] and wiberg bond index[27] (WBI) analyses at the MP2/aug-cc-pVTZ level were performed to provide insight into the bonding nature of H-Ar and Ar-F. The topological properties of the electron density distribution were studied by atoms in molecules (AIM)[28] theory at the MP2/aug-cc-pVTZ level. In this work, the first hyperpolarizabilities were evaluated by a finite-field approach at the MP2 level. In our previous articles, the MP2 method has been chosen for calculating the first hyperpolarizability (6). This is because, with reasonable computation costs, the MP2 results are also very close to those obtained from the more sophisticated correlation methods (for example, the QCISD[34]). The magnitude of the applied electric field was chosen as 0.001 au for the calculation of the hyperpolarizability, which is proven to be the most adequate value for the numerical differentiations[29–32,34]. As shown in Supporting Information (Supporting Information Table S2), MP2 is suitable for the system.

The static first hyperpolarizability was obtained as

$$\beta_{\text{tot}} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$  \hspace{1cm} (1)

Where

$$\beta_i = \beta_{ii} + \beta_{ij} + \beta_{ik}, i, j, k = x, y, z$$  \hspace{1cm} (2)

Furthermore, frequency dependent NLO properties were evaluated by the Coupled Perturbed Hartree-Fork (CPHF) method. The frequency dependent $\beta$ was noted as:

$$\beta(\omega) = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$  \hspace{1cm} (3)

Where,

$$\beta_i = \beta_{ii}(-2\omega; \omega, \omega) + \beta_{ij}(-2\omega; \omega, \omega) + \beta_{ik}(-2\omega; \omega, \omega)$$  \hspace{1cm} (4)

for the second harmonic generation values and

$$\beta_i = \beta_{ii}(-\omega; \omega, 0) + \beta_{ij}(-\omega; \omega, 0) + \beta_{ik}(-\omega; \omega, 0)$$  \hspace{1cm} (5)

for the electro-optical Pockels effect values.

In addition, the MP2 frequency dependent values were estimated using the multiplicative approximation[35,36].

$$\beta(\omega)_{\text{MP2}} \approx \beta(\omega)_{\text{HF}} \beta_{\text{tot}}^{\text{MP2}} / \beta_{\text{tot}}^{\text{HF}}$$  \hspace{1cm} (6)

All of the calculations were performed with Gaussian 09W software package[37]

Result and Discussion

Structures after external field

The optimized geometric structures of HArF with all real frequencies in external electric field (from $-276 \times 10^{-4}$ to $257 \times 10^{-4}$ au) were obtained at MP2/aug-cc-pVTZ level and the important geometrical parameters are collected in Table 1. From Table 1 and Figure 1, it is obvious that the H-Ar length shows a shortest value (1.290) at $E_{\text{ext}} = 189 \times 10^{-4}$ au, which is decreased by 0.030 Å compared with 1.320 Å in no electric field. Interestingly, Ar-F length shows a shortest value (1.881) at $E_{\text{ext}} = 185 \times 10^{-4}$ au which is sharply decreased by 0.102 Å compared with 1.983 Å obtained in the absence of any external field (see in Fig. 2). The discussion of frequencies is in Supporting Information Table S3. The selection of the shortest H-Ar and Ar-F length is also provided in Supporting Information Table S4. Furthermore, the HArF

<table>
<thead>
<tr>
<th>$E_{\text{ext}} \times 10^{-4}$ au</th>
<th>$r_{\text{H-Ar}}$ (Å)</th>
<th>$r_{\text{Ar-F}}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-276$</td>
<td>1.297</td>
<td>2.637</td>
</tr>
<tr>
<td>$-250$</td>
<td>1.293</td>
<td>2.402</td>
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<td>1.291</td>
<td>2.254</td>
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<td>$-189$</td>
<td>1.290</td>
<td>2.231</td>
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<tr>
<td>$-150$</td>
<td>1.292</td>
<td>2.161</td>
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<td>2.090</td>
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<td>1.881</td>
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<tr>
<td>$200$</td>
<td>1.481</td>
<td>1.882</td>
</tr>
<tr>
<td>$250$</td>
<td>1.591</td>
<td>1.922</td>
</tr>
<tr>
<td>$257$</td>
<td>1.616</td>
<td>1.940</td>
</tr>
</tbody>
</table>

![Figure 1](image-url)
molecules in a series of external electric fields are all linear molecules.

How do these HArF structures affect their chemical bond and NLO properties?

The chemical bonding in the HArF

At present, the Laplacian of the electron density of the bond critical points (BCP) was used to differentiate the types of chemical bonds.\[38–40\] For ionic bond, hydrogen bonds, and van der Waals interactions, the Laplacian of the electron density $\nabla^2 \rho(r)$ is positive, while the $\nabla^2 \rho(r)$ is negative for covalent bond. The $\nabla^2 \rho(r)$ value of hydrogen bond lies in the proposed range of 0.014–0.139 au. For the HArF structures, the $\nabla^2 \rho(r)$ values of BCPs are calculated using the AIM theory at the MP2/aug-cc-pVTZ level and the result are listed in Table 2. The results show that the $\nabla^2 \rho(r)$ values for H-Ar range from −0.13 to −0.90 au indicating that there are mainly covalent bonds between the H atoms and the Ar atoms. On the other hand, the $\nabla^2 \rho(r)$ values for Ar-F are all positive indicating that they may be ionic bonds. Interestingly, when the $E_{\text{ext}} = -276 \times 10^{-4}$ au, the $\nabla^2 \rho(r)$ value of Ar-F is 0.07 au which is very similar to the value of hydrogen bond.

According to the bonding motif found by Last and George, an electron transfers from the closed-shell Ar atom to electronegative F atom and the outer electronic shell of Ar$^+$ is an open one, with an unpaired electron in a p-type orbital that forms a strong $\Sigma$ bond with the unpaired s electron of the H atom.\[41\] As a result of this bonding motif, there is strong (HAr)$^+$F$^-$ charge transfer in the HArF electronic structure. And the stabilization of HArF could be rationalized in terms of the strong Coulomb attraction between HAr$^+$ and F$^-$. The NBO calculations (in Table 2) show that, for HArF structure ($E_{\text{ext}} = 0$ au), the positive charge locates at H (0.28) and Ar (0.58) and the negative charge on F (0.86). At the same time, it is evident that the WBI of H-Ar bond (0.79) is very close to 0.796 of H-Xe bond in HXeCCH,\[5\] which shows that H-Ar bond in HArF is mainly covalent bond. On the other hand, the WBI of Ar-F bond is 0.14, which indicates that Ar-F bond in HArF may prevailingly be ionic bond.

For HArF structures, the WBI of H-Ar (in Fig. 3) is in good agreement with the H-Ar length which indicates that the

![Figure 2. The trend of Ar-F length with the electric field $\times 10^{-4}$ (−276 to 257 au).](image)

![Figure 3. The WBI of H-Ar and Ar-F in HArF.](image)

Table 2. NBO charge $q$ and WBI. The Laplacian of the electron density ($\nabla^2 \rho$) of the BCPs.

<table>
<thead>
<tr>
<th>$E_{\text{ext}} \times 10^{-4}$ au</th>
<th>$q$(H)</th>
<th>$q$(Ar)</th>
<th>$q$(F)</th>
<th>WBI(H-Ar)</th>
<th>WBI(Ar-F)</th>
<th>$\nabla^2 \rho$(H-Ar)</th>
<th>$\nabla^2 \rho$(Ar-F)</th>
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<tr>
<td>−276</td>
<td>0.402</td>
<td>0.559</td>
<td>−0.961</td>
<td>0.79</td>
<td>0.04</td>
<td>−0.90</td>
<td>0.07</td>
</tr>
<tr>
<td>−250</td>
<td>0.369</td>
<td>0.572</td>
<td>−0.941</td>
<td>0.80</td>
<td>0.06</td>
<td>−0.87</td>
<td>0.14</td>
</tr>
<tr>
<td>−200</td>
<td>0.342</td>
<td>0.582</td>
<td>−0.924</td>
<td>0.80</td>
<td>0.08</td>
<td>−0.85</td>
<td>0.20</td>
</tr>
<tr>
<td>−189</td>
<td>0.337</td>
<td>0.584</td>
<td>−0.921</td>
<td>0.80</td>
<td>0.08</td>
<td>−0.84</td>
<td>0.21</td>
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<tr>
<td>−150</td>
<td>0.330</td>
<td>0.574</td>
<td>−0.904</td>
<td>0.79</td>
<td>0.09</td>
<td>−0.82</td>
<td>0.24</td>
</tr>
<tr>
<td>−100</td>
<td>0.312</td>
<td>0.577</td>
<td>−0.889</td>
<td>0.79</td>
<td>0.11</td>
<td>−0.78</td>
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<tr>
<td>−50</td>
<td>0.296</td>
<td>0.579</td>
<td>−0.874</td>
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<tr>
<td>0</td>
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<td>0.580</td>
<td>−0.859</td>
<td>0.79</td>
<td>0.14</td>
<td>−0.67</td>
<td>0.34</td>
</tr>
<tr>
<td>50</td>
<td>0.264</td>
<td>0.579</td>
<td>−0.843</td>
<td>0.78</td>
<td>0.15</td>
<td>−0.59</td>
<td>0.36</td>
</tr>
<tr>
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<td>0.250</td>
<td>0.576</td>
<td>−0.826</td>
<td>0.77</td>
<td>0.17</td>
<td>−0.50</td>
<td>0.37</td>
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<tr>
<td>150</td>
<td>0.238</td>
<td>0.570</td>
<td>−0.808</td>
<td>0.76</td>
<td>0.18</td>
<td>−0.39</td>
<td>0.38</td>
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<tr>
<td>185</td>
<td>0.233</td>
<td>0.562</td>
<td>−0.794</td>
<td>0.75</td>
<td>0.19</td>
<td>−0.31</td>
<td>0.38</td>
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<tr>
<td>200</td>
<td>0.232</td>
<td>0.557</td>
<td>−0.789</td>
<td>0.74</td>
<td>0.19</td>
<td>−0.28</td>
<td>0.37</td>
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<tr>
<td>250</td>
<td>0.238</td>
<td>0.534</td>
<td>−0.772</td>
<td>0.70</td>
<td>0.17</td>
<td>−0.15</td>
<td>0.35</td>
</tr>
<tr>
<td>257</td>
<td>0.246</td>
<td>0.525</td>
<td>−0.771</td>
<td>0.69</td>
<td>0.17</td>
<td>−0.13</td>
<td>0.34</td>
</tr>
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</table>
shortened H-Ar length strengthens the H-Ar bond. At the same time, the elongated H-Ar length weakens H-Ar bond. Similarly, the WBI of Ar-F is in consistent with the Ar-F length. Obviously, the bonds of H-Ar and Ar-F in HArF change: WBI of H-Ar ranges from 0.79 to 0.525 and WBI of Ar-F ranges from 0.04 to 0.17. The results of WBI values show that H-Ar bond in HArF may prevailingly be ionic bond.

For the NBO calculations in Figure 4 and Table 2, partial positive charges on Ar make little difference which range from 0.525 to 0.580. Interestingly, the negative charge on F monotonously decrease from 0.961 ($E_{\text{ext}} = -276 \times 10^{-4}$) to 0.771 ($E_{\text{ext}} = 257 \times 10^{-4}$ au) which indicates that the electron transfer in our study can be successfully modulated by controlling HArF structures. Significantly, the partial positive charges on H show very special trend which sharply decrease from 0.402 ($E_{\text{ext}} = -276 \times 10^{-4}$) to 0.232 ($E_{\text{ext}} = 200 \times 10^{-4}$) and then slightly increase to 0.246 ($E_{\text{ext}} = 257 \times 10^{-4}$ au). Furthermore, from the detailed fragment contributions to the frontier molecular orbitals of the HArF analyzed with AOMix program[42,43] (in Supporting Information Table S5 and Figure 5), we can find that main contribution to the HOMO comes from F atom. Also, the main contribution to lowest unoccupied molecular orbital (LUMO) is from H atom. Thus, the direction of electron transfer is from F atom to H atom. Can this interesting electron transfer lead to fascinating variation of $\beta_{\text{tot}}$ values?

**NLO property**

From Table 3, it can be obviously found that the major contribution to the $\beta_{\text{tot}}$ values of HArF is $\beta_\parallel$. When the $E_{\text{ext}}$ decrease from $-276 \times 10^{-4}$ to $200 \times 10^{-4}$ au, the $\beta_{\text{tot}}$ values show a sharply downward trend which decrease from 4078 to 1053 au. Interestingly, when the $E_{\text{ext}}$ further increase to $257 \times 10^{-4}$ au, the $\beta_{\text{tot}}$ values show a slight upward trend which increase to 1087 au. This interesting variation of the $\beta_{\text{tot}}$ values is in line with the trend of the partial positive charges on H.

According to the bonding motif found by Last and George, when $E_{\text{ext}}$ along negative direction of Z-axis is introduced into the HArF system (ranges from 0 to $-276 \times 10^{-4}$ au) which is beneficial for electron transfers from the closed-shell Ar atom to electronegative F atom. As a result, $\beta_{\text{tot}}$ values increase from 1233 to 4078 au. However, when $E_{\text{ext}}$ along positive direction of Z-axis affect the HArF system (ranges from 0 to $257 \times 10^{-4}$ au), electron transfer is impeded and $\beta_{\text{tot}}$ values range from 1053 to 1233 au. Investigating further, we focus on the values of electronic spatial extent $<R^2>$.

Shen et al.[44] and Baert and coworker[45] pointed out that the electron density character is related to the electric property of molecule. The electronic spatial extent $<R^2>$ is a physical property which characterizes the electron density volume around the molecule.[46] To the best of our knowledge, NLO effect naturally reflects molecular electronic polarized characteristics and the polarization reflects the molecular electron cloud deformation behavior. Thus, $<R^2>$ may help us understand the hyperpolarizability. Furthermore, it has been demonstrated that $<R^2>$ has a great relationship with the first hyperpolarizability.$[31]$ The greater $<R^2>$ value may lead to the larger first hyperpolarizability. From Figure 6 and Table 3, we

**Table 3.** The first hyperpolarizabilities and $<R^2>$ of HArF structures at different $E_{\text{ext}}$ calculated at MP2/ aug-cc-pVTZ level.

<table>
<thead>
<tr>
<th>$E_{\text{ext}} \times 10^{-4}$ au</th>
<th>$-276$</th>
<th>$-250$</th>
<th>$-200$</th>
<th>$-189$</th>
<th>$-150$</th>
<th>$-100$</th>
<th>$-50$</th>
<th>$50$</th>
<th>$100$</th>
<th>$150$</th>
<th>$185$</th>
<th>$200$</th>
<th>$250$</th>
<th>$257$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_\parallel$ (a.u.)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\beta_\perp$ (a.u.)</td>
<td>0</td>
<td>0</td>
<td>1</td>
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<td>0</td>
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<tr>
<td>$\beta_{\text{tot}}$ (a.u.)</td>
<td>4078</td>
<td>2796</td>
<td>2118</td>
<td>2016</td>
<td>1752</td>
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<td>$&lt;R^2&gt;$ (a.u.)</td>
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<td>132</td>
<td>131</td>
<td>132</td>
<td>137</td>
<td>139</td>
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</table>
can find that the $<R^2>$ values are almost in consistent with the $\beta_{\text{tot}}$ values.

To make our results more useful to experimentalists, the frequency-dependent first hyperpolarizabilities are investigated by using CPHF method. The results show that the $\beta(\omega)$ values of HArF molecules are all larger than the corresponding static $\beta_{\text{tot}}$ values and show the same trend as the values of $\beta_{\text{tot}}$ for the HArF molecules. What is more, the values of $\beta(\omega)$ of HArF show shortest value at $E_{\text{ext}}$ and $E_{\text{tot}}$ values.

**Conclusions**

In this work, we put forward a physical method of external electric field ($E_{\text{ext}}$) to investigate HArF molecule. Interestingly, the H-Ar bond is the shortest at $E_{\text{ext}} = -189 \times 10^{-4}$ and the Ar-F bond show shortest value at $E_{\text{ext}} = -185 \times 10^{-4}$ au. AIM analysis suggests that H-Ar bond exhibits mainly a covalent bond character and Ar-F bonds show a mainly ionic bond character. The WBI analyses show that with the variation of HArF structure, the covalent bond H-Ar shows slightly downtrend (ranging from 0.79 to 0.69) and ionic bond Ar-F shows uptrend (ranging from 0.04 to 0.17). The NBO analysis shows electron transfer of HArF can be successfully modulated by controlling the HArF structure. Furthermore, the detailed fragment contributions to the frontier molecular orbitals of HArF analyzed by AOMix program clearly show the direction of electron transfer from F atom to H atom. As a result of this electron transfer, the $\beta_{\text{tot}}$ values range from 4078 to 1087 au and the first hyperpolarizability can be modulated by controlling HArF structure. In order to give more useful information to experimentalists, the frequency-dependent first hyperpolarizabilities are investigated using CPHF method. The results show that the $\beta(\omega)$ and $\beta(0)$ values are larger than the corresponding static $\beta_{\text{tot}}$ values and the $\beta(\omega)$ increase with increasing frequency ($\omega$) from 0.0000 to 0.0239 au. Our work shows that external electric field may be used as a regulator to modulate electronic and optic properties of HArF molecule by controlling the HArF structure. We hope that our work may provide a new idea for application of noble-gas hydrides.

**Keywords:** argon fluorohydride · external electric field · first hyperpolarizability · noblegas hydrides · charge transfer

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**Additional Supporting Information** may be found in the online version of this article.


