**PAPER**

**Ab initio** investigation of hydrogen-based high $T_c$ superconductor that is stable under ambient environment

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**Abstract**

We report an *ab initio* investigation of a hydrogen-based high-$T_c$ superconductor candidate—crystalized $C_4H_4$ in the cubic-gauche ($cg$-$C_4H_4$) structure, with the symmetry of space group $I\bar{2}13$. We find the $cg$-$C_4H_4$ structure to be stable under ambient environment; and the evaluation of the electron-phonon coupling strength indicates that the heavily doped $cg$-$C_4H_4$ can generate superconductivity with a $T_c \sim 72$ K. The high frequency vibrational modes of hydrogen atoms are found to play an important role in the total electron-phonon interaction strength, and the reduction of structural symmetry compared with graphene further enhances the electron–phonon coupling of the carbon framework. Our investigation illustrates a BCS route to realizing the hydrogen-based high $T_c$ superconductivity.

**1. Introduction**

Within the BCS framework, the critical superconducting temperature can be expressed as $T_c \sim \omega_D^{-1/NV}$, where $\omega_D$ is the Debye frequency, $N$ is the density of states at the Fermi level, and $V$ the averaged electron-phonon interaction strength. To achieve a higher $T_c$, one can either increase $\omega_D$, $N$, $V$, or any combinations of the three parameters. Light elements, such as carbon, boron, beryllium, and especially hydrogen, usually have strong inter-atomic binding strength and light mass, thereby favor high $\omega_D \sim \sqrt{k/m}$, where $k$ is the elastic constant for the bond and $m$ is the atomic mass. Carbon and hydrogen-based compounds, with light atomic mass and strong bonding, can provide both high-frequency phonons as well as strong electron-phonon coupling [1, 2]. Based on this picture, we propose a hydrocarbon compound that is stable under ambient environment, and it can exhibit high-$T_c$ superconductivity under heavy doping. The structure of the compound is illustrated in figure 1. The inspiration for such an as-yet-unrealized structure originates from the high-pressure allotropic of nitrogen, the $cg$-Nitrogen [3–7]. It has the $I\bar{2}13$ symmetry. Each carbon atom, with $sp^3$ hybridization, has 3 bonds connecting it to the neighboring carbon atoms, and the 4th bond is connected to a hydrogen atom. We have performed detailed *ab initio* calculations for this system and found the structure to be dynamically stable under zero pressure. Under heavy doping, its superconductivity transition temperature $T_c$ can be as high as $\sim 72$ K. A detailed analysis shows the hydrogen atoms play a double role in enhancing the superconductivity critical temperature. First, electron–phonon coupling, due to hydrogen-dominated vibration modes, contributes to the superconductivity; second, the presence of the hydrogen atoms reduces the symmetry of carbon framework, thereby removing the symmetry-induced restrictions on the electron–phonon coupling between the carbon atoms. Usually the electron–phonon coupling of carbon atoms can be prohibited by symmetry selection rules, e.g., in graphene or doped-diamonds.

In earlier works on high-$T_c$ BCS superconductors, the role of hydrogen is to provide metallic bonding. For example, metallic hydrogen is regarded as the best candidate of high-temperature superconductors or even room-temperature superconductors [8, 9]. In recent years, people realize it is more convenient to use hydride to stabilize the structure, which can be synthesized under relatively lower pressure compared to
metallic hydrogen. The investigated hydride includes H$_2$S, YH$_x$ and LaH$_x$ compounds [9–35]. With density functional theory simulations, people investigated the structure of sulfur hydride under high pressure, and predicted this compound to be with superconducting transition temperature in the range 50–235 K [10–22]. And in 2015, this H$_2$S system with $T_c = 203$ K was synthesized experimentally [23]. On the other route, metal-hydrides MH$_x$ with $M = Y, La$ were also investigated with first-principle simulation method. Two structures, namely MH$_6$ with metal atom surrounded by 24 hydrogen atoms, and MH$_{10}$ with metal atom surrounded by 32 hydrogen atoms, were suggested under high pressure, and with $T_c$ predicted to be even up to room temperature [24–33]. In 2019, LaH$_{10}$ was reported to be synthesized under 170 Gpa and with $T_c \sim 250$ K [34]. Most recently, a compound made up with sulfur, hydrogen and carbon even show superconductivity at room temperature under 267 Gpa [35]. So this idea is proven to be correct to achieve high-temperature BCS superconductivity. However, such hydrogen compounds are stable only under extremely high pressure, owing to the highly unstable metallic-bonding between the hydrogen atoms under ambient conditions. In contrast, our proposed heavily-doped cg-C$_4$H$_4$ is stable under ambient environment, with a reasonably high $T_c$.

2. Calculation method

In what follows we present our ab initio study in detail. ABINIT code [36–40] is used, with the projector augmented wave (PAW) [41] method. Local density approximation (LDA) is used for the exchange-correlation functional. After structure relaxation and formation energy calculations, density functional perturbation theory (DFPT) [42–44] method is employed to calculate the phonon spectrum, the eigenvectors, and the electron–phonon coupling strength [45, 46]. The corresponding superconductivity critical temperatures are obtained by using the McMillian equation [47–49]. In all the calculations the plane-wave energy cutoff is set to 36 Hartree. In calculating the formation energy of hydrocarbon compound molecules, vacuum cube with 12 Å in side length is used to avoid interplay between image molecules. Molecules are put inside the vacuum cube and we perform full relaxation. The obtained energy is used to calculate formation energy. To find out if there is competing structures with lower energy than cg-C$_4$H$_4$, we perform structure prediction calculations with Calypso [50, 51], which is a popular structure prediction software. In the calculation of phonon spectrum and electron-phonon coupling, the Brillouin zone sampling k-mesh is set to be $16 \times 16 \times 16$, and phonon wave-vectors q-mesh is set to be $4 \times 4 \times 4$, which is an optimized k-mesh density that balances the accuracy and calculation resources required. After
this step, for the doping level 0.3h/cell case, which is with the highest superconducting transition temperature \( T_c \), a more precise calculation is performed with \( k \)-mesh \( 32 \times 32 \times 32 \) and \( q \)-mesh \( 8 \times 8 \times 8 \), to obtain a more accurate estimation of the \( T_c \) for this system.

3. Formation energy, electronic structure, phonon spectrum and superconductivity

The \( cg \text{-C}_4\text{H}_4 \) structure is first relaxed under ambient environment, and the relaxed structure is summarized in table 1. Although this compound has not yet been realized, it can in principle be synthesized by applying extremely high pressure on hydrocarbons, similar to the synthesis method of the \( cg \text{-Nitrogen} \) as well as other hydrogen-based superconducting materials. The important feature is that such \( cg \text{-C}_4\text{H}_4 \) compound is shown to be stable under even ambient environment, which is verified by both formation energy calculations, and the vibration analysis as shown in figure 3. The formation energy analysis is accomplished by the following procedure: we use single layer graphene and \( H_2 \) molecule as energy reference, and calculate the formation energy of \( cg \text{-C}_4\text{H}_4 \), methane (\( \text{CH}_4 \)) and acetylene (\( \text{C}_2\text{H}_2 \)) respectively. Then we can compare the \( cg \text{-C}_4\text{H}_4 \) with typical hydro–carbon compounds with their relative stability. The formation energy of a hydro–carbon compound is defined as:

\[
E_{\text{formation}} = E_{\text{C}_4\text{H}_4} - \left( \frac{x}{2} E_{\text{graphene}} + \frac{y}{2} E_{\text{H}_2} \right),
\]

since there are 2 carbon atoms in a unit cell of graphene, and 2 hydrogen atoms in a molecule. For \( cg \text{-C}_4\text{H}_4 \), \( x = y = 4 \), the formation energy is 0.084 eV, which means the \( cg \text{-C}_4\text{H}_4 \) is less stable than graphene and \( \text{H}_2 \) gas. As comparison, methane (\( \text{CH}_4 \), \( x = 1 \) and \( y = 4 \)) has formation energy \(-1.301 \) eV, which is more stable than graphene and \( \text{H}_2 \), as well as \( cg \text{-C}_4\text{H}_4 \). While for acetylene (\( \text{C}_2\text{H}_2 \), \( x = y = 2 \)), its formation energy is 2.790 eV. Therefore, \( cg \text{-C}_4\text{H}_4 \) is less stable than methane, but more stable than acetylene. As acetylene is stable under ambient environment, we can expect that \( cg \text{-C}_4\text{H}_4 \) is also stable. We also performed structure prediction calculations, trying to find out competing structures with the same hydrogen–carbon component and with similar formation energy. However, no other three-dimensional crystal structures have been found. The predicted structures are chain-like alkanes and alkenes, or graphene based two-dimensional structures, etc. We are not interested in such one-dimensional or two-dimensional hydrogen–carbon systems. This is because superconductivity is hard to emerge in low-dimensional systems due to the Hohenberg–Mermin–Wagner theorem [52, 53], which states in low-dimensional systems fluctuation will destroy long-range orders, like Cooperons. The stability of \( cg \text{-C}_4\text{H}_4 \) arises from the fact that hydrogen atoms are bounded to carbon atoms, and carbon atoms are bonded together to form the framework. These \( C\text{–C}/C\text{–H} \) bonds are much more stable than the metallic bonding in metal-hydrogen compounds and in metallic hydrogens. Therefore, we can expect that the compound could exist under usual condition, while other hydrogen-based superconductivity materials will just disintegrate, which rules out any possible realistic applications.

However, there is also drawback to use carbon to stabilize the structure, since the \( cg \text{-C}_4\text{H}_4 \) is an insulator based on band-structure calculation, as shown in figure 2. It is well known that BCS superconductivity requires free electrons at Fermi energy. To make it metallic, we need to dope it with electrons or with holes. We simulate high concentration doping in \( cg \text{-C}_4\text{H}_4 \) system, from 0.5 electrons/cell to 0.6 holes/cell, and corresponding heavily-doped band structures are shown in figure 2. Actually, the dispersion of band-structures for different doping status are almost the same, and the only difference is the Fermi energy. In figure 2, charge neutral, 0.5 electrons/cell and 0.5 holes/cell cases are shown. Under these heavily-doped situations, the doped \( cg \text{-C}_4\text{H}_4 \) systems are metallic and the Fermi surface can give raise to

| Lattic constants | Atomic coordinates (in lattice coordinate) |
|------------------|-----------------------------------------|
| Length (Å)       | Angle (°)                               |
| \( a = b = c = 3.681 \) | \( \alpha = \beta = \gamma = 109.47 \)   |
| C1 0.5 0.0 0.1774 | C2 0.3226 0.3226 0.3226                 |
| H1 0.5 0.0 0.8795 | H2 0.6205 0.6205 0.6205                 |
| C3 0.1774 0.5 0.0 | C4 0.0 0.1774 0.5                      |
| H3 0.8795 0.5 0.0 | H4 0.0 0.8795 0.3                      |

Table 1. The relaxed lattice constant under ambient environment, and the atomic coordinates of charge neutral \( cg \text{-C}_4\text{H}_4 \). This yet-unrealized hydrocarbon compound is a crystal with the \( I213 \) space group.
superconductivity. Experimentally such heavily doping could be achieved by high-ratio replacement of carbon atoms with nitrogen or boron, or by applying liquid gating technique on a thin film of \( \text{cg-C}_{4}\text{H}_4 \).

The stability can be further verified by calculated vibration properties. Vibration properties are obtained by calculating the phonon spectrum of \( \text{cg-C}_{4}\text{H}_4 \) under different doping levels, as shown in figure 3. The phonon spectrum under certain doping level is obtained with the optimized structure under the doping level, and we find the \( \text{cg-C}_{4}\text{H}_4 \) structure is dynamically stable under all these high doping cases under zero pressure, by identifying that all phonon branches are with real-positive frequencies. Real-positive phonon frequency indicates that the system is at energy minimum, and restoring force exists if the system is out of equilibrium. The most outstanding feature in the phonon spectrum is, around \( \sim 3000 \text{ cm}^{-1} \) there are 4 phonon branches, which originate from the optic phonon of hydrogen atoms. Such phonon branches are with quite high frequencies, since C–H bonding is very strong and mass of hydrogen atom is very light. The strong C–H bond is important for stabilizing the structure against soft phonons. For example, the potentially very high \( T_c \) in pure carbon nano-structure can be compromised by lattice instabilities [54].

The electron–phonon coupling strength is also obtained by DFPT method. The effective \( \alpha^2 F (\omega) \) spectrums for 0.3h/cell doping level is shown in figure 4. The averaged electron-phonon coupling strength can be obtained by integrate the \( \alpha^2 F (\omega) \) function:

\[
\alpha^2 F (\omega) = \frac{1}{N (\varepsilon_f)} \sum_{kk',\nu} |g_{kk',\nu}|^2 \delta (\varepsilon_{k'} - \varepsilon_f) \delta (\varepsilon_k - \varepsilon_f) \delta (\omega - \omega_{q\nu})
\]

\[
\lambda = 2 \int \frac{\alpha^2 F (\omega)}{\omega} d\omega,
\]

in which \( N (\varepsilon_f) \) is the density of states at the Fermi energy, \( g_{kk',\nu} \) is the electron–phonon coupling matrix element that a phonon \( (q, \nu) \) scatters an electron from \( k \) to \( k' \) state, with \( q = k - k' \). \( \omega_{q\nu} \) are the frequency of the phonon mode \( (q, \nu) \). In figure 4, we can see the high-lying hydrogen-related phonon modes play important role in the total electron-phonon coupling strength. More importantly, the lower frequency phonons that are dominated by carbon atoms have significant contribution because they show strong electron–phonon coupling strength, in contrast to the case of graphene or diamond. In addition, almost all phonons give contributions to electron-phonon coupling strength, which arises from the lowering of symmetry due to the presence of hydrogen atoms [55]. The critical temperature of superconductivity
Figure 3. (A) The phonon spectrum of $\text{cg-C}_4\text{H}_4$ with $0.3h/\text{cell}$. No soft mode is present, which indicates the stability of the system under ambient environment. The stability is verified for all the doped cases. The most outstanding feature is observed between $2700\;\text{cm}^{-1}$ and $3000\;\text{cm}^{-1}$ there are $4$ hydrogen-dominated optical phonons. (B) The phonon line-width due to electron-phonon coupling is added to the phonon spectrum, as the error bar. We can see phonon branches at $\sim3000\;\text{cm}^{-1}$, $\sim1320\;\text{cm}^{-1}$, and $\sim880\;\text{cm}^{-1}$ are with strong electron-phonon coupling.

The transition is obtained by the McMillan equation [47–49]:

$$T_c = \frac{\Omega_{\ln}}{1.2} \exp \left( -\frac{1.04 (1 + \lambda)}{\lambda - \mu^* (1 + 0.62\lambda)} \right),$$

$$\Omega_{\ln} = \exp \left( \frac{2}{\lambda} \int d\omega \ln (\omega) \frac{\alpha^2 F(\omega)}{\omega} \right),$$

where $\mu^*$ denotes the Coulomb repulsion potential, and $\Omega_{\ln}$ is a weighted phonon frequency. So with data obtained from $ab\;initio$ calculations, we get the $T_c$ of heavily doped $\text{cg-C}_4\text{H}_4$. We find the highest $T_c$, which occurs at $0.3h/\text{cell}$, is up to $\sim72\;\text{K}$ if $\mu^* = 0$ and to $\sim48\;\text{K}$ if $\mu^* = 0.136$, a typical value of bulk metals. The corresponding $\Omega_{\ln}$ is $\sim514\;\text{K}$ and $\lambda \sim 1.39$ in this $0.3h/\text{cell}$ doping case. The data of other doping levels, which are calculated with a coarse grid, are summarized in the appendix A. N-type doping and p-type doping are both considered in our calculations. In general, the p-type doping is more favorable to induce superconductivity, since the much higher density of states around the top of valance band compared with the bottom of conduction band as shown in figures 2(b)–(d). At the top of the valance band, the density of state arises from p-orbital of carbon atoms and s-orbital of hydrogen atoms. Due to the BCS equation between transition temperature $T_c$ and electronic structure: $T_c \sim \omega_{\text{p-type}} e^{-1/NV}$ with $\lambda \sim NV$, it is easy to see higher density of state favors higher transition temperature. Therefore, at p-type doping it causes a much larger electron-phonon coupling strength $\lambda$. An interesting feature is that if p-type doping level increases to be larger than $0.4h/\text{cell}$, the weighted phonon frequency $\Omega_{\ln}$ significantly suppressed, which is unfavorable.
Figure 4. (A) the $\alpha^2 F(\omega)$ function of heavily-doped $cg\cdot C_4H_4$ with concentration 0.3h/cell. Both carbon dominated low-frequency phonons and hydrogen dominated high-frequency phonons give significant contributions to the electron-phonon coupling spectrum $\alpha^2 F(\omega)$ function. (B) As comparison, we plot the phonon density of states and phonon density of states projected onto different type of atoms. It is clear that above 1100 cm$^{-1}$ the Hydrogen atoms give most the contribution to the total electron–phonon coupling, while below it the carbon atoms are dominate.

4. Discussion and summary

With heavily electron/hole doping, we demonstrate an alternative route to achieve high-temperature superconductivity transition in hydrogen-based compounds. This new paradigm is to use carbon to stabilize the whole hydrogen-containing system. Comparing with the common method, which applies extremely high pressure to hydrogen-metal compounds with metallic bonding, our method has the advantage that the material could be stable under usual ambient conditions. Once synthesized under high-pressure, $cg\cdot C_4H_4$ material can exist in ambient environment, can be mechanically processed, and can even be heavily doped. This makes the material much easier to keep and characterize experimentally, including transport measurements. In our proposed material, $cg\cdot C_4H_4$, both the carbon framework and the hydrogen atoms contribute to electron–phonon coupling, which can greatly enhance the critical temperature $T_c$. Therefore, such C–H materials synthesized under extremely high-pressure could become a platform for searching high-$T_c$ BCS superconductors under heavy-doping. This family of compound is useful for material discovery because carbon and hydrogen can form a large variety of compounds. Although most of them are one-dimensional or two-dimensional, after high pressure processing it is possible to synthesize a variety of three-dimensional crystal structures that could be stable under usual conditions. In addition, the lower symmetry means that the electron–phonon coupling will be easier to occur. This is in contrast to graphene, in which the high symmetry eliminates most of the electron–phonon coupling matrix elements because of the strict electron-phonon symmetry selection rules [55]. The most interesting point of this investigation is hydrogen-dominated phonons can induce strong electron–phonon coupling in this case, while we do not suffer from the unstable hydrogen–hydrogen metallic bonding. Very
recently, when this manuscript is under review, a breaking new progress emerges that room-temperature superconductor is found under extremely high pressure [35]. This compound contains hydrogen, sulfur and carbon, which verifies the correctness of our consideration that carbon will play important role in constructing new Hydrogen based high-\(T_c\) superconductors. In summary, in hydrogen-carbon compounds synthesized under high pressure, hydrogen can play two roles: first it provides strong electron–phonon coupling strength under high-doping, and second it reduces the symmetry of carbon framework, which unlashes potential electron–phonon coupling of carbon. Our next step is to use \textit{ab initio} molecular dynamics (MD) to further verify the stability of this cg-C_4H_4 compound when heavily doped, and to search for possible synthesis condition and route. Another investigation direction is to use structure prediction methods [50, 51, 56–58] to find possible new hydrocarbon crystal structures that can be high-\(T_c\) superconductors or even room-temperature superconductors and can be stable under usual conditions in this material family.

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Appendix A. The BCS superconductivity properties of cg-C_4H_4 at different doping levels

See table A1.

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