

# Time-dependent density functional theory study of the excited-state dihydrogen bonding: clusters of 2-pyridone with diethylmethylsilane and triethylgermanium

Ning-Ning Wei · Ce Hao · Jiao-Jie Tan ·  
Guangyan Zhao · Ruizhou Li · Zhilong Xiu ·  
Jieshan Qiu

Received: 29 May 2010 / Accepted: 3 November 2010 / Published online: 24 November 2010  
© Springer-Verlag 2010

**Abstract** Density functional theory (DFT) was carried out to identify the existence of intermolecular dihydrogen bonds of the 2-pyridone (2PY)-diethylmethylsilane (DEMS) and 2PY-triethylgermanium (TEGH) clusters in the ground state. The H···H distances of both clusters are shorter than the sum of their van der Waals radii. Thus, intermolecular dihydrogen bonds N–H···H–Si and N–H···H–Ge exist in the 2PY-DEMS and 2PY-TEGH clusters, respectively. Based on the ground-state conformations, intermolecular dihydrogen bonds N–H···H–Si and N–H···H–Ge in the electronically excited state of the 2PY-DEMS and 2PY-TEGH clusters were also investigated using time-dependent density functional theory (TDDFT). Electronic transition of the 2PY-DEMS cluster resembles that of the 2PY-TEGH cluster. Their  $S_1$  state is a locally excited (LE) state centered on 2PY moiety. The H···H distances of the 2PY-DEMS and 2PY-TEGH clusters both stretch in the  $S_1$  state compared to those in the ground state. Upon electronic excitation, intermolecular dihydrogen bonding N–H···H–Si and N–H···H–Ge can weaken with decreasing dihydrogen bonding energies.

**Keywords** Density functional theory · Dihydrogen bond · Electronically excited state · Locally excited state · Time-dependent density functional theory

N.-N. Wei · C. Hao (✉) · J.-J. Tan · Z. Xiu · J. Qiu  
State Key Laboratory of Fine Chemicals, School of  
Environmental and Biological Science and Technology,  
Dalian University of Technology,  
Dalian 116024, China  
e-mail: haoce\_dlut@126.com

G. Zhao · R. Li  
Hebei University of Science and Technology,  
College of Textile and Garment,  
Shijiazhuang 050031, China

## Abbreviations

DFT	Density functional theory
TDDFT	Time-dependent density functional theory
2PY	2-pyridone
TEGH	Triethylgermanium
DEMS	Diethylmethylsilane
LE	Locally excited state
CSD	Cambridge Structure Database
BTMA	Borane-trimethylamine
B3LYP	Becke's three-parameter hybrid exchange functional with Lee-Yang-Parr gradient corrected correlation functional
TZVP	Triple zeta valence plus polarization functions
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
Mos	Molecular orbitals
IR	Infrared spectrum

## Introduction

Dihydrogen bond, a novel type of hydrogen bond, can be usually represented as  $X - H^{\delta-} \cdots H^{\delta+} - Y$  [1–8]. The electrostatic attraction between the oppositely charged hydrogen atoms promotes the formation of dihydrogen bond [4–13]. It has caught wide attention with its comparative strength and directionality to conventional hydrogen bond [5, 7–32]. Dihydrogen bond has been characterized by various spectroscopic and crystallographic studies. Experimental investigations have demonstrated that dihydrogen bond has potential applications in catalysis, crystal engineering and materials chemistry [5]. Dihydrogen bond has been a well-established system containing main group and transitional elements in gas and condensed phase.

In the middle of the 1990s, electrostatic interaction  $H^{\delta-} \cdots \delta^+H$  was identified mostly in transition-metal compounds [14–19]. Raston et al. observed an intramolecular interaction  $N-H \cdots H-Al$  in the alane-piperidine adduct using X-ray crystallography in 1994 [20]. Crabtree et al. clarified the term “dihydrogen bonds” for the first time by examining the Cambridge Structure Database (CSD) to find the  $N-H \cdots H-B$  interaction among boron-nitrogen compounds in 1995 [21]. Campbell et al. reported the intermolecular dihydrogen bond  $N-H \cdots H-Ga$  involving gallium by means of Gladfelter’s neutron diffraction crystal structure of cyclotrigallazane [22]. Proton transfer is thought to proceed with the dihydrogen bonding from the protic donor to metal hybrid [23–27]. Moreover, dehydrogenation reaction from a dihydrogen-bonded cluster has been investigated theoretically and experimentally [28–30]. Ishikawa et al. identified dihydrogen bond containing silicon by IR-UV double-resonance spectroscopy in 2005 [31]. Recently, Singh and co-workers reported the formation of intermolecular dihydrogen bond  $O-H \cdots H-Ge$  of dihydrogen-bonded Phenol-Triethylgermanium (TEGH) cluster in the gas phase [32].

Up to now, tremendous spectroscopic and theoretical investigations are focused on the nature of dihydrogen bond in the ground state. Nevertheless, dihydrogen bond in the electronically excited state is scarcely studied due to the extremely short timescales involved. It is difficult to measure the excited-state hydrogen and dihydrogen bonding by time-resolved techniques. Theoretical calculations on the electronically excited states of the hydrogen- and dihydrogen-bonded clusters afford to enrich the knowledge [33–48]. Zhao and Han have contributed significantly to the study of excited-state hydrogen bonding in the world. Based on the research of excited-state hydrogen bonding, they reported the theoretical structure and dynamics of dihydrogen bonding in the electronically excited state between phenol and borane-trimethylamine (BTMA) for the first time [42]. In the  $S_1$  state, the dihydrogen-bonded phenol–BTMA cluster shows no hydroxyl or B–H stretching vibrational mode in the calculated infrared (IR) spectrum in the benchmark work [42]. We have theoretically investigated the intermolecular dihydrogen bonding in the electronically excited state of the phenol–diethylmethylsilane (DEMS) [43], phenol– $H_2O$ –DEMS [44] and phenol–TEGH [45] clusters. These intermolecular dihydrogen bondings involving hydroxyl protic donor all get strengthened upon electronic excitation. Then, we theoretically studied the excited-state 2-pyridone (2PY)–BTMA cluster which contains intermolecular hydrogen and dihydrogen bonding on the basis of experimental research in the ground state [46]. The N–H stretching vibrational mode of the 2PY–BTMA cluster is blueshifted upon electronic excitation. Additionally, carbonyl

character of the 2PY moiety disappears in the excited-state IR spectrum. These were attributed to the weakening of the dihydrogen bonding  $N-H \cdots H-B$  and hydrogen bonding  $C-O \cdots H-C$ . Understanding the properties of dihydrogen bond in the excited state continues as an area of intense experimental and theoretical research.

2PY is a simple molecule having a peptide group. The electronic spectra and vibrational spectra of 2PY and its hydrogen-bonded clusters have been studied in detail [49–54]. The studies found that the hydrogen-bond strengths of 2PY– $H_2O$  and (2PY) $_2$  clusters are weakened in the  $S_1$  state due to a decrease of the acidity of 2PY [50–52]. Nevertheless, spectroscopic studies on the dihydrogen-bonded cluster involving 2PY are less reported so far. In the present work, we propose a theoretical analysis about the intermolecular dihydrogen bonds of the 2PY–DEMS and 2PY–TEGH clusters in different electronic states. Density functional theory (DFT) method was employed to predict the existence of the dihydrogen-bonded 2PY–DEMS and 2PY–TEGH clusters in the ground state. Intermolecular dihydrogen bonds  $N-H \cdots H-Si$  and  $N-H \cdots H-Ge$  in the electronically excited state were studied using time-dependent density functional theory (TDDFT) since it has been proven as a valid method for the investigation of electronically excited state [55–62]. Theoretical calculations cannot only provide useful insights into the structure and dynamics of dihydrogen bonding but also suggest future experiments.

## Computational methods

Density functional theory (DFT) and time-dependent density functional theory (TDDFT) were employed for our ground state and excited state computations, respectively. Becke’s three-parameter hybrid exchange functional with Lee–Yang–Parr gradient corrected correlation functional (B3LYP hybrid functional) can provide satisfying quantitative and qualitative agreement with experiment [36, 45, 46, 63]. Thus, all geometry optimizations in this work were carried out using B3LYP hybrid functional. Triple zeta valence plus polarization (TZVP) functions was chosen as basis set throughout [64]. Fine quadrature grids 4 were employed, too. Harmonic vibrational frequency analyses were performed at the same theoretical level to verify the true energy minima locating in the ground state and the electronically excited state [63–65].

The binding energies  $E_{bind}$ , of the clusters in different electronic states were calculated at the B3LYP/TZVP level by using the geometries optimized at the same level.  $E_{bind}$  was evaluated as [66, 67]:

$$E_{bind} = E_{AB} - (E_A + E_B), \quad (1)$$

where  $E_{AB}$  is the energy of the dihydrogen-bonded complex formed between molecules A and B, and  $E_A$  and  $E_B$  are individual energies of constituent molecules A and B, respectively. These values were determined by DFT and TDDFT energy calculations.

Corrections were made for the basis set superposition error (BSSE) in the calculations. The magnitude of BSSE is estimated by counterpoise calculations [68]. The original counterpoise method of Boys and Bernardi is the procedure most frequently used for computing the BSSE [67–69]. Hence, the overestimation of the interaction energy (Eq. 1) is corrected as  $E_{cp-bind}$ :

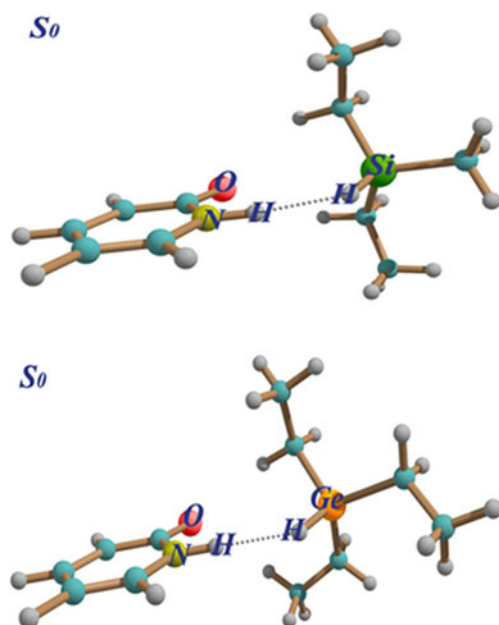
$$E_{cp-bind} = E_{bind} + BSSE. \quad (2)$$

All the computations were performed using the TURBO-MOLE program suite.

## Results and discussion

Geometric conformations of 2PY–DEMS and 2PY–TEGH clusters

Figure 1 shows the optimized conformations of the dihydrogen-bonded 2PY–DEMS and 2PY–TEGH clusters in the ground state. One can find the calculated bond lengths and dihedral angles of the isolated monomers and the clusters in the ground state in Table 3. The C=O and N–H bonds of the 2PY–DEMS cluster are both longer than those of free 2PY. The Si–H bond slightly enlarges



**Fig. 1** Optimized geometries of the dihydrogen-bonded 2PY–DEMS (top) and 2PY–TEGH (bottom) clusters in the ground state. Dotted line denotes the intermolecular dihydrogen bond

because of the formation the 2PY–DEMS cluster. The H···H distance of the 2PY–DEMS cluster is calculated to be 1.984 Å, which is shorter than the sum of their van der Waals radii (2.40 Å). Thus, it indicates the formation of dihydrogen bond N–H···H–Si between 2PY and DEMS in the ground state. Geometric conformation of the 2PY moiety of the 2PY–TEGH cluster is same to that of the 2PY–DEMS cluster. The Ge–H bond also slightly enlarges due to the formation the 2PY–TEGH cluster. The calculated H···H distance of the 2PY–TEGH cluster is 2.055 Å. It conforms that an intermolecular dihydrogen bond N–H···H–Ge exists between 2PY and TEGH in the ground state.

## Electronic transition and frontier molecular orbitals

Based on the geometries with minimum energy, the electronic transition energies and corresponding oscillator strengths for the low-lying electronically excited states of the dihydrogen-bonded 2PY–DEMS and 2PY–TEGH clusters and free monomers were calculated using TDDFT. The results are shown in Table 1 and Table 2. All of the electronic transition energies of the dihydrogen-bonded 2PY–DEMS and 2PY–TEGH clusters are comparable with those of the 2PY monomer but significantly lower than those of the DEMS and TEGH monomers. It can be postulated that the electronically excited state of both dihydrogen-bonded clusters is centered on the 2PY moiety, while the DEMS and TEGH moieties still remain in the ground state.

The oscillator strength of the 2PY–DEMS cluster in the  $S_5$  state is the largest among the low-lying excited states. However, the oscillator strengths are all zero in the  $S_2$ ,  $S_3$  and  $S_4$  states. The  $S_2$ ,  $S_3$  and  $S_4$  states with lower energy are

**Table 1** Calculated electronic transition energies (in eV) and corresponding oscillation strengths (in parentheses) of the low-lying electronically excited states of the dihydrogen-bonded 2PY–DEMS complex and the isolated monomers

	2PY–DEMS	2PY	DEMS
1	4.350(0.082)	4.355(0.097)	7.407(0.005)
	H→L 96.5%	H→L 96.5%	H→L 97.4%
2	4.548(0.000)	4.520(0.000)	7.681(0.023)
3	5.547(0.000)	5.693(0.000)	7.881(0.023)
4	5.691(0.000)	5.879(0.000)	7.919(0.015)
5	5.846(0.150)	5.889(0.117)	8.169(0.010)
6	5.872(0.001)	6.844(0.000)	8.186(0.041)

The orbital transition contributions for the  $S_1$  state are also listed

H: The highest occupied molecular orbital, HOMO

L: The lowest unoccupied molecular orbital, LUMO

**Table 2** Calculated electronic transition energies (in eV) and corresponding oscillation strengths (in parentheses) of the low-lying electronically excited states of the dihydrogen-bonded 2PY–TEGH complex and the isolated monomers

	2PY–TEGH	2PY	TEGH <sup>b</sup>
1	4.349(0.081) H→L 96.5%	4.355(0.097) H→L 96.5%	7.223(0.0129) H→L 72.6% H-1→L 25.4%
2	4.545(0.000)	4.520(0.000)	7.275(0.007)
3	5.346(0.001)	5.693(0.000)	7.406(0.024)
4	5.440(0.000)	5.879(0.000)	7.441(0.005)
5	5.687(0.000)	5.889(0.117)	7.697(0.028)
6	5.842(0.000)	6.844(0.000)	7.709(0.004)

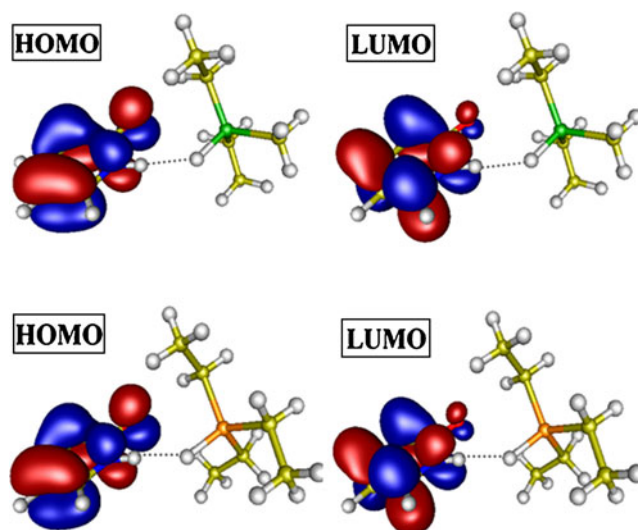
The orbital transition contributions for the  $S_1$  state are also listed

<sup>b</sup> Data taken from Ref. [45]

the dark states of the 2PY–DEMS cluster. It can be speculated that the radiationless transition from the  $S_5$  state to the  $S_1$  state is ultrafast, while the internal conversion from the  $S_1$  state to the ground state occurs on a slower timescale. Therefore, we just discuss the properties of the 2PY–DEMS cluster in the  $S_1$  state here. The oscillator strength of the dihydrogen-bonded 2PY–TEGH cluster is the largest in the  $S_1$  state but is almost zero in other excited states. Hence, the 2PY–TEGH cluster can be initially excited to the  $S_1$  state. Similarly, only the  $S_1$  state of the 2PY–TEGH cluster is taken into our account in this study.

In the  $S_1$  state, the vertical excitation energies of both the clusters are a little lower than that of free 2PY. It infers that a slightly redshift appears in the electronic transition of the dihydrogen-bonded cluster comparing with that of the isolated 2PY. Moreover, the orbital transition contributions for the  $S_1$  state of both clusters are also listed in Table 1 and Table 2. The transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) mainly contributes to the  $S_1$  state of dihydrogen-bonded 2PY–DEMS and 2PY–TEGH clusters.

The molecular orbitals (MOs) analysis can provide direct understanding of the dihydrogen bonding in the



**Fig. 2** Frontier MOs of the dihydrogen-bonded 2PY–DEMS (top) and 2PY–TEGH (bottom) complexes

electronically excited state. Accordingly, we depicted the frontier MOs for the dihydrogen-bonded 2PY–DEMS and 2PY–TEGH clusters in Fig. 2. One can find that the frontier MOs of the 2PY–DEMS and 2PY–TEGH clusters resemble each other. The electron densities of HOMO and LUMO are both localized on the 2PY moiety. Therefore, the  $S_1$  state of the dihydrogen-bonded 2PY–DEMS and 2PY–TEGH clusters is a locally excited (LE) state. The 2PY moiety of both clusters demonstrates a  $\pi\pi^*$  transition upon electronic excitation. In addition, the electron density of the carbonyl oxygen decreases due to the molecular orbital transition from HOMO to LUMO. Intermolecular dihydrogen bonding  $N-H\cdots H-Si$  and  $N-H\cdots H-Ge$  should be influenced by the charge redistribution in the excited state.

### Weakening of dihydrogen bonding in the excited state

The geometries in the  $S_1$  state of the dihydrogen-bonded 2PY–DEMS and 2PY–TEGH clusters were optimized using TDDFT. The changes in structural conformation

**Table 3** Calculated bond lengths  $L$  (Å) and dihedral angles ( $^\circ$ ) of the isolated monomers, dihydrogen-bonded 2PY–DEMS and 2PY–TEGH complexes in different electronic states

	$E_{cp-bind}$	$L(C=O)$	$L(N-H)$	$L(H\cdots H)$	$N-H\cdots H-Si$	$N-H\cdots H-Ge$	$L(Si-H)$	$L(Ge-H)$
monomer( $S_0$ )	—	1.223	1.011	—	—	—	1.498	1.555
2PY–DEMS( $S_0$ )	-15.275	1.227	1.015	1.984	140.127	—	1.511	—
2PY–DEMS( $S_1$ )	-6.517	1.336	1.011	1.990	154.038	—	1.509	—
2PY–TEGH( $S_0$ )	-16.219	1.227	1.015	2.055	—	23.968	—	1.569
2PY–TEGH( $S_1$ )	-6.271	1.337	1.010	2.083	—	43.093	—	1.568

The dihydrogen-binding energies  $E_{cp-bind}$  ( $KJ mol^{-1}$ ) of the dimers are also listed



between the ground state and excited state can obviously affect the intermolecular dihydrogen bonding. Table 3 lists the calculated bond lengths and dihedral angles of the 2PY–DEMS and 2PY–TEGH clusters in different electronic states. The C=O bonds of the 2PY–DEMS and 2PY–TEGH clusters significantly lengthen upon electronic excitation. The N–H and Si–H bonds of the 2PY–DEMS cluster both slightly shorten after being excited to the  $S_1$  state. Likewise, the N–H and Ge–H bonds of the 2PY–TEGH cluster get shortened in the  $S_1$  state, too. In the  $S_1$  state, the H...H distances of the clusters enlarge to 1.990 Å and 2.083 Å, respectively. It can be speculated that intermolecular dihydrogen bonding N–H...H–Si and N–H...H–Ge become very weak in the  $S_1$  state because of the marked structural varieties.

To evaluate the ability of dihydrogen bonding in different electronic states, bonding energies ( $E_{\text{cp-bind}}$ ) of the 2PY–DEMS and 2PY–TEGH clusters were calculated with consideration of BSSE. The values are lists in Table 3. The binding energies of the 2PY–DEMS and 2PY–TEGH clusters are  $-15.275 \text{ kJmol}^{-1}$  and  $-16.219 \text{ kJmol}^{-1}$ , respectively. Upon electronic excitation, the binding energies of both clusters decrease nearly  $10 \text{ kJmol}^{-1}$ . It quantitatively infers that dihydrogen bondings N–H...H–Si and N–H...H–Ge are weaker in the  $S_1$  state than in the ground state.

## Conclusions

Intermolecular dihydrogen bonds N–H...H–Si and N–H...H–Ge were theoretically identified in the ground state of the dihydrogen-bonded 2PY–DEMS and 2PY–TEGH clusters by DFT method. Structural conformations and dynamics of the dihydrogen bonds in the excited state were also investigated using TDDFT method. The dihydrogen-bonded 2PY–DEMS and 2PY–TEGH clusters demonstrate similar electronic transitions upon electronic excitation. The  $S_1$  state of both clusters is a LE state which localized on the 2PY moiety. The 2PY moiety exhibits a  $\pi\pi^*$  transition from HOMO to LUMO in the  $S_1$  state. The H...H distances of both dihydrogen bond significantly enlarge upon electronic excitation. Their dihydrogen bonding energies both decrease in the  $S_1$  state compared to those in the ground state. It suggests that the intermolecular dihydrogen bondings N–H...H–Si and N–H...H–Ge of the 2PY–DEMS and 2PY–TEGH clusters get weaker in the electronically excited state due to the structural varieties and charge redistribution.

**Acknowledgments** This work was supported by the National Natural Science Foundation of China (Grant Nos. 20773018) and the Key Laboratory of Industrial Ecology and Environmental Engineering, China Ministry of Education.

## References

- Bakhmutov VI (2008) Dihydrogen bond: principles, experiments, and applications. Wiley, New York
- Crabtree RH, Eisenstein O, Sini G, Peris E (1998) New types of hydrogen bonds. *J Org Chem* 567:7–11
- Fujimaki E, Fujii A, Ebata T, Mikami N (2000) Autoionization-detected infrared spectroscopy of intramolecular hydrogen bonds in aromatic cations. II. Unconventional intramolecular hydrogen bonds. *J Chem Phys* 112:137–148
- Epstein LM, Shubina ES (2002) New types of hydrogen bonding in organometallic chemistry. *Coord Chem Rev* 231:165–181
- Custelcean R, Jackson JE (2001) Dihydrogen bonding: structures, energetics, and dynamics. *Chem Rev* 101:1963–1980
- Chu TS, Zhang Y, Han KL (2006) The time-dependent quantum wave packet approach to the electronically nonadiabatic processes in chemical reactions. *Int Rev Phys Chem* 25:201–235
- Van der Sluys LS, Eckert J, Eisenstein O, Hall JH, Huffman JC, Jackson SA, Koetzle TF, Kubas GJ, Vergamini PJ, Caulton KGG (1990) An attractive cis-effect of hydride on neighbor ligands: experimental and theoretical studies on the structure and intramolecular rearrangements of  $\text{Fe}(\text{H})_2(\eta^2\text{-H}_2)(\text{PEtPh}_2)_3$ . *J Am Chem Soc* 112:4831–4841
- Matta CF, Hernández-Trujillo J, Tang TH, Bader RFW (2003) Hydrogen-hydrogen bonding: a stabilizing interaction in molecules and crystals. *Chem Eur J* 9:1940–1951
- Marincean S, Jackson JE (2004) Quest for IR-pumped reactions in dihydrogen-bonded complexes. *J Phys Chem A* 108:5521–5526
- Belkova NV, Shubina ES, Epstein LM (2005) Diverse world of unconventional hydrogen bonds. *Acc Chem Res* 38:624–631
- Fanfrlík J, Lepšík M, Horinek D, Havlas Z, Hobza P (2006) Interaction of carboranes with biomolecules: formation of dihydrogen Bonds. *Chem Phys Chem* 7:1100–1105
- Klooster WT, Koetzle TF, Siegbahn PEM, Richardson TB, Crabtree RH (1999) Study of the N–H...H–B dihydrogen bond Including the crystal structure of  $\text{BH}_3\text{NH}_3$  by neutron diffraction. *J Am Chem Soc* 121:6337–6343
- Kar T, Scheiner S (2003) Comparison between hydrogen and dihydrogen bonds among  $\text{H}_3\text{BNH}_3$ ,  $\text{H}_2\text{BNH}_2$ , and  $\text{NH}_3$ . *J Chem Phys* 119:1473–1482
- Feracin S, Bürgi T, Bakhmutov VI, Eremenko I, Vorontsov EV, Vimenits AB, Berke H (1994) Hydrogen/hydrogen exchange and formation of dihydrogen derivatives of rhenium hydride complex in acidic solutions. *Organometallics* 13:4194–4202
- Lough AJ, Park S, Ramachandran R, Morris RH (1994) Switching on and off a new intramolecular hydrogen-hydrogen interaction and the heterolytic splitting of dihydrogen. crystal and molecular structure of  $[\text{Ir}\{\text{H}(\eta\text{-}1\text{-SC}_5\text{H}_4\text{NH})\}_2(\text{PCy}_3)_2]\text{BF}_4 \cdot 2.7\text{CH}_2\text{Cl}_2$ . *J Am Chem Soc* 116:8356–8357
- Park S, Ramachandran R, Lough AJ, Morris RH (1994) A new type of intramolecular H...H...H interaction involving N–H...H(Ir) H–N atoms. Crystal and molecular structure of  $[\text{IrH}(1\text{-SC}_5\text{H}_4\text{NH})_2(2\text{-SC}_5\text{H}_4\text{N})(\text{PCy}_3)]\text{BF}_4 \cdot 0.72\text{CH}_2\text{Cl}_2$ . *J Chem Soc Chem Commun* 19:2201–2202
- Wessel J, Lee JC, Peris E, Yap GPA, Fortin JB, Ricci JS, Sini G, Albinati A, Koetzle TF, Eisenstein O, Rheingold AL, Crabtree RH (1995) An unconventional intermolecular three-center N–H  $\text{H}_2\text{Re}$  hydrogen bond in crystalline  $[\text{ReH}_5(\text{PPh}_3)_3]$  indole- $\text{C}_6\text{H}_6$ . *Angew Chem Int Ed* 34:2507–2509
- Patel BP, Wessel J, Yao W, Lee JC, Peris E, Koetzle TF, Yap GPA, Fortin JB, Ricci JS, Sini G, Albinati A, Eisenstein O, Rheingold AL, Crabtree RH (1997) Intermolecular N–H...H–Re interactions involving rhenium polyhydrides. *New J Chem* 21:413–421
- Shubina ES, Belkova NV, Krylov AN, Vorontsov EV, Epstein LM, Gusev DG, Niedermann M, Berke H (1996) Spectroscopic

- evidence for intermolecular M–H···H–OR hydrogen bonding: interaction of  $\text{WH}(\text{CO})_2(\text{NO})\text{L}_2$  hydrides with acidic alcohols. *J Am Chem Soc* 118:1105–1112
20. Atwood JL, Koutsantonis GA, Lee FC, Raston CL (1994) A thermally stable alane-secondary amine adduct:  $[\text{H3Al}(2, 2, 6, 6\text{-tetramethylpiperidine})]$ . *J Chem Soc Chem Commun* 1:91–92
21. Richardson TB, de Gala S, Crabtree RH, Siegbahn PEM (1995) Unconventional hydrogen bonds: intermolecular B–H···H–N interactions. *J Am Chem Soc* 117:12875–12876
22. Campbell JP, Hwang JW, Young VG, von Dreele RB, Cramer CJ, Gladfelter WL (1998) Crystal engineering using the unconventional hydrogen bond. synthesis, structure, and theoretical investigation of cyclotrigallazane. *J Am Chem Soc* 120:521–531
23. Kubas GJ (1998) Molecular hydrogen complexes: coordination of a  $\sigma$  bond to transition metals. *Acc Chem Res* 21:120–128
24. Jessop PG, Morris RH (1992) Reactions of transition metal dihydrogen complexes. *Coord Chem Rev* 121:155–284
25. Maseras F, Lledós A, Clot E, Eisenstein O (2000) Transition metal polyhydrides: from qualitative ideas to reliable computational studies. *Chem Rev* 100:601–636
26. Epstein LM, Krylov AN, Shubina ES (1994) Novel types of hydrogen bonds involving transition metal atoms and proton transfer ( $\text{XH}\cdots\text{M}$ ,  $[\text{MH}]^+ \cdots\text{B}$ ,  $[\text{MH}]^+ \cdots\text{A}^-$ ). *J Mol Struct* 322:345–352
27. Kazarian SG, Hamley PA, Poliakoff M (1993) Is intermolecular hydrogen-bonding to uncharged metal centers of organometallic compounds widespread in solution? A spectroscopic investigation in hydrocarbon, noble gas, and supercritical fluid solutions of the interaction between fluoro alcohols and  $(\eta^5\text{-C}_5\text{R}_5)\text{ML}_2$  ( $\text{R} = \text{H}, \text{Me}; \text{M} = \text{Co}, \text{Rh}, \text{Ir}; \text{L} = \text{CO}, \text{C}_2\text{H}_4, \text{N}_2, \text{PMe}_3$ ) and its relevance to protonation. *J Am Chem Soc* 115:9069–9079
28. Patwari GN, Ebata T, Mikami N (2001) Dehydrogenation reaction from a dihydrogen bonded precursor complex in the gas phase. *J Phys Chem A* 105:10753–10758
29. Avramović N, Höck J, Blacque O, Fox T, Schmalte HW, Berke H (2010) Hydridic reactivity of  $\text{W}(\text{CO})(\text{H})(\text{NO})(\text{PMe}_3)_3$ -Dihydrogen bonding and  $\text{H}_2$  formation with protic donors. *J Organomet Chem* 695:382–391
30. Kulkarni SA (1999) Intramolecular dihydrogen bonding in main group elements. Connection with dehydrogenation reactions. *J Phys Chem A* 103:9330–9335
31. Ishikawa H, Saito A, Sugiyama M, Mikami N (2005) First observation of a dihydrogen bond involving the Si–H group in phenol–diethylmethylsilane clusters by infrared-ultraviolet double-resonance spectroscopy. *J Chem Phys* 123:224–309
32. Singh PC, Maity DK, Patwari GN (2008) Infrared-optical double-resonance measurements on O–H···H–Ge dihydrogen-bonded phenol triethylgermanium hydride complex in the gas phase. *J Phys Chem A* 112:5930–5934
33. Sobolewski AL, Domcke W (2003) Unraveling the molecular mechanisms of photoacidity. *Science* 302:1693–1694
34. Sobolewski AL, Domcke W (2004) Intramolecular hydrogen bonding in the  $\text{S}_1(\pi\pi^*)$  excited state of anthranilic acid and salicylic acid: TDDFT calculation of excited-state geometries and infrared spectra. *J Phys Chem A* 108:10917–10922
35. Zhao GJ, Liu JY, Zhou LC, Han KL (2007) Site-selective photoinduced electron transfer from alcoholic solvents to the chromophore facilitated by hydrogen bonding: a new fluorescence quenching mechanism. *J Phys Chem B* 111:8940–8945
36. Zhao GJ, Han KL (2008) Time-dependent density functional theory (tddft) study on the hydrogen-bonded intramolecular charge-transfer excited state of 4-dimethylamino-benzonitrile (DMABN) in methanol. *J Comput Chem* 29:2010–2017
37. Zhao GJ, Han KL (2009) Effects of hydrogen bonding on tuning photochemistry: concerted hydrogen bond strengthening and weakening. *Chem Phys Chem* 9:1842–1846
38. Perun S, Sobolewski AL, Domcke W (2005) Ab Initio studies on the radiationless decay mechanisms of the lowest excited singlet states of 9 H-adenine. *J Am Chem Soc* 127:6257–6265
39. Sobolewski AL, Domcke W (2007) Computational studies of the photophysics of hydrogen-bonded molecular systems. *J Phys Chem A* 111:11725–11735
40. Zhao GJ, Han KL (2007) Ultrafast hydrogen bond strengthening of the photoexcited fluorenone in alcohols for facilitating the fluorescence quenching. *J Phys Chem A* 111:9218–9223
41. Zhao GJ, Han KL, Stang PJ (2009) Theoretical insights into hydrogen bonding and its influence on the structural and spectral properties of aquo palladium(II) complexes:  $\text{cis}-[(\text{dppp})\text{Pd}(\text{H}_2\text{O})_2]^{2+}$ ,  $\text{cis}-[(\text{dppp})\text{Pd}(\text{H}_2\text{O})(\text{OSO}_2\text{CF}_3)]^+(\text{OSO}_2\text{CF}_3)^-$ , and  $\text{cis}-[(\text{dppp})\text{Pd}(\text{H}_2\text{O})_2]^{2+}(\text{OSO}_2\text{CF}_3)^-$ . *J Chem Theor Comput* 5:1955–1958
42. Zhao GJ, Han KL (2007) Novel infrared spectra for intermolecular dihydrogen bonding of the phenol–borane-trimethylamine complex in electronically excited state. *J Chem Phys* 127:024306
43. Wei NN, Li P, Hao C, Wang R, Xiu ZL, Chen JW, Song P (2010) Time-dependent density functional theory study of the excited-state dihydrogen bond O–H···H–Si. *J Photochem Photobiol A Chem* 210:77–81
44. Wei NN, Hao C, Xiu ZL, Chen JW, Qiu JS (2010) Time-dependent density functional theory study on the coexistent intermolecular hydrogen-bonding and dihydrogen-bonding of the phenol– $\text{H}_2\text{O}$ –diethylmethylsilane complex in electronic excited states. *Phys Chem Chem Phys* 12:9445–9451
45. Wei NN, Hao C, Xiu ZL, Chen JW, Qiu JS (2010) Time-dependent density functional theory study on excited-state dihydrogen bonding O–H···H–Ge of the dihydrogen-bonded phenol-triethylgermanium complex. *J Comput Chem*. doi:10.1002/jcc
46. Patwari GN, Ebata T, Mikami N (2001) Electronic and vibrational spectroscopy of dihydrogen bonded 2-pyridone-borane-trimethylamine complex in supersonic jets. *J Phys Chem A* 105:8642–8645
47. Zhao GJ, Han KL (2008) Site-specific solvation of the photoexcited protochloro-phyllide in methanol: formation of the hydrogen-bonded intermediate state induced by hydrogen bond strengthening. *Biophys J* 94:38–46
48. Zhao GJ, Han KL (2009) Role of intramolecular and intermolecular hydrogen bonding in both singlet and triplet excited states of aminofluorenes on internal conversion, intersystem crossing, and twisted intramolecular charge transfer. *J Phys Chem A* 113:14329–14335
49. Frey JA, Leist R, Tanner C, Frey HM, Leutwyler S (2006) 2-pyridone: The role of out-of-plane vibrations on the  $\text{S}_1 \leftrightarrow \text{S}_0$  spectra and  $\text{S}_1$  state reactivity. *J Chem Phys* 125:114308
50. Mastuda Y, Ebata T, Mikami N (1999) Vibrational spectroscopy of 2-pyridone and its clusters in supersonic jets: Structures of the clusters as revealed by characteristic shifts of the NH and C=O bands. *J Chem Phys* 110:8397–8407
51. Mastuda Y, Ebata T, Mikami N (2000) Population labeling spectroscopy for the electronic and the vibrational transitions of 2-pyridone and its hydrogen-bonded clusters. *J Chem Phys* 113:573–580
52. Borst DR, Roscioli JR, Pratt DW, Florio GM, Zwier TS, Müller A, Leutwyler S (2002) Hydrogen bonding and tunneling in the 2-pyridone. 2-hydroxypyridine dimer. Effect of electronic excitation. *Chem Phys* 283:341–354
53. Hazra MK, Chakraborty T (2008) Impact of methyl rotor in the excited state level mixing of doubly hydrogen-bonded complexes of 2-pyridone. *J Phys Chem A* 112:1100–1104
54. Sagvolden E, Furche F, Köhn A (2009) Förster energy transfer and davydov splittings in time-dependent density functional theory: lessons from 2-pyridone dimer. *J Chem Theor Comput* 5:873–880

55. Zhao GJ, Han KL (2008) pH-Controlled twisted intramolecular charge transfer (TICT) excited state via changing the charge transfer direction. *Phys Chem Chem Phys* 12:8914–8918
56. Zhao GJ, Han KL, Lei YB, Dou YS (2007) Ultrafast excited-state dynamics of tetraphenylethylene (TPE) studied by semiclassical simulation. *J Chem Phys* 127:094307
57. Zhao GJ, Northrop BH, Han KL, Stang PJ (2010) The effect of intermolecular hydrogen bonding on the fluorescence of a bimetallic platinum complex. *J Phys Chem A* 114:9007–9013
58. Zhao GJ, Chen RK, Sun MT, Li GY, Liu JY, Gao YL, Han KL, Yang XC, Sun LC (2008) Photoinduced intramolecular charge transfer in thiophene- $\pi$ -conjugated donor-acceptor systems: combined experimental and TDDFT studies. *Chem Eur J* 14:6935–6947
59. Zhao GJ, Han KL (2007) Early time hydrogen-bonding dynamics of photoexcited coumarin 102 in hydrogen-donating solvents: theoretical study. *J Phys Chem A* 111:2469–2474
60. Li GY, Zhao GJ, Liu YH, Han KL, He GZ (2010) TD-DFT study on the sensing mechanism of a fluorescent chemosensor for fluoride: Excited-state proton transfer. *J Comput Chem* 31:1759–1765
61. Zhao GJ, Han KL (2009) Excited-state electronic structures and photochemistry of heterocyclic annulated perylenes (HAPs) materials tuned by heteroatoms: S, Se, N, O, C, Si, and B. *J Phys Chem A* 113:4788–4794
62. Zhao GJ, Northrop BH, Stang PJ, Han KL (2010) Photophysical properties of coordination-driven self-assembled metallosupramolecular rhomboids: experimental and theoretical investigations. *J Phys Chem A* 114:3418–3422
63. Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* 98:5648–5652
64. Schäfer A, Huber C, Ahlrichs R (1994) Fully optimized contracted Gaussian basis sets of triple zeta valence quality for atoms Li to Kr. *J Chem Phys* 100:5829–5835
65. Ahlrichs R, Bär M, Horn H, Kölmel C (1989) Electronic structure calculations on workstation computers: the programssystemturbo-mole. *Chem Phys Lett* 162:165–169
66. Jakalian A, Jack DB, Bayly CI (2002) Fast, efficient generation of high-quality atomic Charges. AM1-BCC model: II. parameterization and validation. *J Comput Chem* 23:1623–1641
67. Dmitrova Y, Peyerimboff SD (1993) Theoretical study of hydrogen-bonded formaldehyde-water complexes. *J Phys Chem* 97:12731–12736
68. Boys SF, Bernardi F (1970) The calculation of small molecular interactions by the differences of separate total energies. Some procedures with reduced errors. *Mol Phys* 19:553–566
69. Gutowski M (1993) Critical evaluation of some computational approaches to the problem of basis set superposition error. *J Chem Phys* 98:5440–5554