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Tunable Dipole Induced Hydrogen Bonds Between a Hydrogen Molecule and Alkali Halides

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Hydrogen bonding (HB) systems are known to be X-H···Y type complexes which are called conventional HB systems if the X and Y are strongly electronegative atoms such as O, N and halides or unconventional ones if the X is replaced by C. In this work, we devise a new dipole-induced HB that is formed between a hydrogen molecule and an alkali halide using *ab initio* calculations. The HB is depicted as H-H ···Y-M, with MY being alkali halides. Analysis of the possible structures and properties of the proposed compounds, including their geometries, frequencies, bond strength, natural charge distribution, and a topological analysis of electronic density, shows that the large dipole moment of the Y-M molecule is responsible for the generation of the proposed HB. We also find that the strength of HB can be tuned by adopting MY with various polarities. We hope our findings could provide a new insight into HB.

1. Introduction

Hydrogen bonds (HB) are formed between two molecules with strongly contrasting electronegativity, one of which is terminated by a hydrogen atom. This form of bonding has been studied for more than a century, and remains an active topic in contemporary scientific research.[1,2] The reason for this widespread and long-lasting attention is due to the important role of HB in numerous physical, chemical, and biochemical processes.[3-7] One of the first definitions of HB was formulated by Pauling in 1939, in his classic *The Nature of the Chemical Bond*.[8] According to him, HB may be depicted as X-H···Y, where X-H is the typical polarized covalent bond and proton donating moiety and Y is a proton-accepting center. In conventional HB, X and Y are electronegative atoms such as O, N, F, and Cl. Consider the most common case, H_2O in the water phase and ice in various phases. The Coulomb attraction between the proton (H) and the acceptor (O) is mainly responsible for the formation energy of the HB. As a result, HB usually occurs with group VII, VI, and V elements, due to their large electron affinity and a certain iconicity in the directional assembling which keeps the surrounding molecules locally ordered (for example, ice in the Ih phase). However, it is still a weak interaction within the extent of the van de Waals interacting distance, since it is induced by electrostatic dipole-dipole interactions. Over time, the concept of HB has continued to evolve,[9-11] with a new International Union of Pure and Applied Chemistry (IUPAC) definition having recently been put forward.[12,13] The previous model has now been extended to include some so-called unconventional HB, which may be generalized in four ways; 1) HB with C-H bonds as unconventional proton donors;[14,15] 2) HB with unconventional acceptors (π electrons within aromatic systems, the other π-electronic moieties, the simple C-atom, the C≡C bond, or even the transition metal atoms);[16-19] 3) HB with unconventional donors and acceptors such as C-H···C (or C-H···π) systems;[20-24] and 4) dihydrogen bonds (X-H···H-M or X-H···Si-H or C-H···H-C, where M represents a metal atom).[25-30]

HB involving the C-H group is usually weaker, with a bond strength of 3 kcal/mol or less, because the CH group is less electronegative.[31] Brammer's work on ligand domain HB shows that the polarity $M^{\delta+}–Y^{\delta-}$ (where M denotes a metal atom and Y halogen atoms such as F, Cl, Br, and I) could be a good HB acceptor, forming substantially shorter (and hence stronger) HB than the corresponding Y-C acceptor groups.[32] This illustrates that the presence of a metal atom can enhance the HB capability of halogens. Moreover, many spectroscopic and theoretical studies have shown that the H_2 molecule tends to establish a linear hydrogen bond with halide anions,[33-35] while the integrity of the H_2 subunit is largely maintained in the complex..

According to these spectroscopic and theoretical prototypes, poorly electronegative atoms can form HB through the strong polarity molecular induction. To test this proposition, we devise and elaborate a new type of HB geometry; H-H···Y-M. Here, M=Li, Na, K; Y = F, Cl, Br. In the present paper, the structural possibilities, energy, and characteristics of the H-H···Y-M type HB will be explored using *ab initio* calculations. The possible structures and some properties as frequencies, bond strength, natural charge distribution, and a topological analysis of electronic density will be discussed also.

2. Computational details

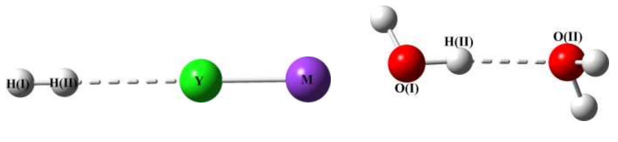
London dispersion forces are important or even dominant in noncovalent HB interactions, which are caused by favorable instantaneous or induced multipolar charges.[36] The second-order Møller-Plesset perturbation theory (MP2) is the most commonly used method for describing the properties of HB because it includes the electron correlation for capturing the dispersion interaction which approximately accounts for the uncoupled and two-body electron correlations.[16,22] However, some *ab initio* studies indicate that the MP2 method tends to overestimate binding in noncovalent interactions. The CCSD(T) method including the perturbative estimate of three-body correlations is very reliable and has been referred to as the "gold standard" of quantum chemistry calculations.[36,37] The Pople type basis sets, such as 6-31G, 6-311G, etc., and the Dunning correlation consistent basis sets, such as aug-cc-pVDZ, aug-cc-pVTZ, etc., are widely used. However, the potassium (K) in the present study systems is not included in Dunning type basis set. Wiberg's study[38] have proved the 6-311++G** basis set generally gives more satisfactory geometries than aug-cc-pVDZ. Moreover, the 6-311++G** basis set is smaller, and therefore has significantly higher computational efficiency than aug-cc-pVDZ. As a consequence, the geometric optimization and vibrational frequencies were performed by MP2 method with the largest basis set 6-311++G(3df, 3pd), and the 6-311++G** basis set was used for comparison. The frequencies of all optimized structures were calculated at the same level and without soft modes, indicating that the systems genuinely corresponded to local minima. The charge distributions were analyzed using the natural bond orbital (NBO)[39] partitioning scheme at the MP2/6-311++G(3df,3pd) level. Based on the MP2/6-311++G(3df,3pd) optimized geometries, the binding energies calculations were carried out at the CCSD(T) level, and the counterpoise procedure was also considered for removing the basis-set superposition error (BSSE). All the calculations were performed using the GAUSSIAN 09 package.[40]

In this work, a series of H-H ⋯Y-M (Y=F, Cl, Br; M=Li, Na, K) HB complexes was considered and tested. The H-H molecule was chosen as a proton donor while the strongly polarized metal halides such as LiF, KF, NaBr, and so on were chosen as proton acceptors. Moreover, to offer more intuitionistic information of this newly proposed HB, the HB in a water dimer was also calculated following the same calculation procedure.

3. Results and discussion

3.1 Geometric structures

As shown in Figure 1, all the atoms of the H-H ⋯Y-M geometries are in line, so we can define this type of HB complex by three scalar quantities; the H(I)-H(II) covalent bond length, the H(II)⋯Y HB length, and the Y-M distance. It is well known that the formation of HB is usually associated with the change of the proton-donating and -accepting bonds, so we not only list the above-mentioned three scalar quantities, but also the bond lengths of the independent Y-M and H(I)-H(II) in Table 1, calculated by the MP2 method with 6-311++G(3df, 3pd) and 6-311++G** basis set, respectively. The bond length results of the two basis set are basically unanimous. The bond lengths of H(I)-H(II) and M-Y are all elongated with the formation of HB. The H(II)⋯Y distance is much longer than the conventional type HB (usually less than 2 Å), while close to the H⋯C distance (2.66 Å) of the O-H⋯C and the H⋯π distance (2.86 Å) of C-H⋯π,[41] which indicates that the H-H⋯Y-M HB should be weak.



a b

Fig. 1 Schematic drawing of H-H⋯Y-M (a) complexes (Y=F, Cl, Br; M=Li, Na, K) and water dimer complex (b).

Table 1 demonstrates some trends in the geometrical parameters. To clarify these, the relationship between the H(I)-H(II) bond length (in Å) versus (vs.) the H⋯Y distance (Å) and M-Y bond length (Å) vs. the H⋯Y distance (Å) for a series of alkali halide as HB acceptors is shown in Figure 2. It can be seen from Figure 2 and Table 1 that for the same halide Y, the same set of alkali metals M, or the same alkali with difference halides, the shorter the H((I)-H(II) bond length, the longer the H⋯Y distance (as denoted by the red line in Figure 2). Furthermore, for the same halide Y and the different alkali metals M, the shorter the M-Y bond length, the longer the H⋯Y distance, and for the same alkali M and different Y, the shorter the M-Y bond length, the shorter the H⋯Y distances (denoted by the purple line in Figure 2). The HB distances of H(II)⋯Y in H-H ⋯Y-M are all longer than that of the water dimer ($r_{H(II)\cdots O(II)}$ =1.9425 Å).

Table 1. Bond length parameters (Å) (r^0 represents the independent bond length of M-Y and H-H; r the bond length of the complex M-Y ⋯ H-H) and frequencies ν/cm^{-1} calculated using MP2 with 6-311++G** and 6-311++G(3df, 3pd) basis set, respectively.

Proton acceptor	MP2	$r_{H(I)-H(II)}$	$r_{H(II)\cdots Y}$	r_{Y-M}	r^0_{Y-M}
LiF	6-311++G**	0.7425	2.3710	1.6010	1.5997
	6-311++G(3df,3pd)	0.7414	2.3174	1.5937	1.5917
NaF	6-311++G**	0.7449	2.2705	1.9929	1.9914
	6-311++G(3df,3pd)	0.7440	2.2110	1.9876	1.9843
KF	6-311++G**	0.7460	2.2216	2.2309	2.2255
	6-311++G(3df,3pd)	0.7447	2.1965	2.2030	2.1985
LiCl	6-311++G**	0.7396	3.2038	2.0221	2.0210
	6-311++G(3df,3pd)	0.7387	2.9520	2.0438	2.0421
NaCl	6-311++G**	0.7402	3.1385	2.3810	2.3789
	6-311++G(3df,3pd)	0.7394	2.8949	2.4033	2.4014
KCl	6-311++G**	0.7408	3.0176	2.7028	2.6986
	6-311++G(3df,3pd)	0.7399	2.8824	2.7030	2.7002
LiBr	6-311++G**	0.7394	3.3752	2.1882	2.1827
	6-311++G(3df,3pd)	0.7382	3.1806	2.2012	2.1993
NaBr	6-311++G**	0.7397	3.3258	2.5384	2.5346
	6-311++G(3df,3pd)	0.7388	3.1293	2.5506	2.5490
KBr	6-311++G**	0.7407	3.3297	2.8634	2.8517
	6-311++G(3df,3pd)	0.7392	3.1139	2.8596	2.8574

$r^0_{H(I)-H(II)}$ = 0.7366 [6-311++G(3df,3pd)], 0.7431(6-311++G**)

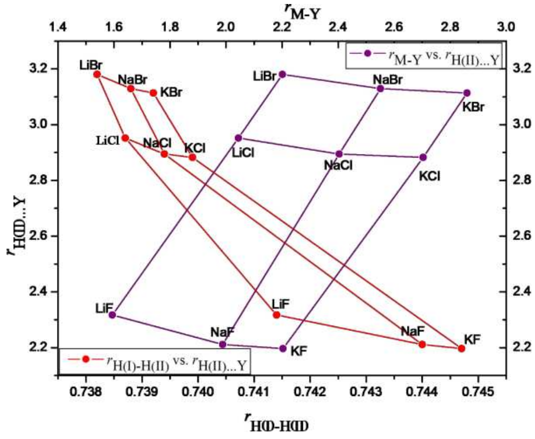


Fig. 2 Relationship between the H(I)-H(II) bond length $r_{H(I)-H(II)}$ (Å) vs. H(II)⋯Y distance $r_{H(II)\cdots Y}$ (Å) and M-Y bond length r_{M-Y}(Å) vs H(II)⋯Y distance $r_{H(II)\cdots Y}$ (Å) for a series of alkali halides as HB acceptors at MP2/6-311++G(3df, 3pd) level of calculations.

3.2. Vibrational frequency analysis

With the formation of HB, the H-H bond in all configurations is elongated, and the H-H bond stretching vibration frequency decreases (that is, red shifts) associated with the increase of intensity in the infra-red (IR) spectrum. This is a so-called proper red-shift type HB.[42] The frequency of H(II)···Y and the corresponding intensity on the IR spectrum are also listed in Table 2. It can be seen that the frequency of the H(II)···Y vibration tends to be higher as the bond length of H-H, $r_{H\text{-}H}$, increases. In terms of the intensity of the H-H bond vibration, the trend is varied and does not show a monotonous transition, in order to equilibrate the charge redistribution and stabilize the total energy of the H-H···Y-M complex system. For the water dimer, the frequency of H(II)···O(II) vibration is at 3768.21 cm^{-1}, and the corresponding intensity is 296.5252 kM/mol).

Table 2. Correlation of H-H bond length, H-H stretching vibrational frequency, and IR intensity of H-H with a series of alkali halides (results calculated using MP2/ 6-311++G(3df, 3pd)).

	LiF	NaF	KF	LiCl	NaCl	KCl	LiBr	NaBr	KBr
$r_{H\text{-}H}$(Å)	0.7414	0.7440	0.7447	0.7387	0.7394	0.7399	0.7382	0.7388	0.7392
Frequency $\omega_{H\text{-}H}$ (cm^{-1})	4434.83	4386.84	4371.87	4482.94	4468.95	4460.13	4490.62	4479.74	4471.55
Intensity (kM/mol) for H-H	69.6611	124.4388	160.8448	26.9180	44.8093	58.9932	19.6279	32.4518	44.2875
Frequency $\omega_{H(II)\cdot\cdot Y}$ (cm^{-1})	204.44	223.75	226.64	147.80	159.98	163.12	121.07	132.67	137.18
Intensity (kM/mol) for H(II)··Y	3.6198	4.44078	3.6358	0.5860	0.4558	0.135	0.3481	0.3565	0.2250

The IR vibration mode of an isolate H_2 molecule is at ω^0=4517.64 cm^{-1} (MP2) with zero intensity.

3.3 Charge analysis

The NBO, AIM and ESP charge calculations were performed at the MP2/6-311++G(3df, 3pd) level for the H-H ··· Y-M complex structures. The results of calculations are summarized in Table 3. It is seen that the AIM results compare better than the ESP results with the NBO results.

Previous work on X-H···Y type HB shows that X-H is a polarity, while in our X-H ··· Y-M type HB, the X-H part is just the neutral H_2 molecule. The isolate H_2 molecule is neutral, and the charges of both atoms are zero. However, with the HB forming, the charge of the H_2 molecule changes induced by the strong polarity of the alkali halide. The H(II) which are near Y are all positive, while H(I) are all negative. Based on NBO and AIM calculations, the total charge of the H(I)-H(II) units in all structures are slightly negative, so that when the H_2 molecule interacts with the MY, H(I)-H(II) unit as a proton donor transfers a small amount to the proton acceptor MY. The negative charges of Y are all less than q_{Y_0}, and the positive charges of M are all more than q_{M_0} (equal in magnitude to q_{Y_0}, while opposite in sign), indicating that both M and Y accept some protons during HB formation and so M has promoted the proton transfer.

Table 3. NBO, AIM and ESP charges *q* (e) for the H-H ··· Y-M complexes and the charge of of the isolate molecule MY.

H(I)-H(II)···		$q_{H(I)}$	$q_{H(II)}$	q_Y	q_M	q_{Y_0}
LiF	NBO	-0.066	0.062	-0.945	0.949	-0.947
	AIM	-0.081	0.080	-0.944	0.945	-0.945
	ESP	-0.069	0.081	-0.903	0.891	-0.862
NaF	NBO	-0.086	0.080	-0.979	0.985	-0.983
	AIM	-0.107	0.104	-0.948	0.949	-0.949
	ESP	-0.085	0.087	-0.921	0.919	-0.901
KF	NBO	-0.090	0.084	-0.969	0.975	-0.973
	AIM	-0.112	0.109	-0.937	0.940	-0.938
	ESP	-0.059	0.024	-0.081	0.847	-0.853
LiCl	NBO	-0.033	0.029	-0.886	0.889	-0.886
	AIM	-0.041	0.036	-0.930	0.934	-0.934
	ESP	-0.100	0.164	-0.881	0.817	-0.886
NaCl	NBO	-0.042	0.037	-0.943	0.947	-0.944
	AIM	-0.052	0.046	-0.917	0.923	-0.923
	ESP	-0.096	0.145	-0.911	0.862	-0.820
KCl	NBO	-0.048	0.043	-0.948	0.952	-0.950
	AIM	-0.060	0.051	-0.914	0.922	-0.920
	ESP	-0.089	0.107	-0.854	0.836	-0.819
LiBr	NBO	-0.026	0.023	-0.860	0.863	-0.860
	AIM	-0.033	0.027	-0.927	0.932	-0.932
	ESP	-0.065	0.131	-0.882	0.816	-0.753
NaBr	NBO	-0.034	0.029	-0.924	0.928	-0.925
	AIM	-0.042	0.035	-0.907	0.914	-0.914
	ESP	-0.070	0.132	-0.918	0.856	-0.801
KBr	NBO	-0.040	0.035	-0.935	0.939	-0.938
	AIM	-0.046	0.039	-0.891	0.897	-0.916
	ESP	-0.060	0.054	-0.946	0.952	-0.95

3.4. Bond strength analysis

3.4.1 Bond strength and BSSE estimation

Table 4 presents the total and HB energies between a series of alkali halides and one H_2 molecule (MP2 and CCSD(T) results). The estimation of BSSE for all of the structures presented here was performed using the full counterpoise method at both the MP2 and CCSD(T) levels. The HB energies can be derived from the following formula:

$$E_{HB} = E_{MY} + E_{H_2} - E_{complex} - E_{BSSE} \qquad (1)$$

The calculated HB energies range from 0.48-2.04 kcal/mol, putting them in the range of weak HB interactions.[31] The energies in this scale can be compared with C-H/π and NH/π interactions.[16] The HB energy of the water dimer is 5.13 kcal/mol by CCSD(T)/6-311++G(3df,3pd) calculation.

Because the proton donors are the same as the H_2 molecule, the bond strength will reside in the acceptor MY. We can see from Table 4 that the same Y with different M does not correspond to the same HB strength, so M should be also the factor restricting the bond strength. When Y is the same, the influence of M on the bond strength should run in the order K > Na > Li. The more electropositive M is, the stronger the polarization of MY (when Y is the same atom), leading to the stronger HB.

Table 4. Total energies, BSSE, and corrected H-bond energies for H-H ··· Y-M type HB complexes

Proton acceptor		$E_{complex(a.u.)}$	$E_{MY(a.u.)}$	E_{HB} (kcal/mol)
LiF	CCSD(T)	-108.44025	-107.26505	1.40
	MP2	-108.42737	-107.25990	1.31
NaF	CCSD(T)	-262.81880	-261.64278	1.86
	MP2	-262.80644	-261.63823	1.74
KF	CCSD(T)	-700.37556	-699.19914	2.04
	MP2	-700.33659	-699.16800	1.90
LiCl	CCSD(T)	-468.44326	-467.26920	0.58
	MP2	-468.41066	-467.24420	0.60
NaCl	CCSD(T)	-622.83579	-621.66135	0.73
	MP2	-622.80340	-621.63655	0.74
KCl	CCSD(T)	-1060.3907	-1059.2161	0.83
	MP2	-1060.3325	-1059.1655	0.83
LiBr	CCSD(T)	-2581.2797	-2580.1061	0.48
	MP2	-2581.2503	-2580.0842	0.50
NaBr	CCSD(T)	-2735.6752	-2734.5013	0.59
	MP2	-2735.6460	-2734.4797	0.61
KBr	CCSD(T)	-3173.2305	-3172.0565	0.68
	MP2	-3173.1755	-3172.0090	0.69

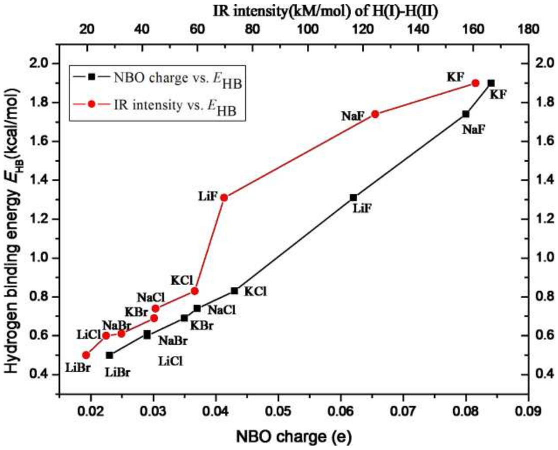


Fig. 3 Relationship between the HB energy, IR intensity of H(I)-H(II), and NBO charge of H(II).

3.4.2 Bond strength with IR intensity and NBO charge

Moreover, we find some interesting relationships between the intensity of the IR spectrum, NBO charge distributions, and corresponding HB strength. As seen in Figure 3, as the HB length increases, so also does the NBO charge of H_2 and the intensity of the and IR intensity might be practical and useful criteria for measuring the relative values strength of HB.

3.4.3 Bond strength and dipole moment

As is well known, the strength of conventional HB is partly related to the dipole-dipole interaction. When the H atom bonds with a strongly electronegative X, the charges are unevenly distributed between the two atoms (H and X) leading H to almost become a positive proton. When this encounters a strongly electronegative Y atom, there will be an electrostatic attraction. Our H-H ··· Y-M type HB represents the other style of bonding. The dipole moment of the neutral H_2 molecule is zero, as is the charge on both H atoms. However, when the H_2 molecule approaches the strongly polarized alkali halide complexes, an induced dipole will occur. Then, the H(II) and MY will mainly be bound through the well-known induced energy. The induced energy and dipole moment can be calculated from the following equation[43]:

$$E = -\frac{a_2 \mu_1^2}{(4\pi\varepsilon_0) r^6} \qquad (2)$$

where E is the induced energy, a_2 is the polarizability of the induced molecule H(II), μ_1 is the dipole moment of MY, and r is the distance H(II)···Y.

Table 5. MP2/6-311++G(3df, 3pd) calculated isolate dipole moment μ_0 (Debye) of MY and the HB energy between one H_2 molecule.

	FLi	FNa	FK	ClLi	ClNa	ClK	BrLi	BrNa	BrK
μ_0	6.5916	8.6134	8.9789	7.3729	9.4201	10.7435	7.5787	9.6211	11.1694
E_{HB} (kcal/mol)	1.31	1.74	1.90	0.60	0.74	0.83	0.50	0.61	0.69

To further understand the relationship between HB strength and the dipole moment, we list the calculated dipole moment values in Table 5, and also illustrate their relationship in Figure 4.

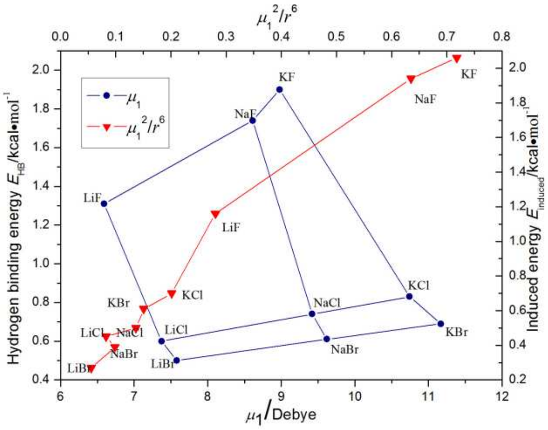


Fig. 4 The HB energy via dipole moment of isolate MY (blue lines) and the induced energy via μ_1^2 / r^6 (red line).

From Table 5 and Figure 4 (blue line), we can see that complexes with different M and the same Y correspond to the difference in dipole moment as well as the binding energy. In MY where Y is the same and M is different, the binding energy increases with the dipole moment, so M as well as Y influences the strength of HB. The order of the influence of M on HB strength runs K > Na > Li. Consequently, we propose that one can use the metal decorating method to increase the energy of HB and can even use different metals to produce "tuneable" HB strength in compounds. However, the HB strength decreases with the increase of the dipole moment when M aligns with the same element, since the change in bonding distance is significant between different Y atoms.

Moreover, to search for the relationship of the induced energy with μ_1^2 / r^6 as represented in the equation 2, the energy decompostion scheme has been used to obtain the induced force. The total interaction energy i.e. HB strength, can be decomposed according to the following equation [44]:

$$\Delta E_{HB} = \Delta E_{electrostatic} + \Delta E_{exchange-repulsion} + \Delta E_{orbital} + \Delta E_{dispersion} \qquad (3)$$

where $\Delta E_{electrostatic}$ corresponds to the electrostatic interaction energy, $\Delta E_{exchange\text{-}repulsion}$ is the exchange repulsion interaction energy, and the $\Delta E_{orbital}$ arises from the mix of occupied molecular orbitals and virtual molecular orbitals, also known as induced strength or polariton strength [45,46]. As seen from the Figure 4 about the induced energy with μ_1^2 / r^6 (red line), the induced strength increases with μ_1^2 / r^6, and the relationship between induced strength and μ_1^2 / r^6 is close to a straight line through the origin point. This is consistent with the linear relationship of the equation 2.

3.5. Topological analyses

Bader et al. proposed the "atoms in molecules" (AIM) methodology in 1970[47] to evaluate the charge density by means of topological parameters such as the proper electronic density ρ(r) and the Laplacian field $\nabla^2\rho(r)$. However, it has become more popular in recent years due to its extensive application to understanding the properties of molecules and the relationships between geometrical and energetic parameters. In addition, the AIM methodology has been successfully applied in the study of the properties of a variety of conventional and unconventional HB.[48-50] Such topological analyses enable us to know more about HB through the recognition of the critical points (CP) of chemical bonds and HB.

Table 6 AIM topological parameters $\rho(r)$ and $\nabla^2\rho(r)$.

	H(I)-H(II)···Y-M complex						Isolated	
	H-H bond		H(II)···Y bond		M-Y bond		M-Y bond	
	$\rho(r)$	$\nabla^2\rho(r)$	$\rho(r)$	$\nabla^2\rho(r)$	$\rho(r)$	$\nabla^2\rho(r)$	$\rho(r)$	$\nabla^2\rho(r)$
LiF	0.270	-1.23	0.010	0.039	0.070	0.677	0.070	0.680
NaF	0.268	-1.218	0.013	0.050	0.045	0.365	0.045	0.370
KF	0.268	-1.214	0.013	0.052	0.051	0.301	0.052	0.305
LiCl	0.272	-1.245	0.005	0.018	0.044	0.257	0.044	0.259
NaCl	0.272	-1.241	0.006	0.020	0.032	0.181	0.032	0.182
KCl	0.271	-1.238	0.006	0.020	0.031	0.134	0.031	0.135
LiBr	0.272	-1.247	0.004	0.013	0.038	0.192	0.038	0.193
NaBr	0.272	-1.244	0.005	0.014	0.028	0.142	0.028	0.142
KBr	0.272	-1.242	0.005	0.015	0.027	0.106	0.027	0.104

* For the isolate H-H bond: $\rho(r)=0.273$, $\nabla^2\rho(r) =-1.255$

* $\rho(r)$ and $\nabla^2\rho(r)$ are given in e/a_0^3 and e/a_0^5 respectively.

Table 6 presents the values of $\rho(r)$ and $\nabla^2\rho(r)$ for the complexes and isolated monomers analyzed here. It lists the values for the covalent H-H bond, ionic accepting bond (M-Y), and the nonbonding HB (H···Y). Usually, $\rho(r)$ is used to estimate the strength of a bond, with a larger value denoting a stronger bond, while $\nabla^2\rho(r)$ is used to describe the properties of the bond. From Table 6, we can see that there is a positive correlation between the $\rho(r)$ of H···Y bond and the HB energy, which is consistent with AIM theory. The positive values of $\nabla^2\rho(r)$ in the H···Y bond indicate the possibility of this type of HB. The electron density $\rho(r)$ and its Laplacian $\nabla^2\rho(r)$ for the H(II)···Y contact within the conventional X-H···Y bond are all positive and should lie within the following ranges; 0.002-0.04 for $\rho(r)$ and 0.02-0.15 for $\nabla^2\rho(r)$.[51] As can be seen from Table 6, the calculated values of $\rho(r)$ are strictly within the range, while some of the $\nabla^2\rho(r)$ values are less than its lower bounding limit, so the HB strength of H-H···Y-M is weaker than for conventional HB.

4. Conclusions

H-H is found to be a proton donor forming a new type of HB depicted as H-H···Y-M. The four-atom complex of this type of HB is all in a line, with the bond length of M-Y and H-H slightly elongated when forming HB and the H···Y distance longer than in conventional HB. This is a proper red-shift type of HB because the bond length of H-H is elongated and the vibration frequency of the H-H stretch has decreased. The bond strength from 0.48 kcal/mol to 2.04 kcal/mol, which belongs to the range of weak HB interaction, and also the long distance of H··Y and the low values for the electronic density $\rho(r)$ and the Laplacian field $\nabla^2\rho(r)$, confirm the conclusion that the bond is weak. The NBO charge of H_2 and the IR spectrum intensity of H-H stretching are positively correlated with the strength of HB so might act as the criteria for relative HB strength. The strong polarization of the alkali halide promotes the formation of HB with the neutral H_2 molecule.

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Notes and references

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