The intrinsic strength of non-covalent interactions described by coupled cluster theory.

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Introduction:

Directional non-covalent interactions guide self-assembly of complex supramolecular structure, stabilize the tertiary structure of proteins and DNA/RNA, lead to drug-receptor recognition to name a few applications [1]. Recently, our group have systematically investigated more than 300 complexes formed by different kinds of non-covalent interactions [2-4]. We compare here the strength of some of these complexes including also tetrel bonded complexes not previously studied.

Computational Methods:

In the present study we combine vibrational spectroscopy with high accuracy CCSD(T)/aug-cc-pVTZ calculations to investigate the strength of 14 different complexes involving hydrogen (HB), halogen (XB), chalcogen (ChB), pnictogen (PnB) and tetrel bond (TrB) (Figure 1). The parameter chosen for the quantitative evaluation of the strength of these interactions is the local stretching force constant (k^a). The k^a of a noncovalent interaction measures the rate of change in the energy for an infinitesimal change in the intermonomer separation, providing a way to probe the strength of a bond without having to break it.

Results

Figure 1. Representation of 14 non-covalently bonded complexes with intermolecular distances.

Table 1. Binding energies (ΔE) in kcal/mol, local stretching forces constants (k^a) in mdyn/Å and type of non-covalent interaction for complexes **1-14**.

#	Complex	ΔE (kcal/mol)	k^a (mdyn/Å)	Type
1	$F_2 \cdots NH_3$	1.7	0.062	XB
2	$Cl_2 \cdots NH_3$	4.4	0.132	XB
3	$FCI \cdots NH_3$	9.4	0.311	XB
4	$FBr \cdots NH_3$	14.1	0.587	XB
5	$FCI \cdots Cl^-$	29.0	0.855	XB
6	$FH \cdots NH_3$	12.1	0.353	HB
7	$FSH \cdots NH_3$	7.6	0.194	ChB
8	$FPH_2 \cdots NH_3$	6.1	0.144	PnB
9	$FSiH_3 \cdots NH_3$	5.9	0.103	TrB
10	$SiF_4 \cdots NH_3$	8.9	0.678	TrB
11	$(FCI)_2$	1.2	0.054	XB
12	$(FCI)_2$	0.7	0.027	XB
13	$(FSH)_2$	3.6	0.097	ChB
14	$(FPH_2)_2$	4.9	0.143	PnB

Discussion:

The halogen bond strength depends on the polarizability of the halogen, the polarizing power of its substituent and the electron donor ability of the halogen-acceptor (complexes **1-5**). By increasing the polarizability of the halogens (complexes **1**, **3**, and **4**) a non-covalent interaction which is stronger than hydrogen bond (complexes **6**) can be achieved. Halogen bond is stronger than the chalcogen, pnictogen or tetrel bonds formed by taking ammonia as a prototypical electron donor in monofluorinated compounds (complexes **3**, **7**, **8**, **9**). Complex **10** forms a stronger interaction than **3** (evidenced by a large k^a). However, its ΔE is lower due to the energetic cost involved in the reorganization of the electronic structure upon complex dissociation, evidencing the limitations of ΔE as an intrinsic strength descriptor. Halogen compounds form the weakest homodimers due to the poor electron donor ability of halogens (complexes **11-14**).

Conclusions:

The local stretching force constants provide a direct and reliable measure of the intrinsic strength of a noncovalent interaction. Halogen bond strength can be easily tuned, making it a versatile tool to be used in the development of new materials. Other types of non-covalent interactions involving main-group elements such as pnictogens and chalcogens are especially useful in systems where a single monomer acts as electron-donor and electron-acceptor as it was shown for the homodimers.

References:

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