Effect of the electronic structure computations on the accuracy of non-reactive collision rates: Application to HCl and DCl in collision with He

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Introduction: Calculations of inelastic rate coefficients need the calculation of highly accurate potential energy surfaces (PESs). These PESs are usually obtained from standard Coupled Clusters methods together large atomic orbital basis sets. However, these calculations are costly in term of CPU time and disk used. A compromise between CPU time and accuracy has to be found. In this poster, we employ the new explicitly correlated coupled clusters methods in order to generate highly accurate PES of HCl-He collision systems in a very reasonable CPU time. Hence, Rotational (de)-excitation cross sections have been calculated for collisions between helium atoms and the diatomic HCl and DCl molecules from a two-Dimensional PES computed at the *ab-initio* CCSD(T)–F12 level using aug-cc-pVTZ basis set. This PES is compared with PESs deduced using standard *ab-initio* methods such as CCSD(T) and Complete Basis Set (CBS) extrapolation. Pressure broadening cross sections were calculated using the Close-Coupling (CC) approach for different transitions and were compared to the experimental values at 300 K.

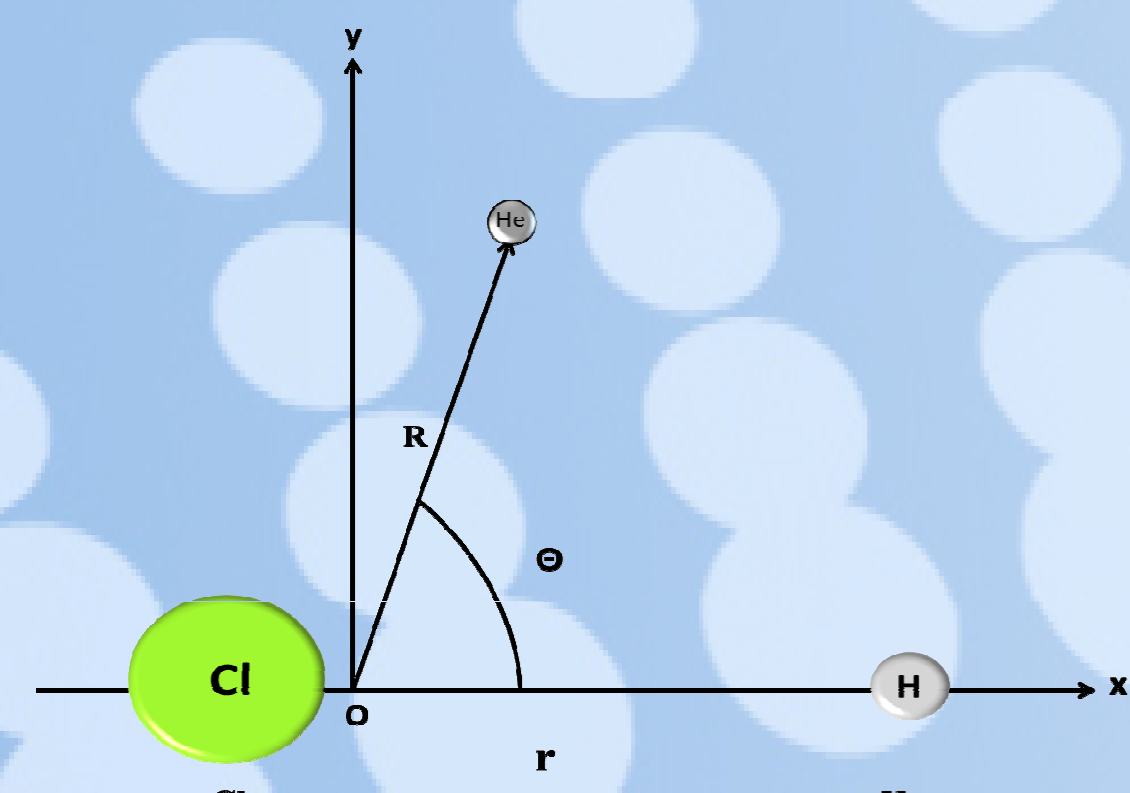## 1- Potential Energy Surfaces (PESs) :

FIG. 1. Jacobi coordinates system of the HCl - He complex.

Tab. 1. Characteristics of a single-point calculation for a total evaluation of the interaction energy of the HCl–He complex.

Method / basis	CCSD(T) / AVTZ	CCSD(T) / AVQZ	CCSD(T) / AV5Z	CCSD(T)-F12 / AVTZ
CPU time/s	13.11	120.00	853.88	14.25
Disk/GB	74.99	731.76	5130	87.43
GTOs [a]	96	176	291	96

[a] Number of contracted Gaussian Functions (GTOs).

- For this work we use the Jacobi coordinates presented in FIG.1.
- Table 1 shows that the computational time (CPU) and the disk usage for a single point calculation is reduced by a factor ~70 for CCSD(T)-F12/aug-cc-pVTZ relative to CCSD(T)/CBS.
- The ab-initio PESs presented in FIG. 2 are calculated for HCl-He system in the supermolecular approach using the CCSD(T)-F12 method with aug-cc-pVTZ basis set for panel (a) and using the CCSD(T) level with CBS extrapolation for panel (b). In all calculations the basis set superposition error (BSSE) is corrected at all geometries. The global minimum in the interaction energy is found to be -32.85 cm^{-1} at R=6.35 bohr and θ=180° for panel (a) and to be -31.96 cm^{-1} at R=6.33 bohr and θ=180° for panel (b) corresponding both of them to collinear He-ClH.
- Compared to standard CCSD(T) calculations with CBS extrapolation we would be required to achieve comparable accuracy with CCSD(T)-F12/aug-cc-pVTZ calculation with a very reduced computing time.
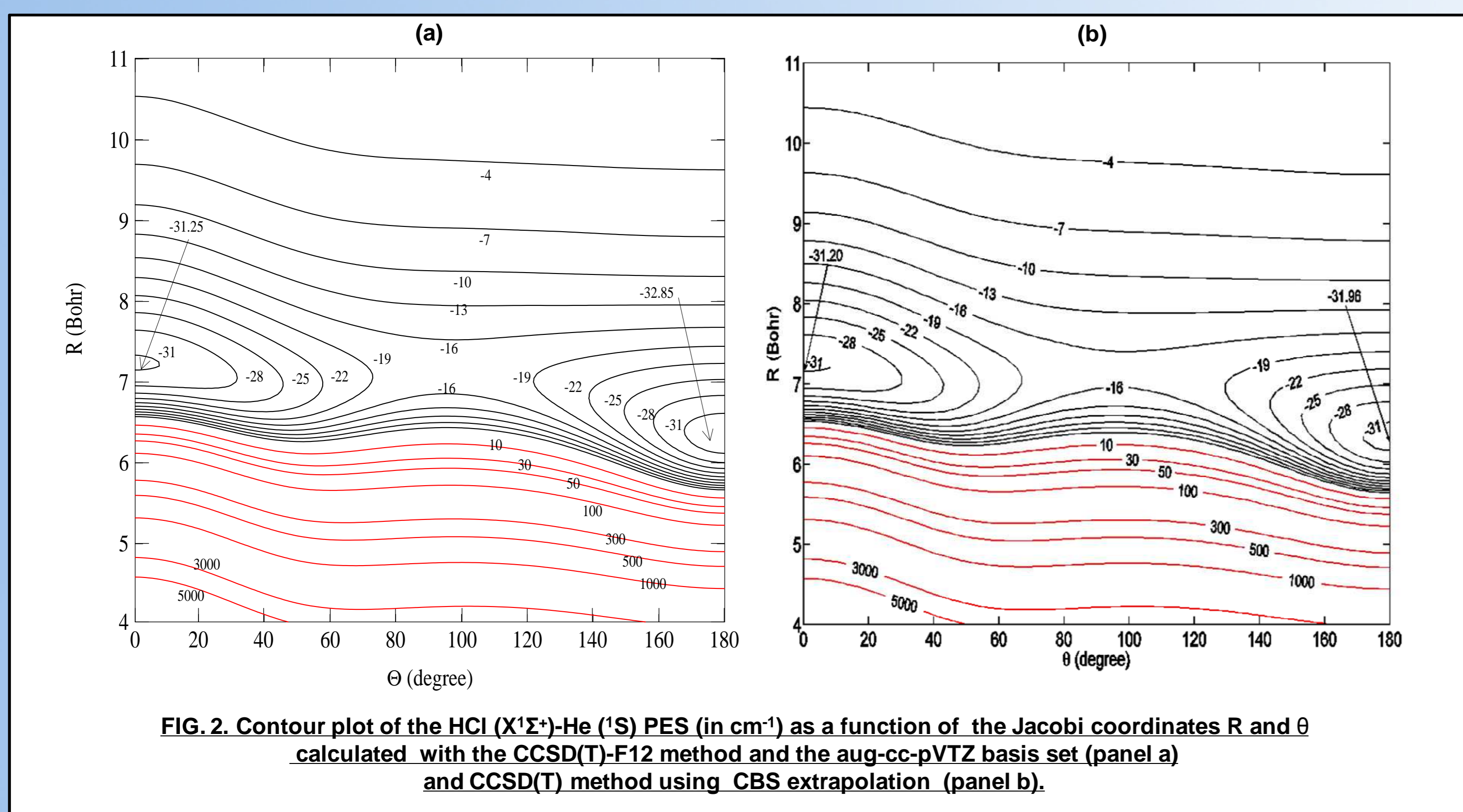

FIG. 2. Contour plot of the HCl ($X^1\Sigma^+$)-He (^1S) PES (in cm^{-1}) as a function of the Jacobi coordinates R and θ calculated with the CCSD(T)-F12 method and the aug-cc-pVTZ basis set (panel a) and CCSD(T) method using CBS extrapolation (panel b).

TAB. 2. Comparison between present and previous minima for selected HCl-He orientations.

Method/Basis	r_{HCl}(bohr)	Θ=0° (HCl-He)		Θ=90°		Θ=180° (He-HCl)	
		R(bohr)	V (cm^{-1})	R(bohr)	V (cm^{-1})	R(bohr)	V (cm^{-1})
CCSD(T)-F12/aug-cc-pVTZ	2.42	7,25	-31,25	7,15	-17,51	6,35	-32,85
CCSD(T)/CBS	2.43	7,24	-31,20	7,15	-16,79	6,33	-31,96
SAPT/A* [1]	2,44	7,28	-30,79	7,16	-17,18	6,33	-32,81
CCSD(T)/aQZ [2]	2,42	7,24	-30,10	7,24	-15,12	6,43	-29,40
CCSD(T)/aug-cc-pV5Z [3]	2,43	7,24	-31,16	7,14	-17,33	6,33	-32,74
EP2 [4]	-	7,33	-28,40	7,04	-	6,48	-32,80
EP1 [5,6]	-	7,40	-14,90	7,08	-	6,68	-15,50

- TAB. 2. shows the positions of the minima and of the well depths for three selected He orientations. We compare our results with those published recently. From this table one can see that the position of the minimums of our PES are in good agreement with results obtained by Murdachaew et al. (2004) and Cagidefajin & Fernandez (2006).
- The CCSD(T)-F12 method associated with the aug-cc-pVTZ basis set gives results as accurate as standard Coupled Clusters method with a much larger basis (at least aug-cc-pV5Z). In addition, it leads to a large reduction of the cost of electron structure computations without deterioration of the accuracy. The F12 correction can explain the overestimation of the well depth of the minima in the PES comparing to that computed with CCSD(T)/CBS.

2- Long-Range interactions :

In order to understand which potential has correct asymptotic behavior, we have performed SAPT [7] calculations in CBS limit and analytical calculations of the interaction energy on the basis of multipolar expansion.

In FIG. 3. for the ClH-He arrangement, a good agreement is obtained with the potential calculated at the CCSD(T)/CBS and CCSD(T)/aug-cc-pVTZ with SAPT/CBS. However, in FIG.4. with HCl-He arrangement there is differences between the two potentials and the CCSD(T)-F12 method fails to describe correctly the interaction energy at long-range whereas CCSD(T) leads to an excellent agreement with SAPT and analytical description of the potential. This is because of the non-consistency of F12 methods.
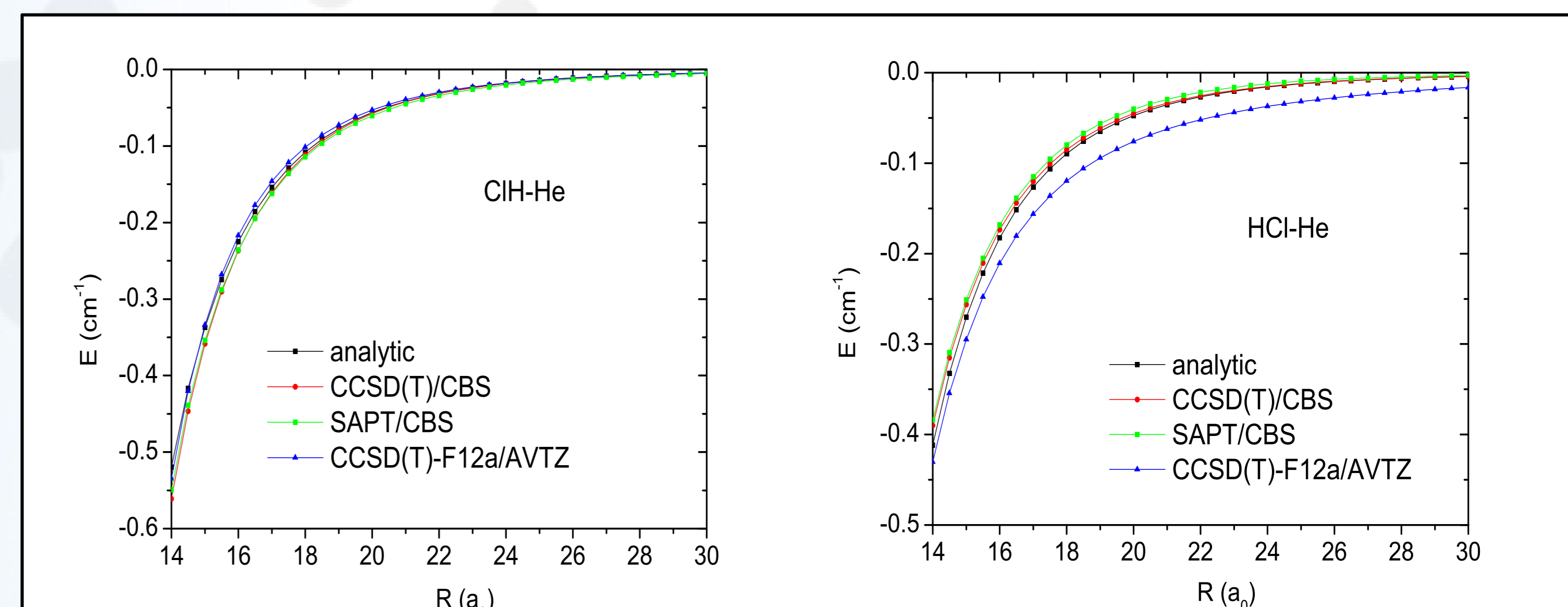

FIG. 3. Interaction potential $V(R)$ of the HCl-He arrangement.

FIG. 4. Interaction potential $V(R)$ of the HCl-He arrangement.

3- Pressure broadening cross sections :

TAB. 3. Pressure broadening cross sections for HCl and DCl broadened by He at 300 K

	J-J'	CCSD(T-)F12/aug-ccpVTZ	CCSD(T)/CBS	Neufeld et al. [8]	Willey et al. [4]	Experimental
HCl	0-1	9.618	9,624	9.8	-	13.20 [9]
	1-2	8.464	8,451	9.4	-	
	2-3	8.099	8,095	9.5		
	3-4	7.791	7,822	-		8.60 [9]
DCl	0-1	11.339	-	-	9.11	9.36 [10]

- Pressure broadening cross sections have been derived from binary scattering *S*-matrix elements computed by MOLSCAT quantum dynamical code using the Close Coupling (CC) method for all the transitions.
- In TAB. 3 we present a comparison of rotational HCl-He and DCl-He pressure broadening cross sections with the experimental values at T=300 K for some transitions. This table shows that our results for HCl-He system are in good agreement with Neufeld et al's theoretical data whereas theirs and ours show differences to the experimental ones. Similar conclusions can be drawn when we compared our data for DCl-He system to those of Willey et al. Further investigations are needed.

4- Conclusions :

The use of our highly correlated CCSD(T)-F12 potential energy surface employing the aug-cc-pVTZ basis set reliably reach conventional aug-cc-pV5Z quality. Our calculations convincingly show that the CCSD(T)-F12 method with Triple-Zeta basis set yields results very close to those one may obtain at the basis set limit, with a very little computational cost. Moreover, the CCSD(T)-F12 method reduces the basis set incompleteness error to an amplitude, which leads to almost no effects on the collision rate constants. Therefore, the application of CCSD(T)-F12 method is highly recommended for all future computations of potential energy surfaces for dynamical purposes.

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