

Ab initio calculations of F-H-Br system with linear geometry

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ABSTRACT

Two potential energy surfaces 1^2A_1 and 1^2B_1 for linear geometry of F-H-Br system have been computed with aug-cc-pVQZ basis set using dynamically weighted state averaged MCSCF followed by MRCI-F12 method. State 1^2A_1 has smaller barrier height (3.49 kcal/mol) than 1^2B_1 . (13.6 kcal/mol). The latter has deep van der Waals well in Br-HF valley (2.12 kcal/mol).

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1. Introduction

Reactions between a halogen atom and hydrogen halide diatomic molecule present a special interest. Many chain reactions comprise them as propagation step. However, first of all an accurate global potential energy surface (PES) is required to initiate the computation. There has been a number of PESs for systems F-H-F¹⁻², F-H-Cl³, Cl-H-Cl⁴⁻⁷, Br-H-Br⁸. Due to open-shell character of such systems multiple electronic states are needed to properly describe the dynamics. To our knowledge systems with bromine and/or iodine atoms were studied using only semiempirical PESs⁹⁻¹⁰. Therefore the goal of this paper is to obtain the accurate *ab initio* PESs for F-H-Br system. Despite the presence of heavy atom, we neglect here by all relativistic effects. Also in this work only linear arrangement of all atoms is considered. Thus this paper represents a first step toward global *ab initio* surfaces for F-H-Br system. The chosen arrangement can be used in the description of the following collinear reactions



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Within chosen linear geometry the molecular system belongs to the C_{2v} point group symmetry. Three lower electronic states are ${}^2\Sigma$ ($1\ {}^2A_1$), ${}^2\Pi_x$ ($1\ {}^2B_1$) and ${}^2\Pi_y$ ($1\ {}^2B_2$) asymptotically correlate to the ground states of $F(^2P)+HBr$ and $Br(^2P)+HF$. The degenerate states ${}^2\Pi_x$ and ${}^2\Pi_y$ are lower at long ranges but in the vicinity of the transition state (TS) area the energy ordering becomes $E({}^2\Sigma) < E({}^2\Pi_x)$. Since these states belong to different symmetry species they cross at some intermediate distances. Such energy reordering is due to different electrostatic interaction. In the TS region the singly occupied p-orbital of the F atom pointing directly towards the H atom of HBr (${}^2\Sigma$ state) gives rise to a more attractive potential than perpendicular singly occupied p-orbital (${}^2\Pi_x$ state) to the FHBr axis. The latter orientation leads to stronger electrostatic interactions at long range. Deviation from linearity reduces the symmetry to C_s and now both ${}^2\Sigma$ and ${}^2\Pi_x$ become the same symmetry states $1\ {}^2A'$ and $2\ {}^2A'$, respectively. They cannot cross anymore and form avoided crossing region.

2. Computational Methods

The geometric configuration of the studied molecular system and notations for internal coordinates is presented in Figure 1. Only two coordinates are needed because as mentioned above it is implied that all three atoms lie along a straight line. These coordinates are interatomic distances R_1 and R_2 as shown in Fig. 1.

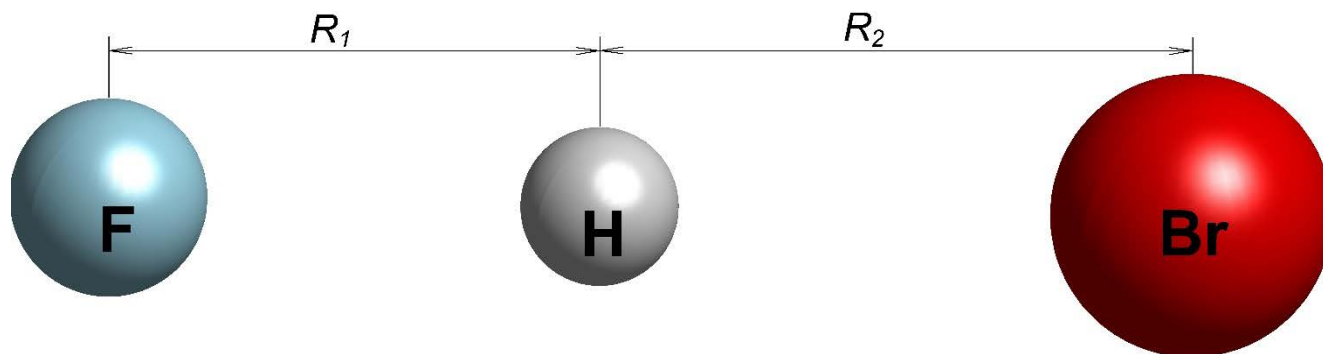


Fig. 1. Geometry of the studied molecular system

All calculations were carried out using Molpro2012 package¹¹. Initial states were calculated using state-averaged multi-configurational self-consistent field (SA-MCSCF) with aug-cc-pVTZ and aug-cc-pVQZ basis sets. As was shown for similar system F-H-Cl³, in the TS area states with charge transfer also must be included in state averaging in order to fully describe molecular system. Therefore a total of six states are included in the dynamically weighting SA-MCSCF calculation (two lowest of each of the following: 2A_1 , 2B_1 , 2B_2) with the decay coefficient $\beta^{-1}=2.78\text{ eV}^{12}$. The active space includes 8 active orbitals ($4A_1$, $2B_1$, $2B_2$, $0A_2$). One valence orbital of A_1 symmetry is closed to excitation in order to keep consistent ordering of orbitals in Molpro and avoid discontinuities in the PESs³. Figure 2 shows six SA-MCSCF states at fixed value of $R_2=3.30a_0$. As seen, states $1\ {}^2A_1$ and $1\ {}^2B_1$ cross at some point. However, the same symmetry states $1\ {}^2B_1$ and $2\ {}^2B_1$ experience avoided crossing. These conical interaction seams make these surfaces unsmooth.

Since MCSCF does not provide sufficiently accurate results, further computations are required. Usually multi-reference configuration interaction (MRCI)¹³ is then employed with initial states obtained within the MCSCF calculation. Our focus is restricted only on three lowest states $1\ {}^2A_1$, $1\ {}^2B_1$ and $1\ {}^2B_2$ (actually two states, because $1\ {}^2B_1$ and $1\ {}^2B_2$ are degenerate everywhere). Instead of conventional MRCI method we used explicitly correlated MRCI-F12¹⁴. This method employs wave functions that explicitly depend on the electron–electron distance. As a result, it has better convergence with basis set. For example, the MRCI-F12 method yields results with near complete basis set limit

accuracy already with triple- ζ basis sets. So the obtained dynamically weighted SA-MCSCF orbitals were used as references in MRCI-F12. The Davidson correction (+ Q) was accounted as well.

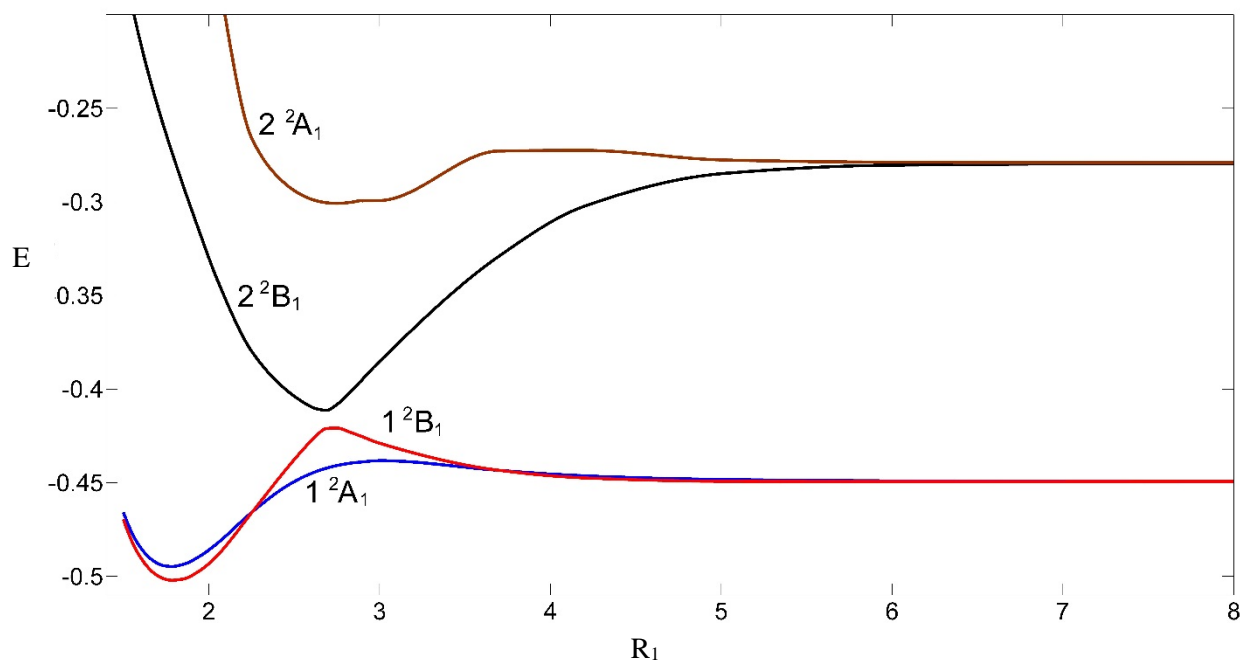


Fig. 2. Six SA-MCSCF states (1^2B_2 and 2^2B_2 coincide with 1^2B_1 and 2^2B_1 , respectively) at $R_2=3.30a_0$ using aug-cc-pVQZ basis set.

A rectangular grid of points $R_1=[1.35-14.0]a_0$ and $R_2=[2.0-14.0]a_0$ was constructed with total number of 567 nodes. The density of the grid was larger in the TS and asymptotic regions. It is necessary to properly sample these important areas of the PESs. Then 2D-cubic spline interpolation was performed using MATLAB® suite and two PESs were generated.

3. Results and Discussion

The first test for *ab initio* calculations is comparison of the asymptotic parameters of the PESs with experimental data. Of course, both PESs coincide here.

Table 1. Parameters for the diatomic molecules derived from the PESs at asymptotic regions compared with experimental data (D_e – dissociation energy, R_e – equilibrium bond length, ZPE – zero point energy, ω_e – harmonic frequency).

	Basis set	D_e , kcal/mol	R_e , a_0	ZPE, kcal/mol	ω_e , cm^{-1}
HF	aug-cc-pVTZ	139.07	1.744	5.93	4144.7
	aug-cc-pVQZ	139.24	1.732	5.92	4138.2
	Experiment ³	141.63	1.733	5.96	4138.3
HBr	aug-cc-pVTZ	92.77	2.696	3.83	2677.3
	aug-cc-pVQZ	92.94	2.692	3.85	2690.5
	Experiment ¹⁵	93.88	2.673	-	2649.3

Table 1 summarizes the dissociation energies, equilibrium distances, zero point energies and harmonic frequencies for two diatomic molecules HF and HBr. The experimental dissociation energy for HBr is given without spin-orbit effect because our calculations neglect it. As seen, there are no significant discrepancies between the results for both basis sets and it would be sufficient to run all computations only with aug-cc-pVTZ basis. However, all further computations used aug-cc-pVQZ basis. It is important to note that even with such a large basis set the computed dissociation energies are not in excellent agreement with the experimental ones. This is not a limitation of MRCI-F12 or basis set convergence but rather the size of the active space. In order to achieve the accuracies of 0.1 kcal/mol, 3sF and 3pF orbitals are to be included into the active space. But this means that all 4dBr orbitals also must be included thus significantly increasing the number of occupied orbitals and making the computation prohibitively expensive. Another check is comparison of exothermicity for $F+HBr \rightarrow Br+HF$ reaction. According to Table 2 the computed ΔH agrees well with the experimental value.

Table 2. Transition state barrier height (E_{barr}), energy difference (ΔE), and exothermicity (ΔH) of reaction (1)

Basis set	E_{barr} , kcal/mol	ΔE , kcal/mol	ΔH , kcal/mol
aug-cc-pVTZ	3.39	-46.30	-48.40
aug-cc-pVQZ	3.49	-46.31	-48.38
Experiment ⁹	-	-	-48.50

Fig. 3a shows the contour plots of 1^2A_1 PES. It is smooth and does not have van der Waals (vdW) wells and conical seams. The TS is located at $R_1=2.85a_0$, $R_2=2.74a_0$ and is of 3.49 kcal/mol high. The 1^2B_1 PES has qualitative differences (Figure 3b). It has the vdW wells in both reactants and product valleys. Also it has conical intersection seams. The saddle point is shifted towards lower F-H and higher H-Br distances ($R_1=2.58a_0$, $R_2=2.86a_0$) and the barrier is much higher namely 13.6 kcal/mol.

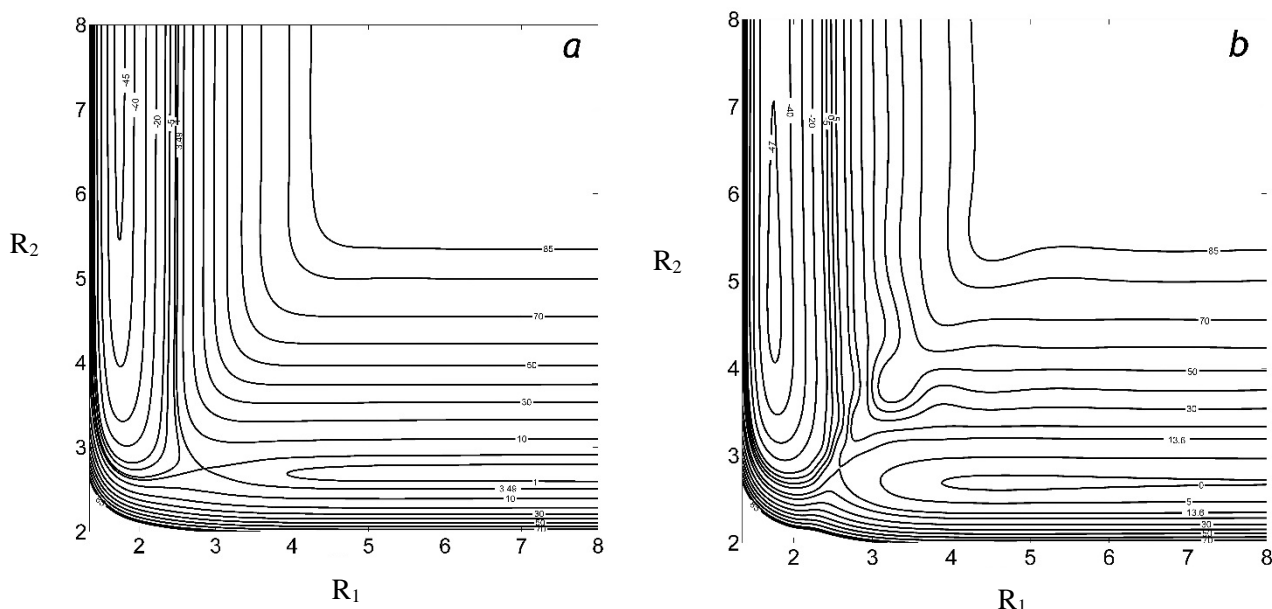


Fig. 3. Contours of 1^2A_1 (a) and 1^2B_1 (b) PESs. The numbers at contour lines represent energy in kcal/mol

The avoided crossing makes this surface discontinuous. Unfortunately these discontinuities lie close to the TS area. But since the barrier height for 1^2A_1 PES is lower, it would not affect the reaction dynamics for this linear configuration.

The 1^2A_1 PES does not exhibit any vdW wells in both reactant and product valleys. It is due to absence of dipole- and quadrupole-quadrupole interaction for this symmetry. However, the 1^2B_1 state has this sort of interaction leading to two vdW wells. The reactant region exhibits a F-HBr well depth of 0.62 kcal/mol at $R_1=4.66a_0$, $R_2=2.69a_0$ (Fig. 4).

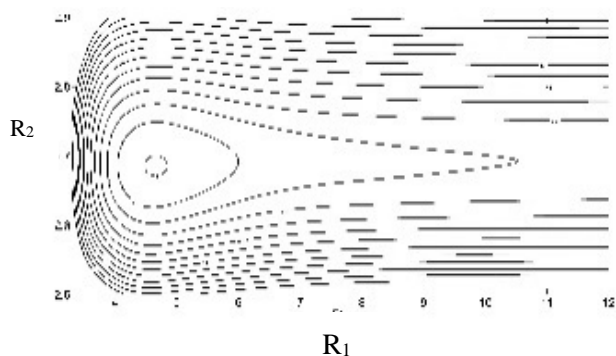


Fig. 4. The vdW well in the reactant valley of 1^2B_1 PES

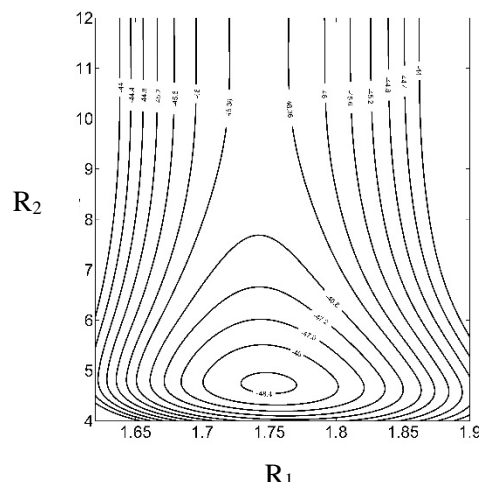


Fig. 5. The vdW well in the product valley of 1^2B_1 PES

The product valley has much deeper well of 2.12 kcal/mol with respect to the asymptote. It is located at $R_1=1.75a_0$, $R_2=4.66a_0$ (Fig. 5). Similar results are derived for the F-H-Cl system³. The wells are 0.67 and 1.95 kcal/mol deep for reactant and product valleys, respectively. Stronger vdW well for Br-HF complex is due to larger bromine atom size. The presence of such vdW wells significantly influences reaction dynamics¹⁶.

4. Conclusions

This paper presents results of *ab initio* computation for linear geometry of F-H-Br system. Two lower states 1^2A_1 and 1^2B_1 (which are degenerate in asymptotic regions) were computed using dynamical weighted SA-MCSCF method followed by MRCI-F12 calculation. Even though this method provides better convergence with basis set than conventional MRCI, the correlation energy is not fully extracted. Better agreement with experimental data is possible if larger portion of the correlation energy is extracted. This can be accomplished only by employment of larger active space. However, in this case the computations may become prohibitively expensive.

State 1^2A_1 has much lower barrier height than state 1^2B_1 . As a result, the reaction dynamics in the TS region will be mainly governed by 1^2A_1 state. However, at long distances between the atom and diatom the dynamics is influenced by both states. A special effect comes from 1^2B_1 state due to the vdW well. As shown in work¹⁶, its presence can quantitatively change the system behavior. Therefore the full reactive dynamics for this system implies non-adiabatic study on two coupled PESs. The number of these PESs grows with deflection from linear configuration. In this case the symmetry reduces and states $2^2A'$ and $1^2A''$ (1^2B_1 and 1^2B_2 for linear arrangement, respectively) are not degenerate anymore. Moreover, since now states $1^2A'$ and $2^2A'$ belong to the same symmetry, they form avoided crossings. *Ab initio* calculations for global PESs with subsequent study of the reactive dynamics are planned for our future research.

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