

An *ab initio* Study of Intermolecular Potential for Ne—HBr Complex

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The potential energy surface of the ground state of the Ne—HBr complex has been calculated at several levels of theory, including the single and double excitation coupled-cluster method with noniterative perturbation treatment of triple excitation CCSD(T). Calculations have been performed using the augmented correlation-consistent polarized quadruple zeta basis set (aug-cc-pVQZ). Using the complete basis set (CBS), the global minimum with a well depth of approximate 70.516 cm^{-1} has been found for the linear Ne—Br—H structure ($\theta = 180.0^\circ$) with the distance between the Ne atom and the center of mass of the HF molecule equals (0.351 nm). In addition to the global minimum, there is a secondary minimum at $R_m = 0.410 \text{ nm}$ and $\theta = 0^\circ$ (a well depth of 57.898 cm^{-1}). At last, the effects of the basis sets, H—Br bond length and theoretical methods on the intermolecular potential calculations of such weakly bound van der Waals complexes were discussed.

Keywords *ab initio*, intermolecular potential, PES

Introduction

The rare-gas hydrogen halide (M—HX) complexes have long been studied for insights into the nature of intermolecular forces and details of inter- and intramolecular dynamics.^{1,2} Systematic investigations of the complexes of Xe, Kr, Ar, and lately Ne with HF, HCl, HBr and their deuterated analogs, have yielded considerable information on their structure and internal dynamics. Yet considering theoretical calculations of such van der Waals complexes, the complexes of Ar—HX (where HX represents hydrogen halide molecules) have been studied frequently, whereas little is known about Ne—HX (where HX represents hy-

drogen halide molecules).³ So in the present paper, we perform a systematic *ab initio* supermolecular calculation for the intermolecular potential surface of Ne—HBr van der Waals complex.

In comparison with the heavier rare-gas hydrogen halide complexes, the Ne—HBr species is expected to be relatively weakly bound. Two phenomena contribute to this effect. First, because the polarizability of neon is only one-fourth that of argon,⁴ the induction and dispersion forces which constitute the attractive part of the intermolecular potential are correspondingly smaller. The intermolecular potential is consequently shallower for this neon complex. Second, the small reduced masses of the neon complex result in relatively large stretching zero-point energies. This further reduces the binding energy for the helium complexes relative to those of the heavier rare gases. In view of the small binding energy, spectroscopic techniques which were successfully applied in the studies of the complexes of the heavier rare gases are more difficult to be applied to the complexes of neon. So compared to the other heavier rare gases, the experimental studies of the weakly bound Ne—HBr complex have not been reported. However, in the view of the small number of electrons, correlation effects can in principle be treated to high order. Consequently, *ab initio* potentials for the Ne—HBr complex are expected to be more reliable than those developed for the heavier M—HBr species.

The goal of this paper is twofold: (1) to give the high quality of the PES of the Ne—HBr complex; (2) to discuss the effects of basis sets, H—Br bond length and

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theoretical methods to the weakly bound Ne—HBr complex. The details of our computational approach and the concluding remarks were given.

Computational details

The supramolecular approach has been employed to examine the interaction of the rare gas atom Ne with the HBr molecule, and that is the interaction energy (ΔE) at a given level of theory is calculated from the expression [Eq. (1)]:

$$\Delta E = E_{AB} - E_A - E_B \quad (1)$$

Where E_{AB} is the energy of the complex, and E_A and E_B are the energies of monomers A and B, respectively. It is well known that for rare-gas complexes the Hartree-Fock interaction potential is repulsive and the dispersion energy is the dominant attractive intermolecular force. An adequate treatment of electron correlation is thus essential in the calculation of the intermolecular potentials of Ne—HBr. In our present study, The level of theory will be indicated by the superscript, *e. g.*, $\Delta E^{\text{CCSD(T)}}$ will denote the CCSD(T) interaction energy. The CCSD(T)⁵ results are, the most accurate, but along the way we also obtained interaction energies at the self-consistent field (SCF), second-order Møller-Plesset (MP2), and the single and double excitation coupled-cluster (CCSD) levels of theory. Calculations have been performed using the augmented correlation-consistent polarized quadruple zeta basis set (aug-cc-pVQZ) of Dunning *et al.*^{6,8} When we investigate the effects of basis sets, the other correlation-consistent basis set aug-cc-pVXZ ($X = D, T, Q, 5$)^{6,8} and the complete basis set (CBS)^{9,10} were used. The electron-correlated calculations for the Ne—HBr complex used frozen core approximation. The counterpoise method of Boys and Bernardi was used to avoid the basis set superposition error (BSSE).¹¹ All calculations were carried out using the GAUSSIAN 94 package¹² in the High Performance Computational Chemistry Laboratory of Guizhou university.

The coordinate system for the Ne—HBr complex is shown in Fig. 1. R is the intermolecular distance from the center of mass of HBr to the rare gas Ne atom, and θ is the angle describing the orientation of the Ne atom with respect to the H—Br bond axis. and $\theta = 0^\circ$ corresponds to the Ne—Br—H colinear arrangement. The equilibrium

structure of HBr in the complex remains unknown. So the H—Br bond length was set at 0.1421 nm according to the calculation at the CCSD(T)/aug-cc-pVQZ theory level and was kept constant in all calculations.

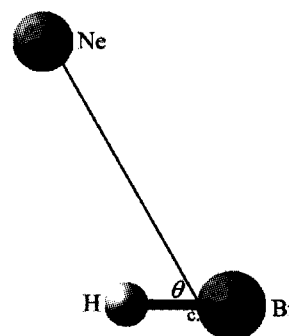


Fig. 1 Coordinate system used for Ne—HBr (c. o. m represents the center of mass).

Results and discussion

Potential surface of Ne—HBr in the ground state

The interaction energies at the SCF, MP2, CCSD, and CCSD(T) levels of theory obtained with the aug-cc-pVQZ basis set are reported in Table 1. We give this extensive set in order to use the original results for other researchers developing their own model potentials. Our calculations probed the potential energy surface most extensively for intermolecular distances in the interval from 0.36 nm to 0.46 nm, and 11 angles in the range from 0° to 180° . For 180° , calculation was performed for an additional distance of 0.353 nm. The PES, which is shown in Fig. 2, could be well fitted to the analytic function described earlier.^{13,14} The global minimum with a well depth of approximate 62.635 cm^{-1} was found on the CCSD(T) surface for the linear Ne—Br—H structure ($\theta = 180.0^\circ$) at $R_m = 0.353 \text{ nm}$. The error due to basis set incompleteness is more difficult to estimate, but a comparison with the estimated complete basis set limit values of interaction energies that we obtained for He—HF suggests that it should not exceed a few percent.¹⁵ It is clear from Table 2 that in addition to the global minimum, there is a secondary minimum at $R_m = 0.4105 \text{ nm}$ and $\theta = 0^\circ$ (a well depth of 57.361 cm^{-1}) corresponding to another linear geometry Ne—H—Br. This is different from the previous studies of Ar—HCl and Ar—FH complexes,^{16,17} where the primary minima are Ar—Cl—H and Ar—F—H. A

potential barrier of 35.299 cm^{-1} separating the two minima occurs around the position ($R_m = 0.393 \text{ nm}$, $\theta = 90^\circ$), corresponding to a T-shaped configuration. This arises because the electron density of the HBr monomer is substantially smaller in this direction than perpendicular

to the internuclear axis, so that the intermolecular repulsion at a given distance is weaker for the two linear ($\text{Ne}-\text{Br}-\text{H}$ and $\text{Ne}-\text{H}-\text{Br}$) and structures than for a T-shaped configuration.

Table 1 SCF, MP2, CCSD, and CCSD(T) interaction energies (in cm^{-1}) of $\text{Ne}-\text{HBr}$ at different distances and different angles

θ ($^\circ$)	R (nm)	ΔE^{HF}	ΔE^{MP2}	ΔE^{CCSD}	$\Delta E^{\text{CCSD(T)}}$
0	0.36	329.165	79.733	109.724	70.886
	0.38	149.238	-18.296	-0.664	-26.933
	0.40	65.951	-47.960	-37.031	-54.960
	0.41	43.173	-51.290	-42.481	-57.357
	0.4105	42.252	-51.341	-42.622	-57.361
	0.411	41.349	-51.383	-42.754	-57.357
	0.42	27.810	-50.841	-43.638	-56.021
	0.44	10.653	-44.557	-39.561	-48.231
	0.46	3.239	-36.234	-32.556	-38.721
20	0.36	241.891	33.500	53.926	21.941
	0.38	110.665	-31.512	-18.721	-40.723
	0.40	49.300	-48.813	-40.444	-55.704
	0.41	32.390	-49.596	-42.644	-55.406
	0.4105	31.705	-49.555	-42.666	-55.317
	0.411	31.033	-49.508	-42.681	-55.219
	0.42	20.949	-47.803	-41.976	-52.679
	0.44	8.132	-40.768	-36.558	-44.157
	0.46	2.542	-32.712	-29.642	-35.103
40	0.36	136.841	-14.306	-5.148	-27.028
	0.38	62.194	-40.740	-33.973	-49.543
	0.40	28.761	-44.538	-39.378	-50.525
	0.41	19.350	-42.719	-38.231	-47.688
	0.4105	18.966	-42.596	-38.137	-47.517
	0.411	18.589	-42.471	-38.040	-47.344
	0.42	12.889	-39.859	-35.911	-43.952
	0.44	5.467	-33.108	-29.885	-35.751
	0.46	2.082	-26.280	-23.866	-28.173
60	0.36	99.737	-17.861	-11.977	-29.313
	0.38	49.200	-34.783	-30.069	-42.584
	0.40	24.128	-36.406	-32.618	-41.696
	0.41	16.848	-34.754	-31.351	-39.101
	0.4105	16.548	-34.648	-31.263	-38.953
	0.411	16.252	-34.479	-31.178	-38.802
	0.42	11.737	-32.261	-29.326	-35.947
	0.44	5.642	-26.793	-24.427	-29.306
	0.46	2.662	-21.511	-19.629	-23.263

Continued

θ ($^{\circ}$)	R (nm)	ΔE^{HF}	ΔE^{MP2}	ΔE^{CCSD}	$\Delta E^{\text{CCSD(T)}}$
80	0.36	103.334	- 8.984	- 2.902	- 19.217
	0.38	51.885	- 27.849	- 23.241	- 34.973
	0.40	26.011	- 31.059	- 27.660	- 36.139
	0.41	18.403	- 30.249	- 27.146	- 34.391
	0.4105	18.087	- 30.179	- 27.094	- 34.283
	0.411	17.776	- 30.098	- 27.040	- 34.172
	0.42	13.010	- 28.531	- 25.773	- 31.972
	0.44	6.481	- 24.124	- 21.908	- 26.485
0.46	3.205	- 19.546	- 17.849	- 21.260	
90	0.36	105.697	- 6.679	- 0.188	- 16.392
	0.38	53.087	- 26.345	- 21.565	- 33.181
	0.40	26.631	- 30.148	- 26.569	- 34.955
	0.41	18.850	- 29.396	- 26.262	- 33.413
	0.4105	18.527	- 29.354	- 26.214	- 33.313
	0.411	18.209	- 29.276	- 26.169	- 33.211
	0.42	13.334	- 27.681	- 25.052	- 31.156
	0.44	6.653	- 23.594	- 21.402	- 25.909
0.46	3.297	- 19.160	- 17.490	- 20.846	
100	0.36	105.203	- 7.142	- 0.222	- 16.318
	0.38	52.715	- 26.401	- 21.404	- 32.909
	0.40	26.388	- 30.196	- 26.299	- 34.603
	0.41	18.659	- 29.191	- 25.996	- 33.052
	0.4105	18.338	- 29.124	- 25.955	- 32.954
	0.411	18.023	- 28.964	- 25.914	- 32.851
	0.42	13.186	- 27.642	- 24.767	- 30.802
	0.44	6.567	- 23.376	- 21.143	- 25.586
0.46	3.250	- 19.039	- 17.265	- 20.575	
120	0.36	93.161	- 16.405	- 8.484	- 24.063
	0.38	46.181	- 30.738	- 25.154	- 36.242
	0.40	22.883	- 31.895	- 27.780	- 35.750
	0.41	16.104	- 30.408	- 26.805	- 33.592
	0.4105	15.823	- 30.313	- 26.734	- 33.467
	0.411	15.548	- 30.217	- 26.662	- 33.342
	0.42	11.330	- 28.282	- 25.141	- 30.935
	0.44	5.598	- 23.454	- 21.035	- 25.298
0.46	2.754	- 18.801	- 16.982	- 20.152	
140	0.36	69.515	- 33.357	- 24.784	- 39.476
	0.38	33.663	- 38.912	- 32.754	- 43.211
	0.40	16.306	- 35.443	- 31.049	- 38.553
	0.41	11.353	- 32.788	- 28.823	- 35.226
	0.4105	11.149	- 32.639	- 28.702	- 35.054
	0.411	10.949	- 32.490	- 28.580	- 34.881
	0.42	7.906	- 29.773	- 26.306	- 31.776
	0.44	3.834	- 23.878	- 21.252	- 25.277
0.46	1.857	- 18.845	- 16.803	- 19.807	

Continued

θ ($^{\circ}$)	R (nm)	ΔE^{HF}	ΔE^{MP2}	ΔE^{CCSD}	$\Delta E^{\text{CCSD(T)}}$
160	0.36	45.701	-49.914	-41.224	-55.055
	0.38	21.092	-46.865	-40.465	-50.314
	0.40	9.709	-39.334	-34.390	-41.490
	0.41	6.584	-35.234	-30.935	-36.985
	0.4105	6.458	-35.032	-30.763	-36.765
	0.411	6.333	-34.831	-30.592	-36.546
	0.42	4.465	-31.355	-27.566	-32.742
	0.44	2.052	-24.456	-21.562	-25.381
180	0.46	0.941	-19.092	-16.703	-19.572
	0.36	35.606	-57.014	-48.171	-61.654
	0.38	15.755	-50.369	-43.724	-53.332
	0.40	6.905	-40.934	-35.813	-42.740
	0.41	4.556	-36.322	-31.834	-37.741
	0.4105	4.462	-36.099	-31.641	-37.502
	0.411	4.370	-35.877	-31.449	-37.263
	0.42	2.999	-32.043	-28.113	-33.167
0.44	1.288	-24.846	-21.696	-25.442	
0.46	0.544	-19.120	-16.680	-19.490	

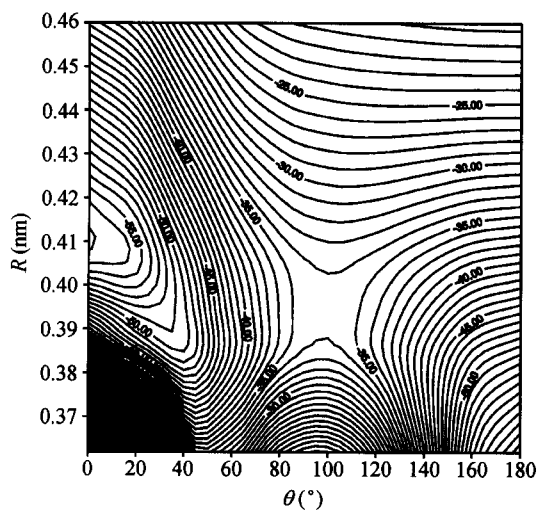


Fig. 2 Potential energy surface of the Ne—HBr complex (contour is labelled in cm^{-1}).

Table 2 Interaction energies ΔE at 0° , 90° and 180°

θ ($^{\circ}$)	R_m (nm)	ΔE (cm^{-1})
0	0.4105	-57.361
90	0.393	-35.299
180	0.353	-62.635

Effects of basis sets and theoretical methods

Different values of different interaction energies with

different correlation consisted basis sets of Dunning at several levels of theory were calculated, as summarized in Table 3. The interaction energies of the two complexes at the complete basis set were estimated by the extrapolation of the calculated interaction energies with the aug-cc-pVXZ basis sets using the fitting of the form $A(x) = A(\infty) + \alpha e^{-\beta x}$ [where $A(x)$ and $A(\infty)$ are the values of molecular properties at the aug-cc-pVXZ ($X = \text{D, T, Q, 5}$) and CBS limit, respectively, with α, β being fitting parameters).^{9,10} It is clear that the change trends of equilibrium distance R_m with basis set are almost all the same for each complex which appears to decrease gradually and displays very good converging behavior. Especially for Ne—H—Br it appears converge completely. At the same time, R_m is a little larger at the MP2 level of theory than that of the CCSD(T) theory level and a little smaller than the value of CCSD level of theory.

The interaction energies and its convergence pattern with basis set for the MP2, CCSD and CCSD(T) level appear to be very similar to R_m . The strength of the interaction is underestimated both at the MP2 theory level and at the CCSD level of theory, in comparison to the CCSD(T) results. Recently, Slavicek *et al.*¹⁸ reported the ground state PES of Ne—HBr at the CCSD(T)/aug-cc-pVDZ level. They stated that the potential minimum and the vibrationally averaged structure of Ne—HBr

Table 3 Interaction energies ΔE (cm^{-1}) of and Ne—H—Br and Ne—Br—H at different levels

	ΔE^{MP2}	ΔE^{CCSD}	$\Delta E^{\text{CCSD(T)}}$
Ne—H—Br			
aug-cc-pVDZ	-36.033(0.425)	-30.622(0.429)	-37.126(0.424)
aug-cc-pVTZ	-49.942(0.416)	-42.504(0.421)	-54.559(0.413)
aug-cc-pVQZ	-51.463(0.413)	-43.639(0.420)	-57.361(0.4105)
aug-cc-pV5Z	-51.629(0.4120)	-43.747(0.420)	-57.811(0.410)
CBS ^a	-51.650(0.4115)	-43.759(0.420)	-57.898(0.410)
Ne—Br—H			
aug-cc-pVDZ	-30.911(0.374)	-24.636(0.381)	-29.541(0.375)
aug-cc-pVTZ	-50.115(0.360)	-41.230(0.364)	-52.546(0.358)
aug-cc-pVQZ	-57.366(0.355)	-48.171(0.360)	-62.635(0.353)
aug-cc-pV5Z	-60.104(0.353)	-51.074(0.359)	-67.060(0.352)
CBS ^a	-61.765(0.352)	-53.162(0.359)	-70.516(0.351)

^a Expected values at the complete basis set, see the text. ^b The corresponding values of R_m (in nm) are all in parentheses.

correspond to the isomer with hydrogen between neon and bromine, which is contrary to our results. From Table 3, it can clearly be seen that the quality of the aug-cc-pVDZ and the aug-cc-pVTZ basis sets are not good. Especially for the aug-cc-pVDZ, the results are contrary to the results of bigger basis sets. They don't fit to calculate these weakly bound complexes. The values with aug-cc-pVQZ and the aug-cc-pV5Z basis sets are very close. It thus appears that the aug-cc-pVQZ basis set is an excellent compromise between the quality and efficiency of calculations, so that it was adopted in the present work.

Effect of H—Br bond length

In the present study, we keep the H—Br bond length constant because the experimental value of H—Br bond length in the Ne—HBr complex is unknown up to now. Can this bring considerable error to the interaction energies? In order to know about this, the interaction energies of the global minimum Ne—Br—H ($\theta = 180.0^\circ$) at different r (H—Br bond length) with different values of R are calculated, respectively (Table 4). With the change of H—Br bond length, the interaction energies at different R are very similar. Note that the interval 0.02 nm selected is very large. The equilibrium distance of H—Br bond length in the Ne—HBr complex must be not far from that in HBr monomer and the difference of interaction energies at different values of r with corresponding values of R must be more smaller. So keeping the H—Br bond length constant at 0.1421 nm can not bring considerable error to the interaction energies and to the PES.

Table 4 Interaction energies ΔE (in cm^{-1}) of Ne—Br—H at different r (H—Br bond length, in nm) with different R (in nm)

r (nm)	R (nm)	ΔE (cm^{-1})
0.1221	0.33	-43.03
	0.35	-60.09
	0.38	-51.75
	0.40	-41.51
	0.42	-32.19
0.1421	0.33	-53.82
	0.35	-62.59
	0.38	-53.33
	0.40	-42.74
	0.42	-33.17
0.1621	0.33	-48.30
	0.35	-63.99
	0.38	-54.57
	0.40	-43.81
	0.42	-34.06

Conclusions

We have investigated the potential energy surface of complex at the CCSD(T) theory level using the aug-cc-pVQZ basis set. At the same time, we also investigated the effects of basis sets, H—Br bond length and theory methods for the calculations of these weakly bound complexes using the correlated MP2, CCSD and CCSD(T) methods with the correlation-consistent aug-cc-pVXZ ($X = D, T, Q, 5$) and completed basis sets. The results show that two minimum energy structures of Ne—HBr

complex have both linear equilibrium geometry. Employing the augmented correlation-consistent polarized basis sets of Dunning *et al.*, the equilibrium distance R_m and interaction energies of the complex all display very good converging behavior and the aug-cc-pVQZ basis set is enough for the calculations of these weakly bound van der Waals complexes.

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