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# The study of interaction potentials and differential cross sections for collisions between He atoms and hydrogen halide molecules*

Sun Gui-Hua(孙桂华)[a)b)], Yang Xiang-Dong(杨向东)[a)†],
Zhu Jun(朱 俊)[c)], and Wang Cai-Xia(王彩霞)[d)]

[a)] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu* 610065, *China*
[b)] *Department of Physics, Hexi University, Zhangye* 734000, *China*
[c)] *Department of Applied Physics, Sichuan University, Chengdu* 610065, *China*
[d)] *Department of Basic Science, Beijing Institute of Information Engineering, Beijing* 100101, *China*

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In this paper, we present the uniform interaction potentials for helium atoms and halogen hydride molecules (HF, HCl and HBr). The differential cross sections are calculated using the above interaction potentials for the He–HF, HCl and HBr systems, respectively, and the results of the calculations are found to be in agreement with the existing theoretical results and experimental data.

**Keywords:** interaction potential, differential cross section, close-coupling approximation
**PACC:** 3430, 3450E

## 1. Introduction

The interaction potential between an atom and a molecule plays an important role in a great variety of physical and chemical phenomena. Intermolecular interactions determine the structure, spectra and dynamical properties of molecular complexes. The interaction between a rare gas atom and a hydrogen halide molecule has been the object of many experimental and theoretical studies.[1,2] In recent years, these systems have become important in the field of chemical lasers, where the collision energy transfer must be well understood. Therefore, it is necessary to thoroughly study their interaction potentials. However, it is difficult to obtain the scattering experimental data because of the strong causticity of hydrogen halide molecules. Hence, a theoretical study is indispensable.

Because of the relatively small number of electrons involved, the He–HF interaction potential and scattering cross section have attracted interest, both from theoreticians and experimentalists. Collins and Lane[3] (CL), using a pseudopotential technique, have published theoretical interaction potentials for the He–HF and HCl systems. Boughton *et al*[4] (BFW) have presented a semi-empirical interaction potential for the He–HF system using the scattering data and the potential model that was employed to describe rare gases interactions. Moszynski *et al*[5] have applied the symmetry-adapted perturbation theory (SAPT) to the computation of He–HF intermolecular potential energy surface. For the He–HCl system, besides the CL pseudopotential interaction potential, Held *et al*[6] have published the Hartree–Fock dispersion (HFD) interaction potential, where the dispersion coefficients $C_6$, $C_8$ and $C_{10}$ have been yielded by the values for the isoelectronic system He–Ar, multiplying all three by the same fitted parameter. Held *et al*[6] have presented the exponential Spline–Morse–Spline–van der Waals (ESMSV) interaction potential for the He–HBr system. The dispersion coefficients $C_6$, $C_8$ and $C_{10}$ were isoelectronic He–Kr values multiplied by the same factor as in the He–HCl fits. However, the ESMSV potential surface is a discontinuous function because of having two interrupted regions.

Although there have been considerable studies on potential energy surfaces and scattering cross sections for collisions between a helium atom and a hydrogen halide molecule (HF, HCl, HBr), some interactions have apparent defects and their expressions are also dissimilar from one another. No uniform potential

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†Author to whom correspondence should be addressed. E-mail: sunhua063@sina.com

functions are available for the interaction potentials of these systems. In this paper, we present the uniform potential surfaces for the interactions between a helium atom and a hydrogen halide molecule (HF, HCl and HBr). We give a systemic investigation and comparison for the three systems based on the above potential energy surfaces.

## 2. Fitted interaction potentials

Held *et al*[6] have given the ESMSV interaction potential for the He–HBr system:

$$V(R)=\begin{cases} A\exp(-\alpha R), & 0<R<0.34\text{nm},\\ \varepsilon\{\exp[-2\beta(R-R_{\rm m})]-2\exp[-\beta(R-R_{\rm m})]\}, & 0.356\text{nm}\le R<0.45\text{nm},\\ -(C_6R^{-6}+C_8R^{-8}+C_{10}R^{-10}), & 0.464\text{nm}\le R<\infty. \end{cases} \tag{1}$$

Equation (1) shows that the ESMSV potential is not evaluated in regions 0.34–0.356 nm and 0.45–0.464 nm, therefore it has two interrupted regions and is not perfect. We add a Morse function in order to describe the interaction potential in the interrupted regions:

$$V(R)=\begin{cases} A\exp(-\alpha R), & 0<R<R_1,\\ \varepsilon\{\exp[-2\beta_1(R-R_{\rm m})]-2\exp[-\beta_1(R-R_{\rm m})]\}, & R_1\le R<R_2,\\ \varepsilon\{\exp[-2\beta_2(R-R_{\rm m})]-2\exp[-\beta_2(R-R_{\rm m})]\}, & R_2\le R<R_3,\\ -(C_6R^{-6}+C_8R^{-8}+C_{10}R^{-10}), & R_3\le R<\infty. \end{cases} \tag{2}$$

Such a smooth and continuous potential function is obtained and shown in Fig.1. Furthermore, the fitted potential is extended to He–HF and He–HCl collision systems, and the uniform interaction potentials are obtained for a helium atom and a halogen hydride molecule (HF, HCl and HBr). The potential parameters for He–HF, HCl and HBr interactions are given in Table 1. The dispersion coefficients $C_6$, $C_8$ and $C_{10}$ for He–HF, HCl and HBr are their isoelectronic He–Ne, Ar and Kr values[7] multiplied by the same factor, respectively. Other parameters are fitted based upon their BFW potential (for He–HF), HFD potential (for He–HCl) and ESMSV potential (for He–HBr).

**Table 1.** The potential parameters for the three systems.

| System | $A$ /eV | $\alpha$ /nm$^{-1}$ | $\varepsilon$ /eV | $\beta_1$ /nm$^{-1}$ | $\beta_2$ /nm$^{-1}$ | $R_{\rm m}$ /nm | $R_1$ /nm | $R_2$ /nm | $R_3$ /nm | $C_6$ /$10^{-6}$eVnm$^6$ | $C_8$ /$10^{-8}$eVnm$^8$ | $C_{10}$ /$10^{-10}$eVnm$^{10}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| He–HF | $1.50\times10^6$ | 72.5 | $2.89\times10^{-3}$ | 22.1 | 17.5 | 0.309 | 0.256 | 0.316 | 0.532 | 2.26 | 6.57 | 24.94 |
| He–HCl | $3.82\times10^8$ | 80.0 | $2.31\times10^{-3}$ | 18.7 | 16.2 | 0.369 | 0.320 | 0.370 | 0.472 | 7.0 | 30.68 | 182.63 |
| He–HBr | $6.42\times10^{13}$ | 111.7 | $1.90\times10^{-3}$ | 14.4 | 13.0 | 0.399 | 0.340 | 0.376 | 0.464 | 10.11 | 43.96 | 274.59 |

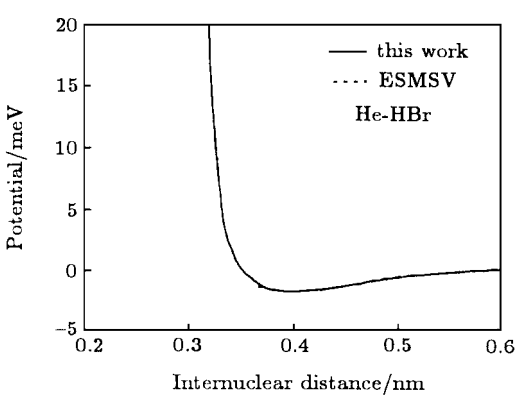



**Fig.1.** Comparison between our fitted potential and ESMSV[6] for the He–HBr system.

Comparisons between our fitted potential energy surfaces and other potentials are shown in Figs.1, 2 and 3 for collision systems He–HBr, HF and HCl, respectively. The fitted potentials for the three systems, the BFW for He–HF, the HDF for He–HCl and the ESMSV for He–HBr, are all spherically symmetric. The SAPT for He–HF, the CL for He–HF and He–HCl are anisotropic potential energy surfaces and their spherical components are shown in the figures. The figures show that our fitted potentials are close to those in potential parameters $R_0$, $R_{\rm m}$, $\varepsilon$, and the shape of potential energy curves, where $R_0$ and $R_{\rm m}$

are the positions of the zero potential and of the attractive minimum, and $\varepsilon$ is the depth of the potential well. Comparisons show that our fitted potentials are quite reasonable.

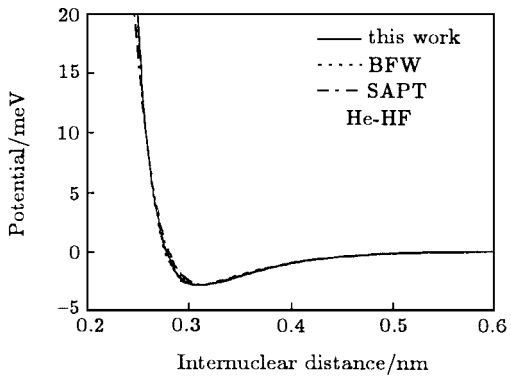



**Fig.2.** Comparison between our fitted potential, the BFW[4], and SAPT[5] for the He–HF system.

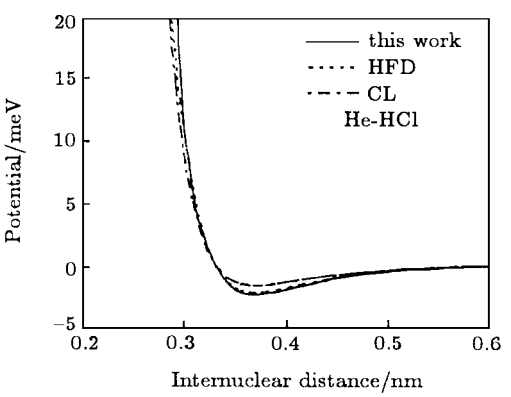



**Fig.3.** Comparison between our fitted potential, the HFD[6], and CL[3] for the He–HCl system.

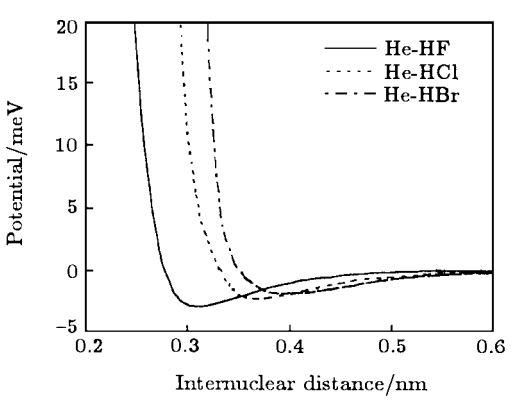



**Fig.4.** Comparison of our fitted potentials for the three collision systems.

Our fitted potentials are illustrated in Fig.4 for the collision systems He–HF, HCl and HBr. In comparing the three systems, we see that, as expected, the largest value of $R_{\rm m}$ is 0.399 nm for the largest system, He–HBr, reflecting the larger size of HBr; the second is 0.369 nm for the He–HCl system; the smallest value is 0.309 nm for the smallest system, He–HF. Also, we see a decreasing well depth in going from He–HF to He–HBr. $\varepsilon$ values are 2.89, 2.31 and 1.90 meV, for He–HF, HCl and HBr, respectively.

## 3. Quantum scattering calculations

The close-coupling (CC) approximation method[8] is employed to calculate the DCSs for the collision systems He–HF, HCl and HBr using our fitted potentials and others. Based on this method, the DCS for the procedure $A + BC(\nu_\alpha = 0, j_\alpha = 0) \rightarrow A + BC(\nu_\beta, j_\beta)$ is given by

$$\frac{{\rm d}\sigma_{\nu_\alpha j_\alpha \rightarrow \nu_\beta j_\beta}}{{\rm d}\Omega} = \frac{1}{(2J_\alpha + 1)} \frac{k_\beta}{k_\alpha} \times \sum_{M_\alpha M_\beta} |f_{\nu_\beta j_\beta M_\beta, \nu_\alpha j_\alpha M_\alpha}(\theta, \phi)|^2, \quad (3)$$

where $\nu$ is the the molecular vibrational number, $j$ is the rotational quantum number, $M$ denotes the projection of the rotation onto a spaced-fixed axis, $l$ is the quantum number of orbital momentum, $k$ is the momentum, and $J$ denotes the total angular momentum quantum number. The scattering amplitude from the initial state $(\nu_\alpha j_\alpha M_\alpha)$ to the final state $(\nu_\beta j_\beta M_\beta)$ is

$$f_{\nu_\beta j_\beta M_\beta, \nu_\alpha j_\alpha M_\alpha}(\theta, \phi) = \left(\frac{4\pi}{k_\alpha k_\beta}\right)^{1/2} \sum_{l_\beta} [2l_\beta + 1]^{1/2} \times A_{l_\beta}(\nu_\alpha j_\alpha M_\alpha \rightarrow \nu_\beta j_\beta M_\beta) {\rm Y}_{l_\beta M_\alpha \rightarrow M_\beta}(\theta, \phi), \quad (4)$$

with

$$A_{l_\beta}(\nu_\alpha j_\alpha M_\alpha \rightarrow \nu_\beta j_\beta M_\beta) = \sum_J \langle l_\beta M_\alpha - M_\beta j_\beta M_\beta | J M_\alpha \rangle T^j_{\nu_\alpha j_\alpha l_\alpha, \nu_\beta j_\beta M_\beta}, \quad (5)$$

where ${\rm Y}_{l_\beta M_\alpha \rightarrow M_\beta}(\theta, \phi)$ is the spherical harmonics and $T^j_{\nu_\alpha j_\alpha l_\alpha, \nu_\beta j_\beta M_\beta}$ is the transition matrix element.

The DCSs calculated using our fitted potentials and the CC method are plotted in Fig.5 for the three systems, He–HF, HCl and HBr, at $E$=88 meV. It can be seen easily that the spacing of the diffraction oscillations in the DCSs for the three systems is different and decreases in going from He–HF to He–HBr. The main reasons for the discrepancy are the difference of the reduced masses, $\mu$, and the positions of the zero

potential, $R_0$, for the systems. It is well known from scattering theory that the spacing of the diffraction oscillations is inversely proportional to $\mu$ and $R_0$. In the three systems, He–HF has the smallest $\mu$ (0.9571a.u.), $R_0$ (0.278 nm), and the greatest spacing; the He–HBr system has the greatest $\mu$ (0.9954a.u.), $R_0$ (0.357 nm), and the smallest spacing; while $\mu$ (0.9796a.u.), $R_0$ (0.332 nm) and the spacing for the He–HCl system lie intermediate between them.

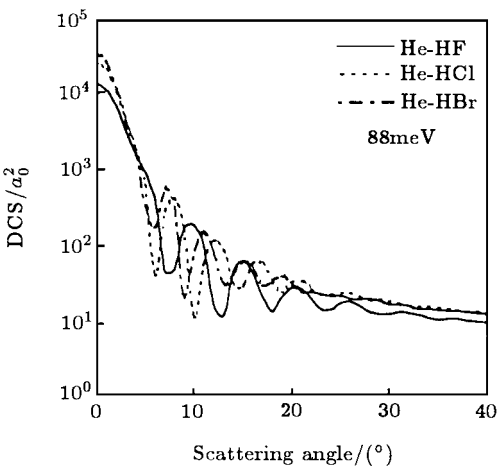



**Fig.5.** Comparison of the DCSs using our fitted potentials for the three systems.

A comparison between the scattering experimental data of the DCS and the predictions of our fitted potential, the BFW and SAPT potential energy surfaces in the CC approximation ($E$=88 meV), is shown in Fig.6 for the He–HF system. As can be seen, the prediction of our fitted potential is quite consonant with that of the BFW and SAPT and the experimental data; this shows further that our potential function and parameters are fairly accurate. The oscillating locations of the calculated DCS by using our fitted potential are coincident with the experimental data, indicating that the positions of the zero potential and potential well are exact. $R_0$ is 0.278 nm for the fitted potential (0.276 nm for the BFW[4] and 0.280 nm for the SAPT) and $R_{\rm m}$ is 0.309 nm for the fitted potential and the BFW[4] (0.315 nm for the SAPT). It is obvious that $R_0$ and $R_{\rm m}$ of the three potentials are very close to one another. It is shown that the amplitudes of diffractions of the differential cross sections (DCSs) are slightly different for the various potential energy surfaces considered for this system. The main cause leading to the difference is the difference of well depth $\varepsilon$. $\varepsilon$ is 2.887 meV for the fitted potential and the BFW (2.834 meV for the SAPT).

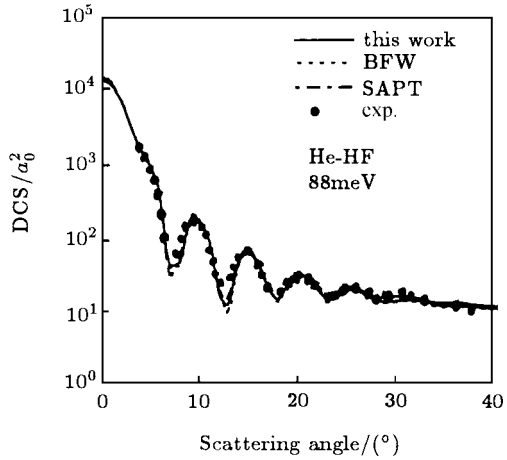



**Fig.6.** DCS data for the scattering of He–HF at $E$=88meV,[6] compared with the predictions of our potential, the BFW and SAPT in the CC approximation.

Figure 7 shows the comparison of the DCSs of the various potential energy surfaces for the He–HCl system. It can be seen that the spacing of the oscillations of the DCSs calculated using the various potential energy surfaces considered for this system is nearly coincident, indicating that their $R_0$ and $R_{\rm m}$ agree quite well. $R_0$ is 0.332nm for the fitted potential (0.331 nm for the HFD and CL) and $R_{\rm m}$ is 0.369 nm for the fitted potential and the HFD (0.371 nm for the CL). The discrepancies of oscillating amplitudes of the DCSs are remarkable for the three potentials. At the same oscillating position, the amplitudes for the CL potential is the greatest, reflecting the shallowest well depth, 1.61 meV, then the HFD, 2.14 meV; the smallest amplitude corresponds to the deepest well for the fitted potential, 2.31 meV.

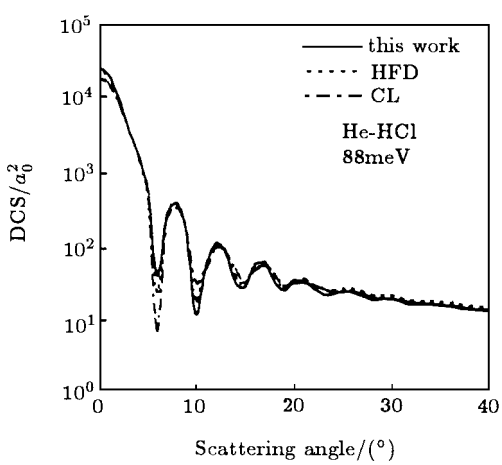



**Fig.7.** Comparison between the predictions of the total DCS of our potential, the HFD and CL for scattering of He–HCl at $E$=88meV in the CC approximation.

## 4. Conclusions

In summary, we have remedied the ESMSV of Held *et al* for the He–HBr system, and then extended it to the He–HF and HCl systems. Thus we propose a new and uniform analytical expression for the interaction between helium atoms and halogen hydride molecules (HF, HCl and HBr). The comparisons between the experimental data and scattering calculations using fitted potentials and other approaches show that our potential energy model is reasonable. The potential parameters are accurate, which can describe the main characteristics of the interactions between helium atoms and halogen hydride molecules (HF, HCl and HBr).

## References

[1] Yang C L and Zhu Z H 1999 *Acta Phys. Sin.* **48** 1852 (in Chinese)
[2] Jiang G, Xie H P, Tan M L and Zhu Z H 2000 *Acta Phys. Sin.* **49** 665 (in Chinese)
[3] Collins L A and Lane N F 1976 *Phys. Rev.* A **14** 1358
[4] Boughton C V, Miller R E, Vohralik P F and Watts R O 1986 *Mol. Phys.* **58** 827
[5] Moszynski R, Wormer P E S, Jeziorski B and Avoird A 1994 *J. Chem. Phys.* **101** 2811
[6] Held W D, Piper E, Ringer G and Toennies J P 1980 *Chem. Phys. Lett.* **75** 260
[7] Tang K T and Toennies J P 1986 *Z. Phys.* D **1** 91
[8] Choi B H and Tang K T 1975 *J. Chem. Phys.* **63** 1775