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Research Paper

Theoretical Study of the Spectroscopic Constants of the Van der Waals Complex ArHF and a Possibility of Fluorine anion from an Excited State

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Abstract: *Ab initio* calculations have been performed for the van der Waals complex ArHF using the multi-reference single and double excitation configuration interaction (MRSDCI) and multi-reference coupled pair approximation (MRCPA) methods to determine the spectroscopic constants of the ground $X^1\Sigma^+$ and first excited $2^1\Sigma^+$ states. The calculated ground state equilibrium constants compared well with the available experimental data. Excited state data may serve as future references. Another aim of this study is the possibility of a fluorine anion from an excited ionic state (ArHF)* produced by Ar colliding with an excited ionic state of HF.

Keywords: Ab initio calculation, van der Waals complex, Spectroscopic constants, Anion production.

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Introduction

Over the last few decades, weakly bound van der Waals complexes have played important roles in both experimental and theoretical investigations. Recent high-resolution spectroscopic techniques have provided spectroscopic data and potential energy surfaces of a variety of van der Waals molecules through vibrational and rotational analyses, which are extremely valuable in the interpretation of chemical and dynamical phenomena.

A class of van der Waals molecules, the rare-gas hydrogen halides (Rg-HX), has been extensively studied both experimentally and theoretically because of their simplicity and to learn more about the true nature of their weak intermolecular forces. The present study is focused on a prototype van der Waals complex ArHF, which has become an important system for the study of weak bonding phenomena.

A variety of experimental techniques¹⁻⁵, based on radio-frequency, microwave, infrared – spectroscopy

and scattering experiments have been performed to study the ArHF complex in its ground vibrational states and also its potential energy surfaces. Among them, Harris et al.¹ determined the structure of ArHF in the ground vibrational state from radio-frequency and microwave spectra using molecular beam electric resonance spectroscopy. Fraser and Pine² observed high-resolution infrared spectra of ArHF and some other rare-gas halide complexes with tunable difference frequency laser spectroscopy. Lovejoy et al.^{3,4} obtained rotationally resolved infrared spectra of ArHF using difference frequency infrared laser spectrometer in an one-dimensional supersonic expansion. Chang et al.⁵ performed experimental as well as ab initio calculations at the Moller-Plesset perturbation theory up to the 4th order (MP4) for ArHF. Dykstra⁶ developed an empirical model MMC (molecular mechanics for clusters) based on high order estimate of induction energy for the ground state of ArHF complex. Hutson⁷ developed a more accurate intermolecular potential designated as H6(4,3,2) by fitting to the results of high-resolution microwave,

infrared and far-infrared spectroscopic investigations. Lotritch et al.⁸ investigated the structure and two-dimensional potential energy surface for the ArHF molecule using the many-body symmetry-adopted perturbation theory (SAPT), where H-F distance was kept at the equilibrium bond length of HF molecule. Tao and Klemperer⁹ also performed MP4 calculations for the ArHF complex at a fixed H-F distance using basis sets including bond functions. Subramanian et al.¹⁰ also examined the geometry and interatomic potentials for the ground state of ArHF at the levels, like MP4, QCISD and DFT using 6-311G* basis set.

For such an anisotropic system, to get the true scenario, one needs more accurate calculations at the multi-reference level with high-level of electron-correlating basis sets containing sufficient diffuse or polarization functions. In the present article, we report the investigations of the ArHF van der Waals complex in its ground $X^1\Sigma^+$ and first excited $2^1\Sigma^+$ states by multi-reference single and double configuration interaction method (MRSDCI) and multi-reference coupled pair approximation (MRCPA) method. However, the potential energy surface is important to get a clear scenario, our aim of this study is to report the spectroscopic constants of this ArHF complex in its ground $X^1\Sigma^+$ and first excited $2^1\Sigma^+$ states. The calculations were performed with a linear Ar-H-F structure, as its equilibrium linear atomic arrangement was proposed by Harris et al.¹. The dependence of both Ar-H and H-F distances was studied to obtain the equilibrium structure. Another aim of this study is to clarify the reaction $\text{Ar} + (\text{H}^+\text{F})^* \rightarrow (\text{ArHF})^* \rightarrow \text{ArH}^+ + \text{F}^-$, which reveals a possibility of fluorine anion from the excited $(\text{ArHF})^*$ state formed during collision between the ground state of Ar atom and an excited ionic state of HF molecule. In the subsequent sections, we will discuss our computational schemes and the results of our present investigations.

Computational details

We used ALCHEMY II program¹¹ for MRSDCI calculations and MRCPA program developed by Tanaka et al.¹² for MRCPA calculations. Two types of MRCPA schemes, viz. MRCPA(2) and MRCPA(4) are used to include second order and approximate fourth order energy corrections¹².

We primarily used aug-cc-pvTZ basis sets proposed by Dunning and co-workers¹³ with modifying a part to reduce computational cost. The basis set for Ar was [6s,5p,3d,2f], where [5s,4p,2d] was contracted from (15s,9p,2d) and diffuse s- (0.0685), p- (0.0487), d- (0.169) and two f- (0.890, 0.406) functions were augmented (numbers in parentheses are exponents). The basis set for H was [4s,3p,1d], where [3s,2p] was contracted from (5s,2p) and diffuse functions s- (0.02526), p- (0.102) and d- (1.057) types were

augmented. For F, the basis set was [7s,5p,2d], where [4s,3p,1d] was contracted from (10s,5p,1d) and diffuse functions s- (0.09158, 0.03, 0.01), p- (0.0891, 0.0297) and d- (0.52) types were augmented. Thus we finally composed a [6s,5p,3d,2f / 4s,3p,1d / 7s,5p,2d] basis set for the Ar-H-F complex. Using this basis set, we first carried out CASSCF calculations to prepare MOs, in which 12 electrons were distributed among four σ and three π orbitals. We used the point group C_{2v} , a subgroup of $C_{\infty v}$. For CASSCF calculations, we used a state-average option to obtain a proper description of both the ground $X^1\Sigma^+$ and first excited $2^1\Sigma^+$ bound states. We performed state-averaged CASSCF calculations over a wide range of Ar-H and H-F internuclear distances and found that 11 configurations are predominant over the entire range. The total number of configuration state functions generated was 485,956. The total weights of the reference CSFs in MRSDCI and MRCPA calculations for the ground and excited states at their equilibrium positions were 0.920 and 0.890, respectively.

It is to be mentioned at this point that for the ground state optimization of ArHF, Huston⁷ used a fixed value for the $R(\text{H-F})=1.73258$ a.u. in Lotritch et al.⁸ calculation $R(\text{H-F})$ was kept constant at its equilibrium value of 1.7328 a.u., which was optimized by Cade and Huo¹⁴ at the Hartree-Fock level. Tao and Klemperer⁹ used another fixed value of $R(\text{H-F})=1.7624$ a.u., which was the vibrationally averaged value for the $v=0$ state. In our investigation, we performed calculations by varying both Ar-H and H-F distances to obtain global minimum in its linear structure.

We also optimized the ground $X^1\Sigma^+$ and first excited $B^1\Sigma^+$ states of HF molecule and ground $X^1\Sigma^+$ state of ArH^+ ion. For HF molecule, we performed MRSDCI and MRCPA calculations with six electrons in two σ and two π orbitals with seven reference configurations. For ArH^+ ion, we performed calculations with six electrons correlated in three σ and two π orbitals with five reference configurations. In the following sections we will report our results of the present investigation.

(A) Spectroscopic constants of HF

The calculated spectroscopic constants of the HF monomer in its ground and first excited states are listed in Table 1 along with the experimental data for comparison. Table 1 shows that our calculated spectroscopic constants, particularly at the MRCPA(4) level, for both the states are in very good agreement with the observed values. Our ground state bond length of 1.737 a.u. by MRCPA(4) is close to the observed value of 1.733 a.u.¹⁵. For the excited state, the bond length is 3.942 a.u. at the MRCPA(4) level in comparison to the observed value of 3.951 a.u. The vibrational frequencies obtained by MRCPA(4) for

both states are in good agreement with the observed values¹⁵. The excited state $B^1\Sigma^+$ is valence ionic type, which is clear from the gross population of H and F at the equilibrium position of 0.17 and 9.83, respectively. The adiabatic excitation energy from the ground to excited state is 10.81 eV at the MRSDCI level and 10.94 eV at the MRCPA(4) level, in comparison to the observed value of 10.51 eV¹⁵.

(B)s Spectroscopic constants of ArH^+

The spectroscopic constants for the ArH^+ ion are listed in Table 2 along with the available experimental values. The bond length is found to be better obtained at the MRCPA(4) level, however the vibrational frequency and dissociation energy are in close agreement with the MRSDCI values in comparison to experimental data^[15-17].

Table 1: Spectroscopic constants of HF

Method	R_e (a.u.)	ω_e (cm^{-1})	T_e (eV)
$X^1\Sigma^+$ state			
MRSDCI	1.740	4138.5	
MRCPA(2)	1.737	4195.5	
MRCPA(4)	1.737	4198.5	
Expt. ^a	1.7325	4138.3	
$B^1\Sigma^+$ state			
MRSDCI	3.908	1186.1	10.81
MRCPA(2)	3.940	1161.5	10.93
MRCPA(4)	3.942	1162.6	10.94
Expt. ^a	3.951	1159.2	10.51

Abbreviations: ^aReference¹⁵

(C) Spectroscopic constants of $ArHF$

The spectroscopic constants for the $ArHF$ complex for both the states are listed in Table 3 along with the

Table 3: Spectroscopic constants of the ground $X^1\Sigma^+$ state of $ArHF$

Method	R_e (Ar-H) (a.u.)	R_e (H-F) (a.u.)	ω_e (Ar-HF) (cm^{-1})	ω_e (H-F) (cm^{-1})	D_e (eV)	D_e^{corre} (eV)
MRSDCI	5.437	1.731	40.3	4278.8	0.0264	0.0221
MRCPA(2)	5.037	1.731	40.2	4364.6	0.0271	0.0215
MRCPA(4)	5.028	1.731	40.1	4399.5	0.0272	0.0213
Exptl.	4.803 ^a , 4.858 ^b	(1.7325 [*])	42.1 ^a , 39.2 ^b	(4138.3 [*])	0.0144 ^a , 0.0156 ^b	
Empirical Calc.	4.855 ^d	1.7326 ^{d,*}			0.0238 ^c , 0.0262 ^d	
Ab initio Calc.	4.884 ^e , 4.886 ^f	1.7328 ^{e,*} , 1.7624 ^{f,*}			0.0258 ^e , 0.0248 ^f	

Abbreviations: ^aReference¹; ^breference²; ^creference⁶; ^dreference⁷; ^ereference⁸; ^freference⁹; ^{*}From Table 1.

The dissociation energies, D_e , for the ground state of $ArHF$ complex are found to be overestimated by about 0.013 cm^{-1} from the experimental values, whereas corrected values using counterpoise correction for basis set superposition error (BSSE)¹⁸ at the equilibrium distances are obtained to be better.

The spectroscopic constants for the excited $2^1\Sigma^+$ state of the $ArHF$ complex are listed in Table 4. The excited state has a global minimum at $R_e(Ar-H) = 2.763$ a.u.

available experimental and theoretical data. For the ground state, the $R_e(H-F)$ value (1.731 a.u.) obtained by our methods are close to the experimental HF monomer bond length of 1.7325 a.u.¹⁵, while $R_e(Ar-H)$ values differ slightly from each other due to computational schemes used. We found that the $R_e(Ar-H)$ bond length is found to be slightly better obtained at the MRCPA(4) level, which is due to the inclusion of higher order correction. Our calculated $R_e(H-F)$ values at the MRSDCI level is in better agreement with the observed value of the HF monomer (listed within the parenthesis from the Table 1). The difference with the other's theoretical values were justified as they performed with fixed $R_e(H-F)$.

Table 2: Spectroscopic constants of the ground $X^1\Sigma^+$ state of ArH^+

Method	R_e (a.u.)	ω_e (cm^{-1})	D_e (eV)
$X^1\Sigma^+$ state			
MRSDCI	2.413	2771.8	4.04
MRCPA(2)	2.415	2854.9	3.97
MRCPA(4)	2.415	2869.1	3.98
Expt.	2.419 ^{a,b}	2711.0 ^b	4.17 ^a , 4.04 ^c

Abbreviations: ^aReference¹⁵; ^breference¹⁶; ^creference¹⁷.

The calculated vibrational frequencies for $Ar-HF$ stretching, $\omega_e(Ar-HF)$, range from 40.1 to 40.3 cm^{-1} in the present methods. The vibrational frequency for $H-F$ stretching, $\omega_e(H-F)$, in the $ArHF$ complex was greater than that of experimental value of HF monomer (listed within the parenthesis from the Table 1) by 143 - 261 cm^{-1} . This is justified from the decrease in $R_e(H-F)$ values in $ArHF$ compared to HF monomer.

and $R_e(H-F) = 5.302$ a.u. at the MRCPA(4) level. The global minimum has been shifted towards greater $H-F$ separation compared to the equilibrium bond length of 3.951 a.u. of the HF monomer in the excited $B^1\Sigma^+$ state (Table 1). The adiabatic transition energy to the excited state of $ArHF$ from its ground state is 9.66 eV by the MRSDCI level and 9.62 eV by the MRCPA(4) level. Since there is no data available in literature for the excited state, our results may serve as future references. Note that the excited state is valence-ionic. In Table 5,

we have listed gross populations and charges for the excited state of ArHF at different positions.

Table 4: Spectroscopic constants of the excited $2^1\Sigma^+$ state of ArHF

Method	R_e (Ar-H) (a.u.)	R_e (H-F) (a.u.)	ω_e (Ar-HF) (cm^{-1})	ω_e (H-F) (cm^{-1})	T_e (eV)
MRSDCI	2.762	5.305	196.1	2236.1	9.66
MRCPA(2)	2.762	5.356	195.2	2255.5	9.62
MRCPA(4)	2.763	5.302	195.3	2217.4	9.62

(D) Possibility of fluorine anion from the excited ionic state

We explored a possibility of fluorine anion (F^-) from the excited state $(\text{ArHF})^*$ produced by Ar atom colliding with HF molecule in its excited $B^1\Sigma^+$ state. The first excited state $B^1\Sigma^+$ of the HF molecule is ionic and has an equilibrium bond length of 3.942 a.u. at the MRCPA(4) level (Table 1), which is close to the experimental value of 3.951 a.u. If an Ar atom collides with this excited state, $\text{Ar} + (\text{HF})^*$, it will produce the excited $(\text{ArHF})^*$ state ($2^1\Sigma^+$). The excitation energy of the $\text{Ar} + (\text{HF})^*$ system from the ground state of ArHF is 10.67 eV at the MRSDCI level and 10.69 eV at the MRCPA(4) level. These are listed in Table 6 and denoted by ΔE_1 . The energy of the $\text{Ar} + (\text{HF})^*$ system was calculated with $R_e(\text{H-F})^*=3.942$ a.u. at the optimized value by our MRCPA(4) method. The resulting excited state $(\text{ArHF})^*$ state is valence-ionic in nature and dissociates to ArH^+ and F^- ions at large H-F separation.

Table 5: Mulliken gross population of the excited ionic state

Atom	At the equilibrium position ^a	At the dissociation limit ^b
Ar	17.69 (+0.31) ^c	17.46 (+0.54) ^c
H	0.62 (+0.38)	0.54 (+0.46)
F	9.69 (-0.69)	10.00 (-1.00)

^a $R_e(\text{Ar-H})=2.763$ a.u., $R_e(\text{H-F})=5.302$ a.u.

^b $R(\text{Ar-H})=2.415$ a.u., $R(\text{H-F})=1.0 \times 10^5$ a.u.

^c Values in parentheses are gross charges.

Table 6: Relative energy of ionic dissociation ($\text{ArH}^+ + F^-$)

Method	Energy difference ^a		
	ΔE_1 (eV)	ΔE_2 (eV)	ΔE (eV)
MRSDCI	10.67	1.81	12.46
MRCPA(2)	10.69	1.62	12.28
MRCPA(4)	10.69	1.63	12.29
Exptl.			12.13 ^b , 12.26 ^c

^a $\Delta E_1 = E(\text{Ar} + (\text{HF})^*) - E(\text{ArHF})$.

$\Delta E_2 = E(\text{ArH}^+ + F^-) - E(\text{Ar} + (\text{HF})^*)$.

$\Delta E = E(\text{ArH}^+ + F^-) - E(\text{Ar} + \text{HF})$.

^b Using $D_e(\text{ArH}^+)$ of Reference¹⁵.

^c Using $D_e(\text{ArH}^+)$ of Reference¹⁷.

The population analysis at large H-F separation, listed in Table 5, supports the nature of such ion-pair formation. The energy at the ion-pair formation was calculated with $R_e(\text{ArH}^+)=2.415$ a.u. optimized at the MRCPA(4) level. The ionic state, $(\text{ArH}^+ + F^-)$, is above $\text{Ar} + (\text{HF})^*$ at its equilibrium position by 1.63 eV (tabulated by ΔE_2) at the MRCPA(4) level. Thus, if an Ar atom with a kinetic energy of more than 1.63 eV collides with excited $(\text{HF})^*$ state, a F^- ion is possible to dissociate from the $(\text{ArHF})^*$ excited ionic state. The energy difference between $\text{Ar} + \text{HF}$ (ground state dissociation) and $\text{ArH}^+ + F^-$ (excited state dissociation), denoted as ΔE , is found to be 12.46 eV at the MRSDCI level, 12.28 eV at the MRCPA(2) level and 12.29 eV at the MRCPA(4) level. These are compared with the result obtained using the equation:

$$\Delta E = D_e(\text{HF}) + \text{IP}(\text{H}) - \text{EA}(\text{F}) - D_e(\text{ArH}^+),$$

where the symbols have their usual meanings, and using known experimental values as: $D_e(\text{HF}) = 6.1$ eV¹⁵, $\text{IP}(\text{H}) = 13.60$ eV¹⁹, $\text{EA}(\text{F}) = 3.40$ eV²⁰, $D_e(\text{ArH}^+) = 4.17$ eV¹⁵ and $D_e(\text{ArH}^+) = 4.04$ eV¹⁷.

Conclusion

In summary, we have presented spectroscopic constants of the ground and an excited state of the weakly bound van der Waals complex ArHF, which is potentially important as a prototype complex to study weak bonding phenomena of such molecules. A possibility of fluorine anion production has also been reported from an excited ionic state $(\text{ArHF})^*$ produced by Ar colliding with an excited ionic state of HF. Several data reported here may serve as future references.

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