

Ab initio study of the ground and first excited states of the van der Waals complex ArHF and a possibility of fluorine anion from the excited state

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Abstract: Ab initio study have been performed for this van der Waals complex ArHF using the multi-reference single and double excitation configuration interaction (MRSDCI) method to determine the spectroscopic constants of the ground and first excited states. The excited state results are found to be new in literature. A possibility of a fluorine anion from the excited ionic state (ArHF)* formed by Ar colliding with an excited ionic state of HF has also been examined.

1. Introduction

ArHF, a prototype weakly bound van der Waals complex, has gained substantial importance in recent years because of its simplicity and to know more about the nature of the weak intermolecular force. Among the experimental investigations, Harris et al.[1] determined the structure of ArHF in the ground vibrational state using molecular beam electric resonance spectroscopy. Fraser and Pine [2] observed high-resolution infrared spectra of some rare-gas halides using laser spectroscopy. Dykstra [3] developed an empirical model MMC (molecular mechanics for clusters) for the ground state of ArHF. Hutson [4] developed an intermolecular potential designated as H6(4,3,2) by fitting to the results of high-resolution spectroscopic investigations. Tao and Klemperer [5] also performed MP4 calculation keeping HF distance fixed at its equilibrium value. A broad report has been published recently by Ghosh et al. [10].

2. Computational Schemes

A modified aug-cc-pvTZ basis sets [6s,5p,3d,2f/ 4s,3p,1d/7s,5p,2d] of Dunning and co-workers [7] has been used for the Ar/H/F systems. We used ALCHEMY II program [8]. First we carried out state-average CASSCF calculations to prepare MOs and then performed MRSDCI calculations. Other than spectroscopic constants of the ground $X^1\Sigma^+$ and first excited $2^1\Sigma^+$ states, our aim is to study the possibility of the fluorine anion from an excited ionic state (ArHF)* produced by Ar colliding with an excited ionic state of HF.

3. Results and Discussion:

3.1 Spectroscopic Constants

The calculated spectroscopic constants of the HF monomer, ArH^+ ion and ArHF complex are listed in Table 1-3. The vibrational frequency for H-F stretching, $\omega_e(\text{H-F})$, in the ArHF complex was greater than that of experimental value of HF monomer. This is justified from the decrease in $R_e(\text{H-F})$ values in ArHF compared to HF monomer. The dissociation energies, for the ground state of ArHF complex are found to be overestimated. The global minimum for the excited $2^1\Sigma^+$ state of the ArHF has been shifted towards greater H-F separation compared to the R_e of 3.908 a.u. of the HF in excited state. The transition energy to excited state from its ground state is 10.81 eV as compared to experimental value 10.51 eV [9].

3.2 Possibility of Fluorine Anion from the Excited Ionic State

If an Ar atom collides with the HF 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 found to be 10.67 eV (denoted by E_1 in Table 4). The ionic state, $(\text{ArH}^+ + \text{F}^-)$, is above $\text{Ar} + (\text{HF})^*$ at its equilibrium position by 1.81 eV (tabulated as E_2). Thus, if an Ar atom with a kinetic energy of more than 1.81 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 $\text{ArH}^+ + \text{F}^-$ (excited state dissociation), denoted as E , is found to be 12.46 eV, compared to 12.13 calculated using experimental values and using $E = D_e(\text{HF}) + \text{IP}(\text{H}) - \text{EA}(\text{F}) - D_e(\text{ArH}^+)$.

Table 1 Spectroscopic constants of HF

State	R_e (a.u.)	ω_e (cm^{-1})	T_e (eV)
$X^1\Sigma^+$ state:			
MRSDCI	1.740	4138.5	
Expt. ^a	1.7325	4138.3	
$2^1\Sigma^+$ state:			
MRSDCI	3.908	1186.1	10.81
Expt. ^a	3.951	1159.2	10.51

^aReference [9]; ^breference [10].

Table 2 Spectroscopic Constants of ArH^+

Method	R_e (au)	ω_e (cm^{-1})	D_e (eV)
$X^1\Sigma^+$ state			
MRSDCI	2.413	2771.8	4.04
Expt.	2.419 ^{a,b}	2711.0 ^b	4.17 ^a

^aReference [9].

Table 3 Spectroscopic constants 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)	T_e (eV)
Ground $X^1\Sigma^+$ state						
MRSDCI	5.437	1.731	40.3	4278.8	0.0264	
Exptl.	4.803 ^a	(1.7325 [*])	42.1 ^a	(4138.3 [*])	0.0144 ^a	
Empirical Calc.	4.855 ^b	1.7326 ^{b,*}			0.0238 ^c	
Ab initio Calc.	4.884 ^d	1.7328 ^{d,*}			0.0258 ^d	
Excited $2^1\Sigma^+$ state						
MRSDCI	2.762	5.305	196.1	2236.1		9.66

^aReference [1]; ^breference [3]; ^creference [4]; ^dreference [5]; ^{*}from Table 1

Table 4 Relative energy of ionic dissociation

Method	Energy difference ^a		
	ΔE_1 (eV)	ΔE_2 (eV)	ΔE (eV)
MRSDCI	10.67	1.81	12.46
Exptl.			12.13 ^b

^a $\Delta E_1 = E(\text{Ar} + (\text{HF})^*) - E(\text{ArHF})$, $\Delta E_2 = E(\text{ArH}^+ + \text{F}^-) - E(\text{Ar} + (\text{HF})^*)$.

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

4. Conclusions

Spectroscopic constants of the ground and excited states of ArHF have been reported for the ArHF complex and a possibility of F⁻ ion from the excited state of ArHF has been investigated.

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