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Theoretical Study of Rg·NO (Rg=He, Ne, Ar and Kr) Complexes

Si-sheng Wang^a, Rui-hong Kong^a, Liu-si Sheng^{a*}, Li-qing Hao^b, Shi-kang Zhou^b, Zhen-ya Wang^b

a. National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China; *b.* Environment Spectroscopy Laboratory, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Hefei 230031, China

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Rg·NO (Rg=He, Ne, Ar and Kr) complexes were studied using *ab initio* calculations. The neutral Rg·NO complex geometry and vibrational frequencies were calculated with the cc-pVDZ basis set at the CCSD(T) level of theory. The calculations show that the geometry of the Rg·NO complexes is a skewed T-shape with the Rg atom on the oxygen side of the NO molecule, and that the Rg–N–O bond angle increases with mass. The dissociation energies (DE) and ionization energies (IE) of the neutral Rg·NO complexes, and the dissociation energies of Rg·NO⁺ ionic complexes were calculated using Gaussian-2 (G2) methods and a high accuracy energy model. The ionization energies of the neutral Rg·NO complexes range from 9.265 eV for He·NO to 9.132 eV for Kr·NO and the dissociation energies of Rg·NO⁺ range from 0.017 eV for He·NO⁺ to 0.156 eV for Kr·NO⁺, in line with the expectation based on the increasing polarizability of the Rg atom.

Key words: Rg·NO clusters, Theoretical calculation, Ionization energy, Dissociation energy

I. INTRODUCTION

Research into the structure and energetics of clusters has been central to the molecular theory of matter. A great deal of effort has been expended in an attempt to establish a relationship between the properties of bulk matter and intermolecular forces. Properties of clusters due to their finite size are of particular interest. For many systems, cluster properties can be explained to a large extent in terms of pairwise interactions while three-body and other higher-order terms contribute only small corrections. The properties of clusters have been the subject of intense research over the past decade [1-5]. From the most fundamental perspective, the four basic components of the intermolecular interaction energy include electrostatic, induction, dispersion and exchange interactions [6]. The Rg·NO clusters are open-shell complexes, which are composed of a closed-shell rare gas atom Rg and an open-shell NO molecule. These complexes are of special interest since most chemically active systems involve atoms or molecules with unpaired electrons. Van der Waals interactions involving open shell species will be most important at long range where chemical forces are relatively weak. Systems involving the ²Π radicals NO or OH have emerged as important benchmarks for the understanding and quantitative description of the collision dynamics and the bound state structure. The van der Waals complex consisting of an open-shell diatomic molecule and a rare gas atom has four sources of angular momenta: electron orbital motion, electron spin, inter-

nal rotation of the diatomic molecular part, and overall rotation of the complex framework. Weakly bound complexes of small inorganic molecules with rare gas atoms are of fundamental interest since these complexes represent prototypes for characterizing simple multipole-induced dipole interactions [6-8].

Recently, much information about the equilibrium geometry, vibrational frequencies, ionization energy and dissociation energy of some Rg·NO clusters have been obtained through experimental and theoretical studies [9-23]. The adiabatic ionization energy of Ar·NO, $IE=9.148\pm 0.005$ eV, was first determined by Sato and coworkers [9] using the resonance-enhanced multiphoton ionization (REMPI) spectroscopy. The vibrational series of Ar·NO⁺ complex and its adiabatic ionization energy 73869 ± 6 cm⁻¹ (9.159 ± 0.001 eV) were determined by Takahashi [10] through multiphoton ionization threshold photoelectron spectra. He utilized the method of spectroscopic analysis on the neutral Ar·NO cluster to give the ground state structure ($r(\text{N-O})=1.15077$ Å, $R(\text{N-Ar})=3.711$ Å, $\angle\text{O-N-Ar}=80.483^\circ$), vibrational frequencies (40 cm⁻¹) and dissociation energy (98 cm⁻¹). In addition, for cationic Ar·NO⁺ clusters, he gave the ground state structure ($r(\text{N-O})=1.106322$ Å, $R(\text{N-Ar})=2.68$ Å, $\angle\text{O-N-Ar}=69.2^\circ$), vibrational frequencies (79 and 94 cm⁻¹) and dissociation energy ($DE(951$ cm⁻¹) ≈ 0.118 eV). Tsuji *et al.* studied the bound-bound excitation spectrum of Ar·NO complex associated with the $A^2\Sigma^+-X^2\Pi$ transition via RE2PI and determined the binding energy of 88 cm⁻¹ about the ground state $X^2\Pi$, and the binding energy of 44 cm⁻¹ about excitation $A^2\Sigma^+$ [11]. Being encouraged by this research progress about the high resolution zero kinetic energy photoelectron spectroscopy of Ar·NO⁺, Robbe *et al.* carried out a quantum chemical calculation study about the ground

* Author to whom correspondence should be addressed. E-mail: lssheng@ustc.edu.cn

TABLE I Geometrical structure and vibrational frequencies of Ar·NO

Methods	$r/\text{Å}$	$R/\text{Å}$	$\theta/(\text{°})$	$V_1(\text{bend})/\text{cm}^{-1}$	$V_2(\text{stretch})/\text{cm}^{-1}$	$V_3(\text{N-O}_{\text{str}})/\text{cm}^{-1}$
HF/6-31G*	1.1270	4.3659	58.44	6.1	22.7	2221.2
MP2/6-311G*	1.1347	4.0686	63.65	16.2	32.7	3557.4
MP2/cc-pVTZ	1.1371	3.8646	67.87	27.3	38.1	3338.0
QCISD/6-311G*	1.1586	4.0280	68.67	17.8	30.4	1851.9
QCISD/cc-pVDZ	1.1660	4.3209	47.65	2.2	34.3	1884.6
	1.1530	3.9032	72.38	25.3	31.0	1811.3
CCSD/cc-pVTZ	1.1474	3.9034	72.40	25.5	31.0	1989.4
CCSD(T)/cc-pVDZ	1.1608	3.9882	64.06	29.4	66.4	2052.8
Ref.[10]	1.1508	3.7110	80.48		40.0 [27]	

state potential energy surface of Ar·NO⁺ and He·NO⁺ clusters [12]. Fourre and coworkers *et al.* [13] performed a study of the vibrational structure of Ar·NO⁺. Paul *et al.* researched the rotational spectra of rare gas-nitric oxide van der Waals molecules [14,15]. Alexander studied the bound states and potential energy surfaces of the Ar·NO system using a new and fully ab initio investigation [16,17]. The intermolecular potential energy surface of the He·NO⁺ complex was also studied [18]. Wright *et al.* studied the geometry, vibrational frequencies and dissociation energy of the ground state of cationic Rg·NO⁺ clusters [19-23]. In these theoretical studies of Rg·NO complexes, these researchers only studied the geometry, vibrational frequencies and dissociation energy of Rg·NO⁺. There is little known about the geometry, vibrational frequencies and dissociation energy of the neutral Rg·NO clusters in ground state. Moreover, theoretical studies about the ionization energy of the Rg·NO complexes have not been reported up to now. In this research, in order to have an understanding of Rg·NO clusters in more detail, the CCSD(T) level of theory and cc-pVDZ basis set are used to calculate the geometry and vibrational frequencies of neutral Rg·NO complexes. The G2 method and a high accuracy energy model are used to calculate the ionization energy and dissociation energy of neutral Rg·NO complexes as well as the dissociation energy of cationic Rg·NO⁺ complexes. Furthermore, we compare these results with the experimental results obtained before.

II. THEORETICAL CALCULATIONS

Rg·NO (Rg=He, Ne, Ar and Kr) complexes were studied using the GAUSSIAN 03 program. The equilibrium geometry and vibrational frequencies of Ar·NO complexes were calculated using the 6-31G*, 6-311G*, cc-pVDZ and cc-pVTZ basis sets at the HF, MP2, QCISD and CCSD(T) levels of theory. Based on the calculations mentioned above, the CCSD(T)/cc-pVDZ method was selected to calculate the equilibrium geometries and vibrational frequencies of neutral Rg·NO complexes. The total energies of Rg·NO complexes

and species pertinent to this work were calculated with the G2 methods using the Gaussian Program [24-26]. Briefly, the equilibrium structure of each species was optimized at MP2(full)/6-31G* level. To calculate a G2 energy, single-point energy calculations were carried out at the levels of MP4/6-311G(d,p), MP4/6-311+G(d,p), MP4/6-311G(2df,p), MP2/6-311+G(3df,2p) and QCISD(T)/6-311G(d,p), with a high level correction and a zero-point vibrational correction. Then, the G2 energies could be used to calculate the ionization energies and dissociation energies.

III. RESULTS AND DISCUSSION

A. Geometric structure and vibrational frequencies of Ar·NO

The geometry of the Rg·NO complexes is presented in Fig.1. The R , r and θ are defined as Rg-N distance, N-O bond length and bond angle between Rg-N and N-O bonds respectively. The geometric structure and vibrational frequencies of Ar·NO complex were calculated using *ab initio* methods: HF, MP2, QCISD and CCSD(T), using the 6-31G*, 6-311G*, cc-pVDZ and cc-pVTZ basis sets. The theoretical results are given in Table I.

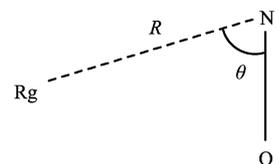


FIG. 1 Definitions of the parameters used in the text.

Because NO is a polar molecule, the induction interaction is an important contribution to the intermolecular interaction. In addition, because the Ar atom has 18 electrons and larger atomic radius, and especially because there is un-paired electron in the outer shell

TABLE II Geometrical structure and vibrational frequencies of Rg·NO

Species	$r/\text{Å}$	$R/\text{Å}$	$\theta/(\text{°})$	$V_1(\text{bend})/\text{cm}^{-1}$	$V_2(\text{strech})/\text{cm}^{-1}$	$V_3(\text{N-O}_{\text{str}})/\text{cm}^{-1}$
He·NO	1.1608	3.5926	59.56	18.4	28.2	2053.5
Ne·NO	1.1607	3.1198	74.81	37.0	85.8	2052.8
Ar·NO	1.1608	3.9882	64.06	29.4	66.4	2052.8
Kr·NO	1.1608	4.0240	73.34	24.3	35.8	2052.8

of the N atom, the dispersion interaction and exchange interaction within Ar·NO complexes also make a contribution to the intermolecular interaction. Within the Ar·NO complex, the bond length of NO is close to the experimental result, 1.15077 Å (coming from the National Institute of Standards and Technology, NIST, US). It can be seen from Table I that the distance between the Ar atom and the N atom or O atom is rather large and the geometry of Ar·NO complex is a skewed T-shape with the Ar atom on the oxygen side of the NO molecule. The symmetry of this cluster is C_s and its geometry is stable because all of its vibrational frequencies are positive.

The parameters of geometrical structure of the ground state $X^2\Pi_{1/2}$ of neutral Ar·NO complex were given by Takahashi as follows: $r(\text{N-O})=1.15077$ Å, $R(\text{N-Ar})=3.711$ Å, $\angle\text{O-N-Ar}=80.483^\circ$ [10]. The results predicted with the QCISD/cc-pVTZ, CCSD/cc-pVTZ and CCSD(T)/cc-pVDZ methods are close to these experimental results on the geometry of the ground state Ar·NO. Based on comparison of the geometry of Ar·NO⁺ complex from Wright and coworkers [19-23] with the geometry of Ar·NO complex from this work, the bond angle in Ar·NO⁺ is larger than that in Ar·NO, perhaps because there are more positive charges in the N atom, so the Ar atom is closer to the N atom within Ar·NO⁺ complex.

As contrasted with the HF method, the effect of the electron correlation on the intermolecular and intramolecular effect is considered by the coupled cluster method, which is suitable for calculating the interaction of complexes.

B. Geometrical structure and vibrational frequencies of Rg·NO

The equilibrium geometries and vibrational frequencies of neutral Rg·NO complexes were calculated using cc-pVDZ basis sets at the CCSD(T) level of theory. The results of the theoretical calculations are listed in the Table II.

Generally speaking, the geometries of Rg·NO complexes are skewed T-shape with their Rg atom on the oxygen atom side of the NO molecule, so the calculated bond length N-O within the Rg·NO complexes is close to that of a free NO molecule. Because the geometrical structures of the neutral Rg·NO complexes are skewed

T-shape structures, the quadrupole-induced dipole interaction should be dominant in the interaction of the complexes. Provided that the dipole-dipole interaction is dominant in the interaction, the complexes should be nearly linear in structure.

Although the geometries of the Rg·NO⁺ complexes predicted by Wright and coworkers [19,23] are also skewed T-shapes, their Rg atoms are all on the nitrogen side of the NO molecule since their bond angles θ are close to 110° . Within the Rg·NO⁺ complexes, the distance of Rg-N is 1 Å shorter than its counterpart in the Rg·NO, which indicates that the positive charge of NO⁺ plays an important role in the charge-induced interaction. The Rg-N distance in the Rg·NO and Rg·NO⁺ increases with the augmentation of the radius of the Rg atoms except for the bond He-N. Because the polarizability of the He atom is lower than others, the binding energy between the He atom and the NO or NO⁺ molecule is very weak. The NO⁺ bond length within the Rg·NO⁺ complexes is close to that of free NO cationic, and the Rg atoms can be polarized by the positive charge of the NO⁺. The Rg atoms are more polarizable with the increasing polarizability of Rg atoms, which enhances the binding energy between Rg and NO.

C. Ionization energy of Rg·NO

The total energies (E_0) of Rg, NO, Rg·NO and the corresponding ions were calculated using the G2 method and are listed in Table III.

TABLE III The total energies of Rg, NO, Rg⁺, NO⁺, Rg·NO and Rg·NO⁺

Species	$E_0/\text{Hartree}$	Species	$E_0/\text{Hartree}$
He·NO	-132.640265	He	-2.900262
He·NO ⁺	-132.299771	He ⁺	-1.998329
Ne·NO	-258.559419	Ne	-128.819459
Ne·NO ⁺	-258.219551	Ne ⁺	-128.025243
Ar·NO	-656.796027	Ar	-527.055700
Ar·NO ⁺	-656.458770	Ar ⁺	-526.478943
Kr·NO	-2881.921180	Kr	-2752.180970
Kr·NO ⁺	-2881.585574	Kr ⁺	-2751.663531
NO	-129.739969	NO ⁺	-129.398881

TABLE IV Ionization energies of Rg·NO $\alpha/10^{-24}\text{cm}^3$

Species	IE/eV		Species	$\alpha^a/10^{-24}\text{cm}^3$	$R^b/\text{\AA}$
	This work	Exp. [10]			
He·NO	9.265		He	0.205	0.49
Ne·NO	9.248		Ne	0.396	0.51
Ar·NO	9.177	9.159±0.01	Ar	1.64	0.88
Kr·NO	9.132		Kr	2.48	1.03

^a Stands for the static polarizability of Rg atom.

^b Stands for the radius of Rg atom.

According to the high precision energy model of GAUSSIAN 03 program, IE of each molecule can be deduced approximately from the different energy between the total energy of the cation in the ground state and that of the corresponding neutral molecules in the ground state. For the ionization course of Rg·NO clusters:



$$IE(\text{Rg} \cdot \text{NO}) = E_0(\text{Rg} \cdot \text{NO}^+) - E_0(\text{Rg} \cdot \text{NO}) \quad (2)$$

The ionization energies of Rg·NO are calculated using this formula (2) and the data of Table III. The theoretical calculation results are listed in Table IV. The radius and polarizability of the Rg atoms are also listed in the Table IV. It is known that the ionization energies of Rg·NO complexes decrease gradually with the Rg atoms from the He to the Kr atom, and they are shifted to red in comparison with the ionization energy of the NO molecule. For example, the ionization energy of NO is 9.264 eV (NIST), that of He·NO is about 9.265 eV, that of which is nearly the same as NO's, while the red shift of ionization energy of Kr·NO is ~ 0.132 eV from that of NO. The theoretical value of the ionization energy of Ar·NO complex is 9.177 eV, which is in agreement with the experimental value ~ 9.159 eV from Takahashi [10] and ~ 9.148 eV from Sato *et al.* [9]. Up to now, the experimental values of the ionization energies of other Rg·NO complexes (Rg=He, Ne and Kr) have not been reported.

In principle, the ionization energies for Rg·NO complexes are dependent on their monomers. Because the ionization energy of monomer NO is smaller than monomer Ar, the NO is ionized more easily than Rg atoms within these complexes. However, because the ionization energy of the NO molecule is affected by Rg atoms, the ionization energy of the Rg·NO complexes is shifted from that of a free NO molecule. A graph about the calculated ionization energy versus the polarizability obtained for the Rg·NO species is shown in Fig.2. As may be seen, a very good straight line is obtained. The IE s decrease linearly with the increment of the polarizability, which confirms that the polar-induced dipole interaction acts a dominant function.

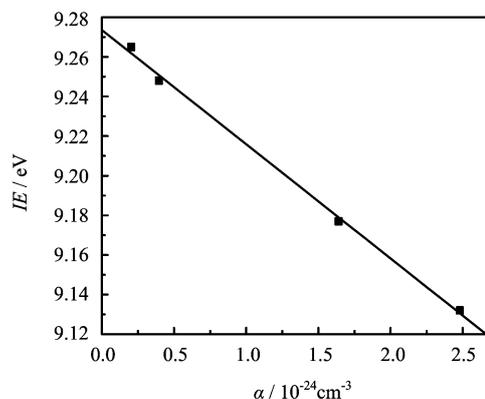
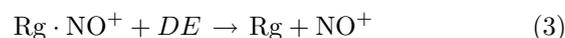


FIG. 2 Graph of Rg·NO ionization energy versus polarizability.

D. Dissociation energies of Rg·NO and Rg·NO⁺ complexes

According to the high precision energy model of the GAUSSIAN 03 program, the dissociation channel of cationic Rg·NO⁺ complexes can be expressed in the following way:



$$DE(\text{Rg} \cdot \text{NO}^+) = E_0(\text{Rg}) + E_0(\text{NO}^+) - E_0(\text{Rg} \cdot \text{NO}^+) \quad (4)$$

The DE s of Rg·NO⁺ were calculated using formula (4) and the datum of Table III. The calculated results are

TABLE V Dissociation energy of Rg·NO⁺

Species	DE/eV	
	This work	Ref.[23]
He·NO ⁺	0.017	0.024
Ne·NO ⁺	0.033	0.042
Ar·NO ⁺	0.114	0.117
Kr·NO ⁺	0.156	0.162

listed in Table V. From Table V, it is seen that the DE s of Rg·NO⁺ complexes increase with increase of the polarizability of Rg atoms. But, as a whole, all of the DE s are rather low. The measured dissociation energy of Ar·NO⁺ by Takahashi was 0.118 eV [10], which is in accord with our theoretical value ~ 0.114 eV. In 2000, the DE s of cationic Rg·NO⁺ complexes were calculated by Wright and coworkers using the QCISD/RCP-41++'G(3df) level of theory and full counterpoise correction [23]. Their results are also listed in Table V. Although different theoretical methods were used in this work, the results are very close to each other.

The main contribution to this interaction energy is expected to be the charge/induced-dipole term, which is dependent on the polarizability of the Rg atom. In principle, the Rg atom should interact with both N and O, which each carry a portion of the +e charge; and then, the average geometry would be expected to be a balance of these effects. Assuming that the dipole moment of NO⁺ is the same for all of the complexes, and ignoring the effects of the distance and angle between the NO⁺ and Rg atoms, the induced energy, U , can be given approximately by [27]:

$$U \propto \alpha \quad (5)$$

where α is the static polarizability of the Rg atom. Figure 3 shows the relationship between the DE s of Rg·NO⁺ complexes and the polarizability of rare gas atoms. As may be seen, a very good straight line is also obtained, which confirmed that the charge/induced dipole interaction is the main contributor to the interaction energy in these species, and also indicating that the errors in the calculated dissociation energies are relatively small.

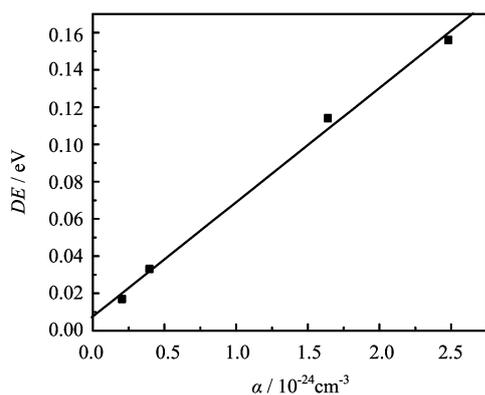


FIG. 3 Graph of Rg·NO⁺ dissociation energy versus polarizability.

In addition, we also calculate the dissociation energy of neutral Ar·NO cluster with a similar method to validate the calculation and the equation as before:



$$\begin{aligned} DE(\text{Ar} \cdot \text{NO}) &= E_0(\text{Ar}) + E_0(\text{NO}) \\ &\quad - E_0(\text{Ar} \cdot \text{NO}) = 0.010 \text{ eV} \end{aligned} \quad (7)$$

In 1984, Sato *et al.* determined the DE (0.013 ± 0.002 eV) of neutral Ar·NO cluster using the multiphoton ionization method [9], which is in accord with our theoretical result.

IV. CONCLUSION

Rg·NO clusters, composed of a rare gas atom and an NO molecule, are prototypes for the study of the intermolecular interactions in van der Waals complexes. The precise equilibrium geometry and vibrational frequencies of complexes were calculated by using the CCSD(T)/cc-PVDZ method. The calculated results indicate that the geometry of the neutral Rg·NO complexes is a skewed T-shape, with the Rg atom on the oxygen side of the NO molecule. The ionization energies and dissociation energies of neutral Rg·NO clusters as well as the dissociation energies of Rg·NO⁺ complexes were calculated through the high precise energy model and G2 method. Our theoretical results are in agreement with the published experimental results. The DE s of cationic Rg·NO⁺ clusters predicted by us with the G2 methods are also close to those predicted by Wright and coworkers [23] using the QCISD/RCP-41++'G(3df) level of theory and full counterpoise correction.

V. ACKNOWLEDGMENT

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