

# Interaction dipole moment in Rg–Xe (Rg = He, Ne, Ar, and Kr) heterodiatoms from conventional *ab initio* and density functional theory calculations

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We have obtained interaction dipole moment curves for the rare gas heterodiatoms Rg...Xe (Rg = He, Ne, Ar, and Kr) from conventional *ab initio* and density functional theory calculations with flexible Gaussian-type basis sets. All methods seem to reproduce fairly similar dipole moment curves for all pairs. Our best values for the interaction dipole moment (at the respective experimental equilibrium separation  $R_e$ ) were obtained at the coupled-cluster theory with single, double, and perturbatively linked triple excitations level of theory:  $\mu_{\text{int}}(\text{RgXe})/ea_0 = -0.0025(\text{He}), -0.0047(\text{Ne}), -0.0055(\text{Ar}),$  and  $-0.0037(\text{Kr})$ . The same trend (in absolute terms) is observed at the MP2 level of theory for the derivative of the dipole moment at  $R_e$ , as  $(d\mu_{\text{int}}(\text{RgXe})/dR)_e/e = 0.0043(\text{He}), 0.0082(\text{Ne}), 0.0091(\text{Ar}),$  and  $0.0059(\text{Kr})$ . Around  $R_e$ ,  $\mu_{\text{int}}(\text{HeXe}) \equiv \mu_{\text{HeXe}}$  varies at the MP2 level of theory as  $[\mu_{\text{HeXe}}(R) - \mu_{\text{HeXe}}(R_e)]/ea_0 = 0.0043(R - R_e) - 0.0033(R - R_e)^2 + 0.0018(R - R_e)^3 - 0.0005(R - R_e)^4$ .

**KEY WORDS:** rare gas heterodiatoms, interaction dipole moment, collision-induced absorption, MP2, CCSD(T), DFT

## 1. Introduction and theory

Rare gas dimers constitute the favorite ground for fundamental experimental observations [1]. Collision-induced absorption (CIA) and collision-induced light scattering (CILS) in these systems are routinely associated with interaction dipole moment and dipole polarizability curves [1,2]. A recent study on the NeAr heterodiatom [3] has brought forth the observation of hyper-Rayleigh scattering and the importance of interaction dipole hyperpolarizability curves for its interpretation. The importance of the interaction electric property dipole moment and (hyper)polarizability is evidenced by the effort invested in the development of theoretical models [4,5]. These models reproduce the interaction properties of atom pairs relying exclusively on the electric properties of the atoms. A straightforward quantum chemical calculation of interaction

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properties is always possible. In previous work, we have examined closely the possibility of applying conventional *ab initio* methods to the determination of the interaction (hyper)polarizability of Rg<sub>2</sub>, Rg = He, Ne, Ar, and Kr [6]. More recently we extended our efforts to NeAr [7], KrXe [8], and Xe<sub>2</sub> [9]. In this paper, we turn our attention to the interaction dipole moment of the heterodiatoms RgXe, Rg = He, Ne, Ar, and Kr. The properties of these systems attracted some attention early enough [10]. A more recent model study, reported pure rotational spectra of RgXe, Xe = Ne, Ar, and Kr [11]. We mention also an analysis of the CIA spectrum of HeXe [12].

We rely on the finite-field method for a straightforward approach to the calculation of electric polarizabilities [13]. The energy of an uncharged molecule in a weak, homogeneous static electric field can be written as follows [14]:

$$E^P = E^0 - \mu_\alpha F_\alpha - \frac{1}{2} \alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{6} \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma + \dots, \quad (1)$$

where  $F_\alpha$  is the electric field,  $E^0$  the energy of the free molecule,  $\mu_\alpha$  the dipole moment,  $\alpha_{\alpha\beta}$  the dipole polarizability, and  $\beta_{\alpha\beta\gamma}$  is the first dipole hyperpolarizability. The subscripts denote Cartesian components and a repeated subscript implies summation over  $x$ ,  $y$  and  $z$ . The number of independent components needed to specify the dipole moment and (hyper)polarizability tensors is regulated by symmetry [14]. Linear molecules have only one independent dipole moment, so we drop the subscript and write  $\mu \equiv \mu_z$  (where  $z$  is the molecular axis). For very weak fields the expansion of equation (1) converges rapidly. The extraction of electric properties from the field-perturbed energies is straightforward [8].

The interaction properties are obtained via the Boys–Bernardi counterpoise-correction (CP) method [15]. For a given configuration of the system  $A \dots B$  the interaction property  $P_{\text{int}}(A \dots B)$  is obtained as

$$P_{\text{int}}(A \dots B) = P(A \dots B) - P(A \dots X) - P(X \dots B), \quad (2)$$

where  $P(A \dots X)$  denotes the property for the subsystem  $A$  in the presence of the ghost orbitals of subsystem  $B$  and  $P(X \dots B)$  the property of  $B$  in the presence of the ghost orbitals of subsystem  $A$ .

The *ab initio* calculations reported in the present study rely on self-consistent-field (SCF), MP2 and MP4 (second- and fourth-order Møller–Plesset perturbation theory), coupled-cluster theory with singles and doubles (CCSD), and coupled-cluster theory with single, double and perturbatively linked triple excitations (CCSD(T)) methods. Descriptions of these methods are available in standard references [16,17]. We also employ the widely used DFT methods B3LYP, B3PW91, and B3P86 as implemented in the GAUSSIAN 98 program [18]. We are particularly interested in the performance of DFT-based methods in interaction induced electric property calculations.

Table 1  
Basis sets used in the calculations.

Atom	Basis Set	CGTF	$\alpha_{\text{SCF}}$	$\alpha_{\text{NHF}}$
He	[6s4p3d]	33	1.3217	1.32223 <sup>a</sup>
Ne	[7s5p4d1f]	49	2.3719	2.37674 <sup>a</sup>
Ar	[8s6p5d3f]	72	10.6556	10.758 <sup>a</sup>
Kr	[8s7p6d5f]	94	16.4498	16.476 <sup>a</sup>
Xe	[9s8p7d5f]	103	27.05	27.06 <sup>b</sup>

<sup>a</sup>Stiehler and Hinze [19].

<sup>b</sup>McEachran et al. [20].

## 2. Computational details

Relying on previous experience [12] we employ in this study flexible basis sets, especially designed for interaction electric properties. We show in table 1 the composition of these basis sets: [6s4p3d] for He [12], [7s5p4d1f] for Ne [12], [8s6p5d3f] for Ar [12,13], [8s7p6d5f] for Kr [12], and [9s7p6d5f] for Xe [9]. Agreement with the available accurate numerical Hartree-Fock (NHF) data [19,20] is better than 1% in all cases.

Technical details about our finite-field approach to the calculation of interaction electric properties are easily found in our recent related work [6–9]. The adopted equilibrium internuclear separation adopted in this work is  $R_e/a_0 = 7.51$  for HeXe [21], 7.33 for NeXe [11], 7.74 for ArXe [11], and 7.94 for KrXe [11]. The 18 innermost MO were frozen in the post-Hartree-Fock calculations on HeXe. Similarly, the 19 innermost MO were frozen on NeXe, the 23 on ArXe, and the 27 on KrXe.

All calculations were performed with GAUSSIAN 94 [22] and GAUSSIAN 98 [18].

Atomic units are used through this work. Conversion factors to SI units are: Energy,  $1 E_h = 4.3597482 \times 10^{-18}$  J, Length,  $1 a_0 = 0.529177249 \times 10^{-10}$  m, dipole moment,  $\mu$ ,  $1 e a_0 = 8.478358 \times 10^{-30}$  cm, and dipole polarizability,  $\alpha$ ,  $1 e^2 a_0^2 E_h^{-1} = 1.648778 \times 10^{-41}$  cm<sup>2</sup> J<sup>-1</sup>.

## 3. Results and discussion

Interaction dipole moments for all heterodiatoms at the equilibrium distance are given in table 2. Results have been obtained for all *ab initio* methods SCF, MP2, MP4, CCSD, CCSDT(T), and the DFT-based B3LYP, B3PW91, and B3P86. In addition to the final BSSE corrected value  $\mu_{\text{int}} \equiv \mu_{\text{int}}(\text{Rg} \dots \text{Xe})$  we give in this table the uncorrected  $\mu(\text{Rg} \dots \text{Xe})$  and the quantities  $\mu(\text{Rg} \dots \text{X})$  and  $\mu(\text{X} \dots \text{Xe})$ . In fact, the closeness of the final to the uncorrected value,

Table 2  
Interaction dipole moment Rg...Xe heterodiatoms<sup>a</sup> calculated at the experimental equilibrium distance (reference values in bold).

Diatom	$R_e$	Method	$\mu(\text{Rg}\dots\text{Xe})$	$\mu(\text{Rg}\cdots\text{X})$	$\mu(\text{X}\dots\text{Xe})$	$\mu_{\text{int}}$
He...Xe	7.51	SCF	−0.0033	0.0000	0.0000	−0.0033
		MP2	−0.0028	0.0000	−0.0001	−0.0028
		MP4	−0.0026	0.0000	−0.0001	−0.0026
		CCSD	−0.0026	0.0000	−0.0001	−0.0026
		<b>CCSD(T)</b>	<b>−0026</b>	0.0000	<b>−0001</b>	<b>−0025</b>
		B3LYP	−0.0025	0.0000	−0.0001	−0.0024
		B3PW91	−0.0037	0.0000	0.0000	−0.0037
		B3P86	−0.0031	0.0000	0.0000	−0.0031
		Ne...Xe	7.33	SCF	−0.0068	−0.0001
MP2	−0.0048			−0.0001	0.0002	−0.0050
MP4	−0.0046			−0.0001	0.0003	−0.0047
CCSD	−0.0048			−0.0001	0.0002	−0.0049
<b>CCSD(T)</b>	<b>−0045</b>			<b>−0001</b>	<b>0002</b>	<b>−0047</b>
B3LYP	−0.0034			−0.0001	−0.0001	−0.0032
B3PW91	−0.0062			−0.0001	0.0000	−0.0061
B3P86	−0.0049			−0.0001	0.0000	−0.0047
Ar...Xe	7.74			SCF	−0.0086	0.0000
		MP2	−0.0055	−0.0002	0.0001	−0.0054
		MP4	−0.0056	−0.0002	0.0001	−0.0055
		CCSD	−0.0060	−0.0002	0.0001	−0.0058
		<b>CCSD(T)</b>	<b>−0056</b>	<b>−0002</b>	<b>0001</b>	<b>−0055</b>
		B3LYP	−0.0057	0.0000	−0.0002	−0.0056
		B3PW91	−0.0063	−0.0001	−0.0001	−0.0061
		B3P86	−0.0052	0.0000	−0.0001	−0.0050
		Kr...Xe	7.94	SCF	−0.0059	0.0002
MP2	−0.0033			0.0002	0.0001	−0.0036
MP4	−0.0034			0.0002	0.0002	−0.0037
CCSD	−0.0037			0.0002	0.0001	−0.0040
<b>CCSD(T)</b>	<b>−0034</b>			<b>0002</b>	<b>0001</b>	<b>−0037</b>
B3LYP	−0.0035			0.0003	−0.0002	−0.0036
B3PW91	−0.0041			0.0002	−0.0001	−0.0041
B3P86	−0.0033			0.0003	−0.0001	−0.0035

<sup>a</sup>Xe on the positive z-axis.

$\mu_{\text{int}}(\text{Rg}\dots\text{Xe}) \approx \mu(\text{Rg}\dots\text{Xe})$  constitutes further evidence of the completeness of the basis sets used in the calculations.

As seen in Table 1 the BSSE affects the uncorrected  $\mu(\text{Rg}\dots\text{Xe})$  at the fourth decimal place, so uncertainties to such effects are of the order of  $1 \times 10^{-4} ea_0$ . The SCF values of the interaction dipole moment are  $\mu_{\text{int}}/ea_0 = -0.0033$  (HeXe),  $-0.0068$  (NeXe),  $-0.0085$  (ArXe), and  $-0.0060$  (KrXe). The electron correlation correction to these values is relatively large. Our most accurate values are, presumably, those obtained at the CCSD(T) level. The

Table 3  
R-dependence of the interaction dipole moment of the He...Xe diatom.

$R/a_0$	SCF	MP2	B3LYP	B3PW91
3.0	-0.6716	-0.6671	-0.6399	-0.6451
3.5	-0.4163	-0.4141	-0.3953	-0.3974
4.0	-0.2563	-0.2545	-0.2418	-0.2414
4.5	-0.1538	-0.1522	-0.1434	-0.1420
5.0	-0.0890	-0.0875	-0.0813	-0.0801
5.5	-0.0494	-0.0481	-0.0438	-0.0436
6.0	-0.0265	-0.0253	-0.0226	-0.0232
6.5	-0.0137	-0.0127	-0.0111	-0.0124
7.0	-0.0069	-0.0061	-0.0051	-0.0069
7.5	-0.0034	-0.0028	-0.0025	-0.0038
8.0	-0.0016	-0.0012	-0.0009	-0.0020
8.5	-0.0008	-0.0005	-0.0006	-0.0011
9.0	-0.0003	-0.0002	-0.0004	-0.0007
10.0	-0.0001	0.0000	-0.0002	-0.0004

Table 4  
R-dependence of the interaction dipole moment of the Ne...Xe diatom.

$R/a_0$	SCF	MP2	B3LYP	B3PW91
3.0	-1.1727	-1.1023	-1.0399	-1.0978
3.5	-0.8222	-0.8027	-0.7733	-0.7952
4.0	-0.4897	-0.4792	-0.4637	-0.4729
4.5	-0.2777	-0.2684	-0.2573	-0.2619
5.0	-0.1532	-0.1453	-0.1363	-0.1392
5.5	-0.0824	-0.0762	-0.0690	-0.0714
6.0	-0.0431	-0.0385	-0.0331	-0.0357
6.5	-0.0220	-0.0187	-0.0149	-0.0177
7.0	-0.0109	-0.0086	-0.0064	-0.0089
7.5	-0.0053	-0.0037	-0.0023	-0.0050
8.0	-0.0025	-0.0015	-0.0008	-0.0025
8.5	-0.0012	-0.0005	-0.0001	-0.0015
9.0	-0.0005	-0.0001	-0.0002	-0.0009
10.0	-0.0001	0.0001	-0.0003	-0.0005

total electron correlation, defined as  $ECC = CCSD(T) - SCF$ , is positive for all diatoms. In absolute terms the magnitude of the SCF  $\mu_{\text{int}}$  is significantly reduced. We see that MP2, MP4, and CCSD methods yield very reliable estimates for the interaction dipole moment. It is also interesting and instructive to observe clearly the performance of the DFT methods in comparison to the conventional *ab initio*. The popular B3LYP method is closest to the CCSD(T) for HeXe, ArXe, and KrXe. For NeXe the B3P86 method yields practically a value identical to that of the most accurate CCSD(T).

Table 5  
R-dependence of the interaction dipole moment of the Ar...Xe diatom.

$R/a_0$	SCF	MP2	B3LYP	B3PW91
4.0	-0.7301	-0.6784	-0.6468	-0.6613
4.5	-0.4189	-0.3941	-0.3849	-0.3902
5.0	-0.2388	-0.2217	-0.2193	-0.2217
5.5	-0.1353	-0.1224	-0.1220	-0.1228
6.0	-0.0757	-0.0660	-0.0660	-0.0663
6.5	-0.0416	-0.0343	-0.0342	-0.0348
7.0	-0.0223	-0.0171	-0.0170	-0.0177
7.5	-0.0117	-0.0080	-0.0082	-0.0088
8.0	-0.0060	-0.0034	-0.0030	-0.0046
8.5	-0.0030	-0.0012	-0.0018	-0.0018
9.0	-0.0015	-0.0003	-0.0002	-0.0016
10.0	-0.0003	0.0003	0.0001	-0.0007

Table 6  
R-dependence of the interaction dipole moment of the Kr...Xe diatom.

$R/a_0$	SCF	MP2 <sup>a</sup>	B3LYP <sup>a</sup>	B3PW91
4.0	-0.6079	-0.5351	-0.4889	-0.5083
4.5	-0.3466	-0.3223	-0.3038	-0.3107
5.0	-0.1972	-0.1834	-0.1760	-0.1792
5.5	-0.1124	-0.1024	-0.0991	-0.1006
6.0	-0.0638	-0.0560	-0.0546	-0.0551
6.5	-0.0357	-0.0297	-0.0290	-0.0292
7.0	-0.0196	-0.0151	-0.0147	-0.0150
7.5	-0.0106	-0.0073	-0.0072	-0.0078
8.0	-0.0056	-0.0033	-0.0033	-0.0039
8.5	-0.0029	-0.0013	-0.0012	-0.0018
9.0	-0.0015	-0.0004	-0.0006	-0.0008
10.0	-0.0004	0.0002	-0.0001	-0.0004

<sup>a</sup>Taken from Ref. [8].

In tables 3–6, we give the R-dependence of  $\mu_{\text{int}}$  for all heterodiatoms calculated at the SCF, MP2, B3LYP, and B3PW91 level of theory. The contents of these tables show clearly that the DFT methods reproduce qualitatively the R-dependence of the interaction dipole moment. We used our MP2 curves to obtain the variation of the curves around the respective  $R_e$ :

$$\begin{aligned}
 [\mu_{\text{HeXe}}(R) - \mu_{\text{HeXe}}(R_e)]/ea_0 &= 0.0043(R - R_e) - 0.0033(R - R_e)^2 \\
 &\quad + 0.0018(R - R_e)^3 - 0.0005(R - R_e)^4, \\
 [\mu_{\text{NeXe}}(R) - \mu_{\text{NeXe}}(R_e)]/ea_0 &= 0.0082(R - R_e) - 0.0067(R - R_e)^2 \\
 &\quad + 0.0035(R - R_e)^3 - 0.0008(R - R_e)^4,
 \end{aligned}
 \tag{3}$$

Table 7  
Theoretical predictions<sup>a</sup> and experimental estimates of the interaction dipole moment of the Rg...Xe heterodiatoms.

Diatom	$R_e$	$ \mu_{\text{int}} _e$	$\left(\frac{d\mu}{dR}\right)_e$
He...Xe	7.51	0.0025 0.001 <sup>b</sup>	0.0043
Ne...Xe	7.33	0.0047 0.003 <sup>b</sup>	0.0082
Ar...Xe	7.74	0.0055 0.005 <sup>b</sup>	0.0091
Kr...Xe	7.94	0.006 <sup>c</sup> 0.0037 0.003 <sup>c</sup>	0.0059

<sup>a</sup>Present investigation. CCSD(T) values for the interaction dipole moment, MP2 for its derivative at  $R_e$ .

<sup>b</sup>Bar-Ziv and Weiss [10].

<sup>c</sup>Jäger et al. [11].

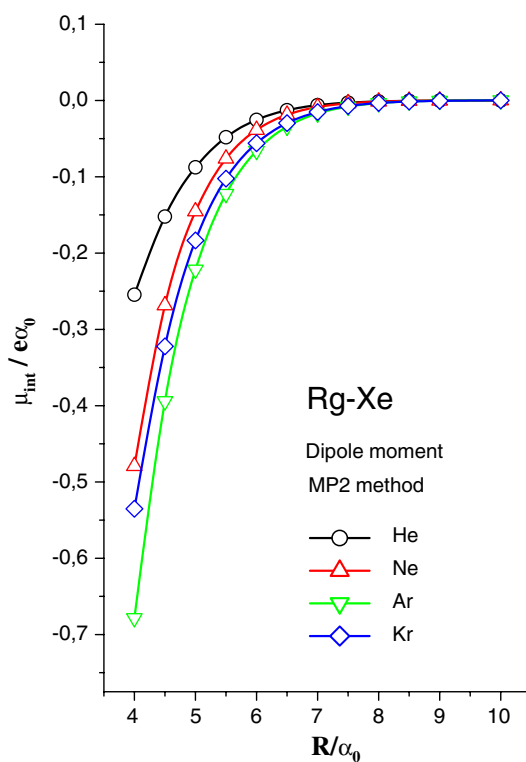


Figure 1.  $R$ -dependence of the interaction dipole moment of the complexes Rg...Xe at the MP2 level of theory.

$$\begin{aligned}
 [\mu_{\text{ArXe}}(R) - \mu_{\text{ArXe}}(R_e)]/ea_0 &= 0.0091(R - R_e) - 0.0065(R - R_e)^2 \\
 &\quad + 0.0030(R - R_e)^3 - 0.0008(R - R_e)^4, \\
 [\mu_{\text{KrXe}}(R) - \mu_{\text{KrXe}}(R_e)]/ea_0 &= 0.0059(R - R_e) - 0.0043(R - R_e)^2 \\
 &\quad + 0.0021(R - R_e)^3 - 0.0005(R - R_e)^4.
 \end{aligned}$$

We rely on the above expansions to deduce the derivatives of the interaction dipole moments at  $R_e$ ,

$$\left(\frac{d\mu_{\text{int}}(\text{RgXe})}{dR}\right)_e.$$

Our findings are shown in table 7 along with the calculated  $|\mu_{\text{int}}|$  and previous values deduced from experimental data. Our value for HeXe is somewhat above the old one of Bar-Ziv and Weiss [10]. For NeXe, ArXe, and KrXe our results are quite close to the more recent data obtained by Jäger et al. [11]. The overall agreement is quite good and encouraging.

Last, we have traced in figure 1 the  $R$ -dependence of the MP2 values of the dipole moment for all heterodiatoms. The effect is similar for all pairs although not monotonic:  $|\mu_{\text{int}}(\text{HeXe})| < |\mu_{\text{int}}(\text{NeXe})| < |\mu_{\text{int}}(\text{ArXe})|$  but  $|\mu_{\text{int}}(\text{HeXe})| < |\mu_{\text{int}}(\text{KrXe})| < |\mu_{\text{int}}(\text{ArXe})|$ .

#### 4. Conclusions

We have calculated the interaction dipole moment  $\mu_{\text{int}}$  for the systems Rg...Xe, Rg = He, Ne, Ar, and Kr. Electron correlation effects are of importance for  $\mu_{\text{int}}$ . Our best CCSD(T) values agree quite well with the available experimental estimates. The DFT methods B3LYP and B3PW91 provide a qualitative correct description of the  $R$ -dependence of the interaction dipole moment and the agreement with the MP2 method is improved as we move from He...Xe to Kr...Xe. We have calculated for the first time derivatives  $\left(\frac{d\mu_{\text{int}}(\text{RgXe})}{dR}\right)_e$  for all pairs.

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