

***Ab initio* ground state potential energy surfaces for Rg–Br₂ (Rg=He, Ne, Ar) complexes**

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High-level *ab initio* molecular electronic structure calculations are performed for Rg–Br₂ (Rg = He, Ne, Ar) complexes at CCSD(T) (coupled cluster using single and double excitations with a noniterative perturbation treatment of triple excitations) level of theory. Specific augmented correlation consistent basis sets are used for each noble atom (Rg), supplemented with an additional set of bond functions. Effective-core potentials (ECPs), augmented with diffusion (*sp*) and polarization (3*df*) functions, have been employed for the bromine atoms. For all complexes, the CCSD(T) potential energy surfaces (PESs) show double-minimum topology, with wells at both linear and T-shaped configurations; the linear minimum is found to be deeper than the T-shaped one. Vibrational corrections are taken into account for all the complexes and their effects in the stability of the linear and T-shaped conformers are examined. For each complex and each configuration (linear and T-shaped), R_e equilibrium intermolecular distances, D_e and D_0 dissociation energies, are evaluated and compared with previous theoretical and/or experimental results. © 2002 American Institute of Physics. [DOI: 10.1063/1.1473800]

I. INTRODUCTION

The rare gas–halogen van der Waals (vdW) molecules provide relatively simple systems for which intermolecular potentials and dynamical processes can be studied in great detail by both experimentalists and theoreticians (see Refs. 1 and 2). One of the most interesting subjects of the rare gas dihalogen complexes turns out to be the structural analysis of their ground electronic state. *Ab initio* results predict global minima for linear configurations of these complexes^{3–7} whereas experimental data were consistent with the T-shaped configuration for the ground (*X*) and electronically excited (*B*) states. Huang *et al.*⁸ have shown that this disagreement between theory and experiment is due to the zero-point vibrational energy that favors the T-shaped isomer.

Among the rare gas–dihalogen species, the most detailed theoretical studies have been performed for Rg–Cl₂ complexes (see Ref. 9 and references therein) and, in contrast, less attention has been paid to Rg–Br₂ systems, despite the experimental data available. In studying the dynamics of rare gas–dihalogen molecules, pairwise additive atom–atom potentials have been commonly used (see Refs. 10 and 11) with success in describing some important phenomena, but more detailed theoretical studies have shown¹² that atom–atom forms are not consistent with experimental observations. Therefore, high-level *ab initio* theory should be employed to describe the weak van der Waals interactions.

He–Br₂ is one of the most studied complexes. Potential energy surfaces based on MP4 *ab initio* calculations have been reported¹² for its ground (*X*) and excited (*B*) states and dynamical quantum calculations have been carried out^{10,12,13} emphasizing the importance of the anisotropy of the PES for

the ground electronic state of He–Br₂. Later, another MP4 surface has been calculated¹⁴ and used to calculate an excitation spectrum of He–Br₂. Recently, a study based on CCSD(T) approach has been presented for Ne–Br₂ (Ref. 15) and, for Ar–Br₂, *ab initio* results¹⁶ at CCSD(T) level have established the double minimum topology of its potential energy surface but show a considerable underestimation of the binding energy of the complex.

The aim of this study is to present high-level *ab initio* calculations, as accurately as currently possible at an *ab initio* level, and to reproduce reliable PESs comparable to the available experimental data for weakly bound systems, for Rg–Br₂ complexes. Thus, we report on theoretical predictions of the linear and T-shaped structures, energies, and vibrational frequencies of Rg–Br₂ systems, and we compare our results with the best available values.

The paper is organized as follows. In Sec. II we outline the computational details of our *ab initio* calculations. In Sec. III we discuss our *ab initio* results for each complex, we present the parametrized potential energy surfaces and discuss on equilibrium geometries, binding energies, and vibrational frequencies and compare with experimental data or previous *ab initio* studies. Conclusions constitute the closing section.

II. COMPUTATIONAL DETAILS

The *ab initio* calculations are performed using the GAUSSIAN 98 package.¹⁷ All computations are carried out at the CCSD(T) level of theory. For bromine atoms the Stuttgart group (SDD) effective core potential¹⁸ is employed. The valence electrons are described using the SDD basis set augmented with (*sp*) diffusion and (3*df*) polarization functions, denoted as SDD+G(3*df*). The exponents of diffusion and polarization functions used for bromine associated with

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the SDD ECP were those specified in the literature.^{15,19,20} Such ECPs basis sets have been used^{19–21} in calculations of halogen-containing molecules. In particular, CCSD(T) calculations for the Br₂ molecule using the SDD+G(3df) basis set¹⁵ are in very good agreement with experimental data and recent CCSD(T) *ab initio* calculations using the extended SDB-cc-pVQZ basis set.²²

For van der Waals complexes, efficient basis sets can be constructed with the use of midbond functions. Studies by Tao and Pan²³ have shown the importance of these property specific basis sets; they provide an efficient way^{3,24} to saturate the dispersion energy, the dominant attractive force in the case of vdW complexes (e.g., Rg–X₂, X=F, Cl, Br). The justification for using basis sets with bond functions is based on comparison with results obtained using larger basis sets in recent studies on weakly bound systems.^{9,25–28} For example, potential energy surfaces for Rg–F₂ and Rg–Cl₂ complexes have been already re-examined^{9,26} using basis sets augmented with bond functions. The high quality of the results obtained with basis sets augmented with bond functions became even more convincing when comparison has been made²⁵ with interaction energies for Ar–HCl at the complete basis set limit.

The exponents of the bond functions are known to be quite system independent²⁹ and, after studying the efficiency of some of them performing systematic calculations, we select the (3s3p2d2f1g) bond functions with exponents given in Ref. 27. Therefore, for the Rg atom we used augmented correlation consistent (aug-cc-pVnZ, n=Q,5) basis sets incorporated in the GAUSSIAN 98 programs supplemented with an additional set (3s3p2d2f1g) of bond functions²⁷ and will be denoted as aug-cc-pVnZ+(3s3p2d2f1g), n=Q,5. We place the bond functions in the middle of the van der Waals bond and in all calculations 6d and 10f Cartesian functions are used.

In our study, for each complex, the results obtained with aug-cc-pVnZ+(3s3p2d2f1g) basis sets were in better agreement with experimental data than those obtained using aug-cc-pVnZ basis sets, demonstrating that the use of bond functions clearly gives much more efficient basis sets. To better illustrate the importance of bond functions we report on the dissociation energies for the Rg–Br₂ complexes, taken using aug-cc-pVnZ basis sets with and without (3s3p2d2f1g) bond functions. For He–Br₂ we get a difference of 11 cm^{–1} in the *D_e* values of the T-shaped and linear configurations, for Ne–Br₂ a difference of 35 cm^{–1} and for Ar–Br₂ is 98 cm^{–1}, resulting in a significant improvement with respect to the corresponding values when using aug-cc-pVnZ, n=Q,5 basis sets for the Rg atoms. We should note that results obtained with the aug-cc-pVnZ, n=Q,5 basis with and without bond functions are qualitatively similar. The difference between the energies of the linear and the T-shaped structures is preserved, with the T-shaped configurations being always higher in energy than the linear ones, independently of the use of the bond functions.

III. RESULTS

A. *Ab initio* calculations

The potential energy surfaces for He–Br₂, Ne–Br₂, and Ar–Br₂ complexes are examined using the supermolecular approach. In a supermolecular calculation, the interaction energy between a pair of atoms or molecules, is given by

$$\Delta E = E_{\text{Rg-Br}_2} - E_{\text{BSSE}} - E_{\text{Rg}} - E_{\text{Br}_2}, \quad (1)$$

where *E_{Rg-Br₂}*

 is the energy of the complex (Rg = He, Ne, Ar) and the *E_{Rg}*, *E_{Br₂}* are the energies of the monomers. The results are corrected for the basis-set superposition error (*E_{BSSE}*) using the standard counterpoise method.³⁰ We used Jacobi coordinates (*r*, *R*, *θ*) to describe the triatomic complexes, where *R* is the intermolecular distance of Rg atom from the center of mass of Br₂, *r* is the bond length of Br₂, and *θ* is the angle between the **R** and **r** vectors. For each of the Rg–Br₂ molecules, we examined several intermolecular distances *R* (2.5 ≤ *R* ≤ 10 Å), and for each of them we performed calculations for *θ* = 0°, 30°, 60°, 90° with fixed *r* = 2.28 Å. The results for each system are listed in three tables: Table I contains the CCSD(T) interaction energies for He–Br₂, Table II for Ne–Br₂ and Table III for the Ar–Br₂ complex.

For He–Br₂, we get [see Figs. 1(a), 2(a), and Table IV] at *θ* = 0°, *D_e* = 222.5 μ*E_h* (48.8 cm^{–1}) and *R* = 4.42 Å, for *θ* = 90° *D_e* = 183.5 μ*E_h* (40.3 cm^{–1}) and *R* = 3.58 Å. These results are in agreement with previous *ab initio* calculations,¹⁴ although our calculations give lower interaction energies (5.8 cm^{–1} for the linear isomer and 1.3 cm^{–1} for the T-shaped one) than in the previous study (see Table IV). Furthermore, our calculations predict a larger (by 8.5 cm^{–1}) difference between the energies of the two structures than the results of Williams.¹⁴ In Table IV we also present results on the *D_e* and *R_e* values given by a IDIM PT1 semiempirical model.¹⁰ This model predicts double mini-

TABLE I. CCSD(T) interaction energies for the He–Br₂ molecule obtained with the aug-cc-pV5Z+(3s3p2d2f1g) basis set for the He and SDD+G(3df) ECP for Br at *θ* = 0°, 30°, 60°, and 90°. *r* fixed at 2.28 Å.

<i>R</i> ^a (Å)	<i>ΔE</i> (μ <i>E_h</i>)			
	<i>θ</i> = 0°	<i>θ</i> = 30°	<i>θ</i> = 60°	<i>θ</i> = 90°
2.5	1914.3			
3.0	–132.0	8084.9	4673.3	249.1
3.25	–222.4			–95.1
3.5	–197.8			–180.1
3.75	–150.0			–171.3
4.0	–109.1		–46.7	–140.7
4.25	–77.6	–16.8	–90.2	–107.2
4.5	–55.2	–104.2	–88.3	–79.4
4.75		–109.5		
5.0	–29.0	–91.3	–56.9	–43.0
5.5		–52.3	–32.3	
7.0	–3.8	–9.6	–6.7	–5.3
9.0	–0.8	–1.7	–1.3	–1.2

^aFor linear configurations *R* is the distance to the nearest Br atom and for all the other configurations the distance from He atom to the Br₂ center of mass.

TABLE II. CCSD(T) interaction energies for the Ne-Br₂ molecule obtained with the aug-cc-pVQZ+(3s3p2d2f1g) basis set for the Ne and SDD+G(3df) ECP for Br at $\theta=0^\circ, 30^\circ, 60^\circ$, and 90° . r fixed at 2.28 Å.

R^a (Å)	ΔE (μE_h)			
	$\theta=0^\circ$	$\theta=30^\circ$	$\theta=60^\circ$	$\theta=90^\circ$
2.5	5413.5			
3.0	-104.4			658.9
3.25	-413.4			-167.5
3.5	-401.6	7682.1	1020.3	-377.6
3.75	-315.3			-369.5
4.0	-230.7		-170.0	-301.0
4.25	-164.4	-95.8	-226.0	-228.4
4.5	-116.8	-252.7	-203.2	-168.5
4.75		-247.5	-161.9	
5.0	-60.9	-200.0	-122.8	-90.4
5.5		-111.1	-67.9	
7.0	-7.6	-19.5	-13.6	-10.8
9.0	-1.8	-3.5	-2.6	-2.3

^aFor linear configurations R is the distance to the nearest Br atom and for all the other configurations the distance from Ne atom to the Br₂ center of mass.

imum topology for the ground He-Br₂ state with almost similar energies for the two isomers; 38.0 cm⁻¹ for the linear and 37.9 cm⁻¹ for the T-shaped.

For Ne-Br₂, we get [see Figs. 1(b), 2(b), and Table IV] at $\theta=0^\circ$ $D_e=426.7\mu E_h$ (93.6 cm⁻¹) and $R=4.49$ Å, and at $\theta=90^\circ$ $D_e=391.6\mu E_h$ (85.9 cm⁻¹) and $R=3.60$ Å. Again, the interaction energies predicted by our calculation are lower than the ones obtained in a previous CCSD(T) *ab initio* calculation¹⁵ for both conformers (see Table IV). The differences account 26.3 cm⁻¹ for the linear structure and 25.4 cm⁻¹ for the T-shaped one, and this improvement in the binding energies for Ne-Br₂ fully justifies the use of the bond functions.

For Ar-Br₂ [see Figs. 1(c), 2(c), and Table IV], $D_e=1197.1\mu E_h$ (262.7 cm⁻¹) and $R=4.63$ Å at $\theta=0^\circ$, and $D_e=1031.3\mu E_h$ (226.4 cm⁻¹) and $R=3.8$ Å at $\theta=90^\circ$.

TABLE III. CCSD(T) interaction energies for the Ar-Br₂ molecule obtained with the aug-cc-pVQZ+(3s3p2d2f1g) basis set for the Ar and SDD+G(3df) ECP for Br at $\theta=0^\circ, 30^\circ, 60^\circ$, and 90° . r fixed at 2.28 Å.

R^a (Å)	ΔE (μE_h)			
	$\theta=0^\circ$	$\theta=30^\circ$	$\theta=60^\circ$	$\theta=90^\circ$
2.5	18 822.4			
3.0	667.9			4636.2
3.25	-926.7			684.9
3.5	-1200.6	26 025.0	5053.7	-701.6
3.75	-1047.8			-1022.0
4.0	-809.3		-115.6	-952.0
4.25	-595.3	334.5	-568.7	-773.0
4.5	-430.0	-567.1	-622.3	-591.8
4.75		-742.6	-538.9	
5.0	-225.3	-666.5	-427.4	-326.8
5.5		-401.2	-245.8	
7.0	-27.4	-71.4	-48.9	-38.5
9.0	-6.1	-12.4	-9.4	-8.0

^aFor linear configurations R is the distance to the nearest Br atom and for all the other configurations the distance from Ar atom to the Br₂ center of mass.

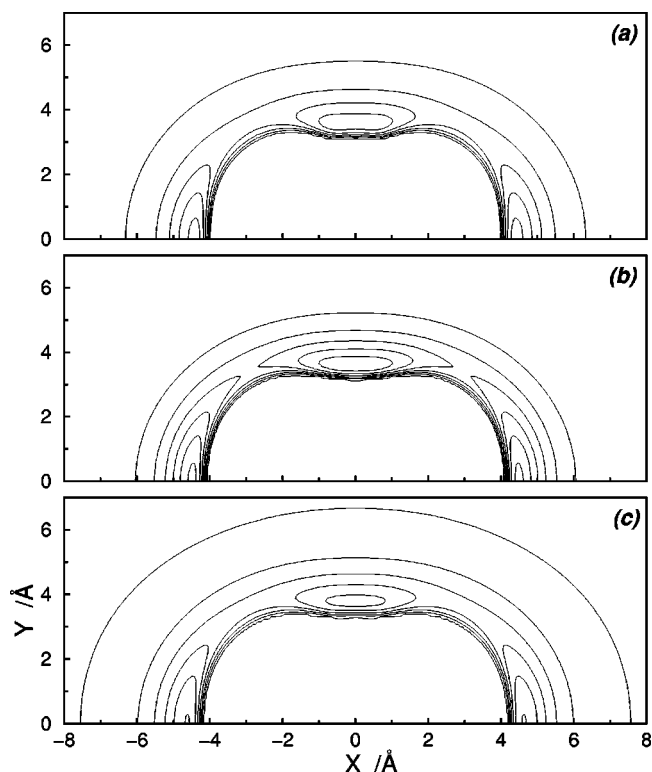


FIG. 1. Contour plots of the Rg-Br₂ potential energy surfaces, $V(R, \theta)$ [Eq. (3)]. (a) For He-Br₂ contour intervals are of 10 cm⁻¹ and for energies from -45 to 15 cm⁻¹. (b) For Ne-Br₂ contour intervals are of 15 cm⁻¹ and for energies from -90 to 15 cm⁻¹. (c) For Ar-Br₂ contour intervals are of 50 cm⁻¹ and for energies from -260 to 40 cm⁻¹. The Br-Br bond length is fixed at 2.28 Å.

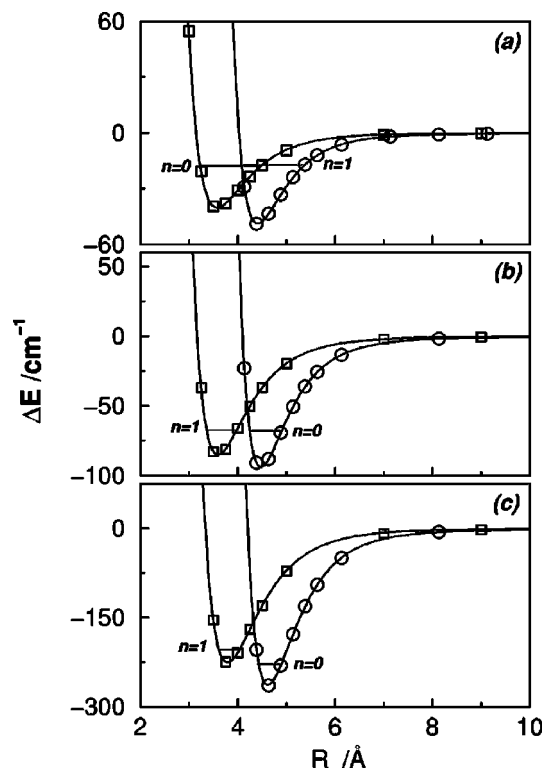


FIG. 2. Potential energy curves for Rg-Br₂ complexes, calculated at CCSD(T) level with the SDD+G(3df) basis set for Br and aug-cc-pV5Z+(3s3p2d2f1g) basis set for He (a), aug-cc-pVQZ+(3s3p2d2f1g) basis set for Ne (b) and Ar (c). *Ab initio* results are indicated by open symbols, circles for $\theta=0^\circ$ and squares for $\theta=90^\circ$. Full lines are for the parametrized potential curves $V(R, \theta)_{i=1,4}$ [Eq. (2)].

TABLE IV. Binding energies (D_e and D_0 in cm^{-1}) and equilibrium distances (in Å) for the indicated Rg-Br₂ (Rg=He, Ne, Ar) complexes.

Complex		Linear			T-shaped		
		D_e	D_0	R_e	D_e	D_0	R_e
He-Br ₂	This work	48.8	17.2	4.42	40.3	17.7	3.58
	Best <i>ab initio</i> value (Refs. 1, 14)	43.0		4.50	39.0		3.70
	Semiempirical value (Ref. 10)	38.0	16.8	4.93	37.9	17.3	3.63
	Experimental value (Refs. 1, 31)					17.0±1.5	
Ne-Br ₂	This work	93.6	68.0	4.49	85.9	67.3	3.60
	Best <i>ab initio</i> value (Ref. 15)	67.3	46.2	4.61	60.5	46.7	3.73
	Semiempirical value (Ref. 33)					71.25	3.64
	Experimental value (Ref. 32)					70.5±2.0	3.67
Ar-Br ₂	This work	262.7	228.0	4.63	226.4	203.5	3.80
	Best <i>ab initio</i> value (Ref. 16)	162.6		4.85	145.3		3.99
	Semiempirical value (Ref. 16)	256.6	220.0	4.60	247.2	213.5	3.65

Recent *ab initio* CCSD(T) calculations by Naumkin and McCourt¹⁶ for the Ar-Br₂ ground state have estimated 162.6 cm^{-1} and 145.3 cm^{-1} for the D_e of the two isomers (see Table IV). In order to represent their *ab initio* data, Naumkin and McCourt¹⁶ have suggested diatomics-in-molecules (DIM) based models predicted a D_e value of 256.1 cm^{-1} for the linear isomer and 247.2 cm^{-1} for the T-shaped (see Table IV). Both estimates (*ab initio* and semiempirical) are higher than our predictions.

B. Analytical representation of the PESs

For each θ , the calculated interaction energies (see Tables I, II, III) are fitted to an analytical expression. Various potential forms are tested for the $V(R, \theta_i)$, $i=1-4$ curves, including Morse, Degli Esposti, and Werner,³⁴ and combinations of Morse-vdW, Morse-Born-Mayer-vdW type. We found that the Morse-vdW type form was the most flexible, allowing for an accurate representation of the *ab initio* points at short ($1.5 \leq R \leq 3.0$ Å) and large ($R \geq 10.0$ Å) distances, ensuring a correct asymptotic behavior. Therefore, we use

this analytical expression to fit the CCSD(T) data for each complex. The potential function has the following form,

$$V(R, \theta_i) = D_e^i (\exp(-2\alpha^i(R - R_e^i)) - 2 \exp(-\alpha^i(R - R_e^i))) - \frac{C_6^i}{R^6} - \frac{C_8^i}{R^8}, \quad (2)$$

with parameters D_e^i , α^i , R_e^i , C_6^i , and C_8^i , $i=1-4$. For each Rg-Br₂ complex, and each angle we fitted the *ab initio* points given in Tables I, II, and III to the expression given in Eq. (2). All adjustable parameters for each Rg-Br₂ complex are listed in Table V using a nonlinear least square calculation. We should note that the above parameters do not have physical meaning and they simply serve the fitting procedure. The average absolute deviation (standard deviation) between the original *ab initio* data and the fit was smaller than 0.55 μE_h (0.12 cm^{-1}) for He-Br₂, 0.64 μE_h (0.14 cm^{-1}) for Ne-Br₂ and 3.0 μE_h (0.7 cm^{-1}) for Ar-Br₂ for energies $\Delta E \leq 1000$ cm^{-1} .

To represent the two-dimensional interaction potentials

TABLE V. Parameters for the $V(R, \theta_i)$, $i=1-4$ potential [Eq. (2)] for the indicated Rg-Br₂ (Rg=He, Ne, Ar) complexes. Distances are in Å and energies in cm^{-1} .

θ	D_e	α	R_e	C_6	C_8
He-Br ₂ complex					
0°	51.1559	1.917 46	4.332 65	351 738.0	-7.053 81e06
30°	6.808 33	1.802 98	4.925 56	206 838.0	38 079.4
60°	8.330 59	1.707 09	4.495 13	180 297.0	-1.795 57e06
90°	5.812 44	1.652 89	4.184 63	97 681.0	137 714.0
Ne-Br ₂ complex					
0°	22.5201	1.977 39	4.784 41	383 914.0	6.349 79e06
30°	15.5201	1.838 80	4.881 77	400 073.0	1.321 19e06
60°	13.3680	1.743 22	4.550 66	334 625.0	-1.509 96e06
90°	10.8445	1.698 59	4.200 71	225 779.0	129 474.0
Ar-Br ₂ complex					
0°	334.0670	1.765 70	4.481 61	2.433 58e06	-6.343 72e07
30°	343.3370	1.683 28	4.405 10	2.565 72e06	-8.745 64e07
60°	23.5244	1.521 75	5.035 27	555 289.0	1.393 25e07
90°	10.8432	1.563 97	4.865 62	545 334.0	1.013 10e07

of the Rg-Br₂ complexes we use an expansion in Legendre polynomials,

$$V(R, \theta) = \sum_{\lambda} V_{\lambda}(R) P_{\lambda}(\cos \theta), \quad (3)$$

where the $V_{\lambda}(R)$ coefficients are obtained by a collocation method. Figure 1 presents two-dimensional contour plots of the $V(R, \theta)$ surfaces for all the Rg-Br₂ complexes in the XY-plane. The equipotential curves are shown for Rg moving around of a Br₂ molecule with fixed $r_e = 2.28$ Å. For each complex, the linear potential well is deeper than the perpendicular well and the barriers between the two wells are at energies -18.1 cm⁻¹ for He-Br₂, -44.5 cm⁻¹ for Ne-Br₂ and -126.5 cm⁻¹ for Ar-Br₂. The isomerization barrier for He-Br₂ is rather low, so the lowest vibrational levels are expected to be extended in both wells. For Ne-Br₂ and Ar-Br₂ the isomerization barriers are high enough, so the lowest vibrational levels of these complexes are expected to be mostly localized in either the linear or T-shaped well.

C. Vibrational analysis

As mentioned before, the zero-point energy plays an extremely important role in the stabilization of the T-shaped structures for all these complexes. Therefore, zero-point energies are calculated here for the Rg-Br₂ complexes. The harmonic approximation is expected to underestimate the zero-point energy for these complexes, therefore, we performed quantum mechanical calculations to evaluate the D_0 for these systems. The Hamiltonian has the form

$$\hat{H} = -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial R^2} + \frac{\hat{j}^2}{2\mu_2 r_e^2} + \frac{\hat{l}^2}{2\mu_1 R^2} + V(r_e, R, \theta), \quad (4)$$

where $\mu_1^{-1} = m_{\text{Rg}}^{-1} + (2m_{\text{Br}})^{-1}$ and $\mu_2^{-1} = m_{\text{Rg}}^{-1} + m_{\text{Br}}^{-1}$ are the reduced masses, m_{Rg} (Rg=He, Ne, Ar) and m_{Br} are the atomic masses, \hat{l} and \hat{j} are the angular momenta associated with the vectors \mathbf{R} and \mathbf{r} , respectively, leading to a total angular momenta $\hat{J} = \hat{l} + \hat{j}$. r_e is fixed to the equilibrium Br-Br bond length, and the potential for each complex is given by the $V(R, \theta)$ expansion [Eq. (3)].

Using the one-dimensional potentials given in Eq. (3), numerical basis functions $\{f_n(R)\}_{n=1, \dots, 12}$ are obtained by solving the one-dimensional Schrödinger equation. For each angle θ , we choose three basis functions and we orthonormalized them using the Gram-Schmidt procedure. For a zero total angular momentum, $\hat{l} = -\hat{j}$, the corresponding two-dimensional Hamiltonian is represented in the radial, $\{f_n(R)\}$, and the angular, $\{P_m(\cos \theta)\}$, basis functions and the calculated eigenvalues correspond to the vibrational energy levels. The results of these calculations, in comparison with the best available data for the Rg-Br₂ complexes are summarized in Table IV. In Fig. 3 we present contour plots of the probability density distributions for the two lowest vdW vibrational levels ($n=0, n=1$) for each of the Rg-Br₂ molecules.

For He-Br₂ complex the lowest two ($n=0, 1$) vdW vibrational levels for $J=0$ are found at energies of -17.7 and -17.2 cm⁻¹, respectively, with a very small energy difference between them (≈ 0.5 cm⁻¹), and slightly above the

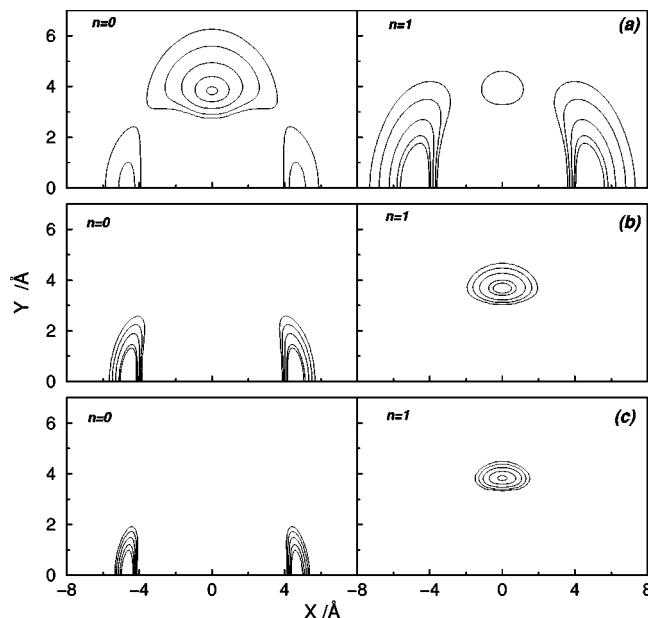


FIG. 3. Contour plots of the probability density distributions for the $n=0$ and $n=1$ vdW levels calculated using the $V(R, \theta)$ [Eq. (3)] for each Rg-Br₂ complex. (a) For He-Br₂ contour lines are for 1.0, 0.5, 0.1, 0.01, 0.001, (b) for Ne-Br₂ contour lines are for 2.0, 1.0, 0.1, 0.01, 0.001, (c) for Ar-Br₂ contour lines are for 5.0, 1.0, 0.1, 0.01, 0.001.

isomerization barrier. The $n=0$ eigenfunction is mainly localized in the T-shaped well, whereas the $n=1$ corresponds to linear configurations [see Figs. 2(a) and 3(a)]. However, we should note [see Fig. 3(a)] that both the $n=0$ and $n=1$ wave functions are extended to linear and T-shaped configurations. As we see, zero-point vibrational corrections bring the energies of the two configurations to approximately the same level and they reverse the ordering of the two minima, with the T-shaped to be the lowest one. This is in accord with predictions based on semiempirical data¹⁰ and on an indirect experimental estimate^{1,31} (see Table IV).

For Ne-Br₂ system, the $n=0, 1$ vdW vibrational levels for $J=0$ are at energies of -68.0 and -67.3 cm⁻¹, respectively, with an energy difference of only 0.7 cm⁻¹. These figures are within the error bar of the experimental estimate³² of $D_0 = 70.5 \pm 2.0$ cm⁻¹ (see Table IV). The $n=0$ eigenfunction localized in the linear isomer and the $n=1$ in the T-shaped one [see Figs. 2(b) and 3(b)]. It is interesting to note that the zero-point corrections does not alter the stability of the two minima for the Ne-Br₂.

For Ar-Br₂ molecule, we found the $n=0, 1$ vdW vibrational levels at energies of -228.0 and -203.5 cm⁻¹ with an energy difference of 24.5 cm⁻¹. Our calculations indicate that the linear well still remains significantly deeper than the T-shaped one, even when the zero-point vibrational energy is included. Figures 2(c) and 3(c) show that the $n=0$ eigenfunction corresponds to linear configurations, while the $n=1$ to T-shaped configurations. To our knowledge there is no experimental information available for the D_0 value of Ar-Br₂ complex. On the other hand, the previous *ab initio* calculations¹⁶ underestimate considerably the binding energy

of Ar-Br₂ (see Table IV). Therefore, we can only make a comparison with an available semiempirical estimate¹⁶ based on a scaled DIM model (see Table IV).

IV. CONCLUSIONS

We have presented results of *ab initio* calculations for the interaction of Rg=He, Ne, Ar, with Br₂ molecule using CCSD(T) approach. The (aug-cc-pVnZ, n=Q,5) + (3s3p2d2f1g) basis sets have been employed for the rare gas atoms and the SDD effective core potential basis sets supplemented with diffusion and polarization functions [SDD+G(3df)] for the Br atoms. The CCSD(T) calculations, the most accurate to date for all the Rg-Br₂ (Rg=He, Ne, Ar) molecules, are in good accord with available experimental data. High quality basis sets and correlation treatments are essential for obtaining an accurate description of van der Waals complexes. As in all previous *ab initio* studies, each surface has a double minimum topology with linear and T-shaped isomers. The CCSD(T) interaction energies for the linear configurations are found to be lower than the T-shaped ones for all the Rg-Br₂ complexes studied.

Zero-point vibrational energy corrections are found to be very important in the stability of the linear and T-shaped isomers. The most interesting appears to be the case of He-Br₂ for which the ground vibrational state is found to correspond mainly to T-shaped structure, whereas the first vibrational state corresponds to the linear configuration and is only 0.4 cm⁻¹ higher than the ground one. For Ne-Br₂ and Ar-Br₂ the zero-point vibrational effects are less important and does not reverse the ordering of the two minima. For He-Br₂ and Ne-Br₂, molecules the geometries and their binding energies predicted by the CCSD(T) calculations are in excellent agreement with experimental estimates.^{12,13,32} For all the Rg-Br₂ complexes, the present results are more reliable than the best available ones. Work is in progress for constructing three-dimensional potential energy surfaces for these complexes to study their dynamics and spectra. Preliminary results³⁵ on the B←X excitation spectrum of HeBr₂ show that the double minimum surface presented here for the ground (X) state describes very well the experimental spectrum of the HeBr₂ complex,¹² indicating that for the HeBr₂ the two structures are likely very close in energy and therefore, both of them can be determined by the experiment.

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