J. Phys. Chem. A **2004,** *108,* 6065−6071

Three-Dimensional ab Initio Potential and Ground State Dynamics of the HeI_2 Complex

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Received: March 18, 2004; In Final Form: May 25, 2004

The interaction potential for the HeI_2 molecule is studied using the coupled-cluster (CCSD(T)) method. A correlation-consistent triple-ζ valence basis set in conjunction with a large-core Stuttgart−Dresden−Bonn (SDB) relativistic pseudopotential is used for the iodine atoms, whereas augmented correlation-consistent basis sets, aug-cc-pV5Z, are used for the He atom, supplemented with a set of bond functions. The potential energy surface of the ground electronic state of HeI_2 shows a double-minimum topology, with an isomerization barrier of 25.64 cm^{-1}. Bound state calculations are carried out for $J = 0$, and the lowest vibrational vdW level corresponds to the linear configuration, while a level found only 0.7 cm^{-1} above is assigned to a T-shaped isomer. The CCSD(T) dissociation energies for the linear and T-shaped configurations are found to be $D_0^L = 15.38$ cm^{-1} and $D_0^T = 14.68$ cm^{-1}, with vibrationally averaged structures of $R_0 = 5.34$ and 4.40 Å, respectively. The above results are in good accord with experimental investigations available for the T-shaped isomer. Further, the present calculations predict the existence of a linear isomer, and the rather small energy difference between them indicates that linear and T-shaped isomers can coexist even at low temperatures for the He−I_2 complex.

I. Introduction

HeI_2 was the first rare gas−dihalogen van der Waals molecule studied by Levy and co-workers.[1,2] Their analysis indicates that the molecule in its ground electronic state has a perpendicular structure with $R_0 = 4.47 \pm 0.13$ Å, and R_e is estimated to be smaller by ≈0.5 Å than R_0.[1] The binding energy has been determined[2] by analyzing the product distribution from vibrational predissociation in the B excited state. The blue-shift values for high v levels have been extrapolated from the lower vibrational ones, and a value of $D_0 = 18.8 \pm 0.6$ cm^{-1} has been reported for the X state of HeI_2.[2] Later, Sharfin et al.[3] measured the blue-shift values for high v levels, and a lower value, by 1.2 cm^{-1}, than the one used by Blazy et al.[2] has been obtained for the $v = 62$ level. Thus, Janda and co-workers[4] have reevaluated the available data for HeI_2 and suggested that the ground state binding energy, D_0, be revised to 17.6 ± 1.0 cm^{-1} from the previous reported value of 18.8 cm^{-1}.

The first attempt to calculate a purely ab initio surface for such complexes was undertaken by Schwenke and Truhlar[5] for the ground electronic state of HeI_2. The authors have calculated the interaction energy for T-shaped geometries using Møller−Plesset perturbation theories up to third order. The well-depth that they obtained, 6 cm^{-1}, was significantly shallow, although they show that the potential derived from the spectra by Levy and co-workers[2] underestimates considerably the steepness of the repulsive wall. On the basis of their ab initio results, they have proposed a more reasonable semiempirical potential[5] with well-depth and well-distance of 2.73 meV (22.02 cm^{-1}) and 7.65 α_0 (4.05 Å), respectively.

Recently, due to an increase in computer power, ab initio electronic structure calculations have advanced to a point that they are useful for determining the potential surface of rare gas−dihalogen complexes.[6−15] The problem of the topology of the ground state rare gas−dihalogen PESs is challenging for the general theory of intermolecular interactions. For such species (homonuclear), there is a general acceptance of the existence of a double-minimum topology, associated with linear and T-shaped isomers. This statement is based on recent experimental observations by the groups of Klemperer and Heaven on ArI_2[16,17] and NeI_2[18] complexes and a series of high-level ab initio calculations[11,19−22] on these systems. One of the goals of such theoretical studies is to assist the experimental search and assignment of the signatures of different isomers.

Thus, in this work, we present results of high-level ab initio calculations at the CCSD(T) level for the HeI_2 complex. In our calculations, relativistic effects are included with the use of large-core pseudopotentials for I atoms, and consistent correlated basis set are employed for the He atom, while for a better description of long-range interactions a set bond function is used. The purpose of this study is to construct a reliable three-dimensional surface reproducing the available experimental data for the ground state of HeI_2, as regards its dynamics and spectra.

II. Results

II.A. Ab Initio Computation. We use the Jacobi coordinates (r,R,θ) to describe the potential surface of the HeI_2 complex, where R is the intermolecular distance of the He atom from the center of mass of I_2, r is the bond length of I_2, and θ is the angle between the $\mathbf{R}$ and $\mathbf{r}$ vectors. Intermolecular energies are calculated for several R distances ranging from $R = 3$ to 9 Å, while the angle θ is varied between 0° and 90° on a seven equally spaced (by $\pi/12$ rad) grid, considering four different I_2 bond lengths with $r = 2.422\,49$, 2.666, 2.909 51, and 3.110 92 Å. The r values are chosen around the equilibrium distance of $r_e = 2.666$ Å in a range that is enough to describe some of the first excited vibrational levels of I_2(X).

The ab initio calculations are performed using the Gaussian 98 package,[23] using the spin-restricted single- and double-excitations coupled-cluster method with perturbative triples [RCCSD(T)] correlating only the valence electrons. For the

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10.1021/jp048787t CCC: $27.50 © 2004 American Chemical Society
Published on Web 06/19/2004

TABLE 1: Experimental and CCSD(T) Theoretical Spectroscopic Constants for the I_2 Molecule[a]

	CCSD(T)		
property	this work	SDB-cc-pVTZ[b]/cc-pTVZ-PP[c]/cc-pV5Z-PP[c]	experiment[d]
D_e /kcal/mol	42.61(32.50)	(26.06)/41.02(30.41)/46.23(36.01)	35.57
r_e /Å	2.6794	2.6831/2.6964/2.6755	2.6663
ω_e /cm^{-1}	213.9	215.8/215.3/221.4	214.5
$\omega_e x_e$ /cm^{-1}	0.53	−/0.53/0.52	0.61

[a] Spin−orbit effects have been approximately included to the theoretical dissociation energy (values in parentheses) using the atomic splittings of Moore (see ref 26). [b] Reference 24. [c] Reference 28. [d] Reference 27.

TABLE 2: CCSD(T) Interaction Energies for the He−I_2 Molecule Obtained with Different Atomic Basis Sets at the Indicated (R,θ) Configurations for R = 2.666 Å[a]

	$\theta = 0°$		$\theta = 90°$	
atom/basis set	R	ΔE	R	ΔE
I/SDB-aug-cc-pVTZ, He/aug-cc-pV5Z	4.5	2.88	3.25	48.81
	5.0	−38.41	3.75	−30.73
	5.25	−32.11	4.25	−27.24
I/SDB-aug-cc-pVTZ, He/aug-cc-pV5Z+bf	4.5	−6.96	3.25	35.64
	5.0	−42.10	3.75	−36.67
	5.25	−34.44	4.25	−29.85
I/SDB-aug-cc-pVTZ, He/aug-cc-pVTZ	4.5	11.98	3.25	61.19
	5.0	−35.58	3.75	−26.34
	5.25	−30.53	4.25	−25.74
I/SDB-aug-cc-pVTZ, He/aug-cc-pVTZ+bf	4.5	−3.14	3.25	37.16
	5.0	−40.67	3.75	−36.30
	5.25	−33.82	4.25	−29.74

[a] The term “bf” stands for the 3s3p2d2f1g set of bond functions.

present calculation of the ground state HeI_2 potential we use an effective core potentials basis set for the I atoms, which is a convenient method to incorporate relativistic effects[24] in standard quantum mechanical calculations. We employ the Stuttgart−Dresden−Bonn (SDB) large-core energy-consistent pseudopotential[25] in conjunction with an augmented correlation-consistent triple-ζ (SDB-aug-cc-pVTZ) valence basis set[24] for the iodine atoms. In order to check the performance of the above atomic basis sets we computed at the CCSD(T) level several properties of the I_2(X) monomer (see Table 1) and compared them with available experimental values,[27] as well as with a recent theoretical study, where the newly developed cc-pVXZ-PP (X = T, 5) basis sets, in conjunction with small-core relativistic pseudopotentials, have been employed.[28] Spin−orbit interaction, as well as core polarization potential (CPP) corrections, are not included in the present calculations. For a better comparison with the experimental results we approximately take into account spin−orbit effects by including in the theoretical dissociation energies the experimental first-order spin−orbit correction given by Moore[26] (see Table 1). Further, for comparing with the small-core cc-pVTZ-PPCPP basis set, CPP-corrected results taken from ref 24 for I_2 are presented in Table 1 for the SDB-cc-pVTZ basis set.

For the He atom the augmented correlation-consistent quintuple-ζ basis set from EMSL library is used.[29] Recent studies have shown,[14,30−33] that the use of midbond functions is an efficient way to saturate the dispersion energy in weakly bound complexes. Thus, an additional set (3s3p2d2f1g) of bond functions is employed.[34] The set of bond functions are centered at the midpoint between the He and the I_2 center of mass. All computations are carried out at the CCSD(T) level of theory, and in all calculations, 6d and 10f Cartesian functions are used.

In order to elucidate the effect of bond functions, test runs are performed using augmented correlation-consistent triple-ζ type basis sets for the He atom, as well as the above-mentioned atom-centered basis sets with and without the additional set (3s3p2d2f1g) of bond functions. The results of these calculations are summarized in Table 2 for configurations around global and local minima. As can be seen, the use of bond functions clearly improves the interaction energies of the complex, demonstrating their efficiency in calculations of such vdW systems. The effect of the extension of the correlation-consistent basis sets is also checked. One can see that at the region of the wells the interaction energies are slightly changed by using the aug-cc-pVTZ or aug-cc-pV5Z basis sets for the He atom. However, in the repulsive wall somewhat larger changes are obtained; thus, the aug-cc-pV5Z basis set is chosen for the He atom in our calculations.

The intermolecular energy between He and I_2 is calculated using the supermolecular approach. The interaction energy, ΔE, is given as the difference between the total energy of the complex, E_{HeI_2}, and the sum of the energies of the monomers, $E_{He} + E_{I_2}$. The standard counterpoise method[35] is used for the correction of basis set superposition error (BSSE). The results of the CCSD(T) interaction energies for HeI_2 are listed in Table 3 for the indicated values of r, R, and θ. The results of the interaction energies for the different I−I bond lengths are qualitatively similar. For all the r values the linear configuration is found to be lower in energy than the T-shaped one. When the I−I bond is lengthened their energy difference increases. We should note that the interaction energies of the T-shaped structures are found to be more sensitive to small changes of the I−I bond length than the ones for the linear configurations.

II.B. Representation of the Potential Energy Surface. In order to represent the potential energy surface for the HeI_2 complex, we used an analytical functional form to fit the CCSD(T) ab initio points. We used an expansion in Legendre polynomials, $P_\lambda(\cos\theta)$, to describe the two-dimensional He···I_2 interaction potential

$$V(R,\theta;r_k) = \sum_\lambda V_{k\lambda}(R) P_\lambda(\cos\theta), \quad k = 1-4 \tag{1}$$

TABLE 3: CCSD(T) Interaction Energies for the $He-I_2$ Molecule Obtained with the aug-cc-pV5Z+ (3s3p2d2f1g) Basis Set for He and the SDB-aug-cc-pVTZ ECP for I for the Indicated *r*, *R*, *θ* Values

	ΔE (cm^{-1})						
R (Å)	$\theta = 0°$	$\theta = 15°$	$\theta = 30°$	$\theta = 45°$	$\theta = 60°$	$\theta = 75°$	$\theta = 90°$
$r = 2.42249$ Å							
3.0							178.13
3.25						206.50	21.55
3.5						53.53	−31.54
3.75					142.66	−5.68	−42.82
4.0	279.52	333.38	319.69	170.22	37.11	−24.21	−39.18
4.25	42.82	79.23	96.28	46.64	−3.69	−26.45	−31.67
4.5	−30.18	−8.14	11.50	−0.44	−16.53	−23.13	−24.30
4.75	−43.74	−31.19	−16.13	−15.39	−18.19		
5.0	−38.78	−31.91	−21.77	−17.71	−16.04	−14.38	−13.63
5.25	−30.31	−26.38	−19.88	−15.74	−12.97		
5.5	−22.45	−20.39	−16.13	−12.73	−10.14		
6.0	−12.03	−11.13	−9.46	−7.59	−5.97	−4.83	−4.46
7.0	−3.73	−3.58	−3.20	−2.70	−2.19	−1.82	−1.69
9.0	−0.64	−0.61	−0.57	−0.50	−0.42	−0.37	−0.37
$r = 2.666$ Å							
3.0							192.11
3.25						216.25	35.64
3.5						61.32	−21.55
3.75					160.85	−0.88	−36.67
4.0	498.71	550.93	465.97	219.34	45.01	−21.62	−35.73
4.25	121.15			66.41		−25.26	−29.85
4.5	−6.96	19.75	32.94	6.39	−15.87	−22.65	−23.40
4.75	−40.80	−24.84	−10.07	−13.87	−18.44		
5.0	−42.09	−32.90	−21.40	−18.13	−16.53	−14.44	−13.43
5.25	−34.44	−29.23	−21.29	−16.70	−13.50		
5.5	−26.03	−23.07	−17.82	−13.70	−10.58		
6.0	−14.05	−12.88	−10.62	−8.25	−6.23	−4.96	−4.50
7.0	−4.28	−4.08	−3.56	−2.90	−2.28	−1.87	−1.73
9.0	−0.70	−0.68	−0.61	−0.53	−0.44	−0.40	−0.37
$r = 2.90951$ Å							
3.0							184.56
3.25						213.61	38.65
3.5						63.60	−16.88
3.75					178.19	1.73	−32.90
4.0		889.49	670.96	280.36	53.40	−19.99	−34.39
4.25	264.23			92.60		−24.21	−28.31
4.5	42.47	71.75	67.36	16.46	−14.70	−22.15	−22.52
4.75	−27.65	−8.71	1.60	−10.82	−18.35		
5.0	−41.72	−30.29	−18.79	−17.84	−16.86	−14.38	−13.19
5.25	−37.75	−30.99	−21.88	−17.36	−13.89		
5.5	−29.69	−25.72	−19.27	−14.57	−10.97		
6.0	−16.29	−14.84	−11.85	−8.87	−6.50	−5.03	−4.50
7.0	−4.92	−4.67	−3.95	−3.12	−2.39	−1.91	−1.76
9.0	−0.75	−0.75	−0.68	−0.57	−0.46	−0.42	−0.37
$r = 3.11092$ Å							
3.0							167.66
3.25						204.02	35.38
3.5						62.07	−15.91
3.75					190.70	2.44	−31.12
4.0		1295.91	892.96	338.76	60.03	−18.83	−31.67
4.25	456.33			118.85		−23.42	−27.21
4.5	116.37	142.77	108.49	27.26	−13.50	−21.66	−21.79
4.75	−3.18	16.68	17.05	−7.00	−18.04		
5.0	−36.21	−23.22	−14.11	−16.99	−16.94	−14.22	−12.91
5.25	−38.63	−30.62	−21.35	−17.62	−14.13		
5.5	−32.20	−27.37	−20.10	−15.12	−11.22		
6.0	−18.22	−16.48	−12.82	−9.39	−6.67	−5.05	−4.48
7.0	−5.51	−5.16	−4.28	−3.29	−2.44	−1.93	−1.76
9.0	−0.83	−0.81	−0.70	−0.57	−0.46	−0.42	−0.37

with $\lambda = 0, 2, 4, 6, 8, 10, 12$, due to the symmetry of the system with respect to $\theta = 90°$. The $V_{k\lambda}(R)$ coefficients are obtained by a collocation method applying the following procedure. For each of the seven values of angle θ, we fitted the CCSD(T) data to a Morse−vdW function

TABLE 4: Parameters for the $V(R,\theta_i;r_k)_{i=1-7,k=1-4}$ Potential (eq 2) for the HeI_2 Complex[a]

$r = 2.42249$ Å

θ_i (deg)	α_0^{i1}	α_1^{i1}	α_2^{i1}	α_3^{i1}	α_4^{i1}	σ
0	89.8779	1.8153	4.47533	727394	−2.47957(07)	0.17
15	54.8805	1.74932	4.64672	581566	−1.88948(07)	0.14
30	39.6858	1.66140	4.72401	507133	−1.75524(07)	0.48
45	22.0724	1.60139	4.76785	363343	−9.94594(06)	0.06
60	5.16017	1.52995	5.04998	187124	−384584	0.16
75	4.11218	1.51458	4.80702	144479	542076	0.13
90	4.82704	1.58517	4.47926	149629	270447	0.14

$r = 2.666$ Å

θ_i (deg)	α_0^{i2}	α_1^{i2}	α_2^{i2}	α_3^{i2}	α_4^{i2}	σ
0	101.573	1.77443	4.56839	815155	−3.21922(07)	0.21
15	45.7720	1.72853	4.82471	592173	−1.86241(07)	0.17
30	26.7291	1.64757	4.95876	470219	−1.38057)07)	0.08
45	20.5726	1.58043	4.8730	347516	−9.36266(06)	0.09
60	23.8978	1.52109	4.49734	270717	−6.84457(06)	0.16
75	3.8303	1.47759	4.88681	137377	798167	0.15
90	4.26079	1.52824	4.57902	146827	280844	0.13

$r = 2.90951$ Å

θ_i deg)	α_0^{i3}	α_1^{i3}	α_2^{i3}	α_3^{i3}	α_4^{i3}	σ
0	64.38	1.76644	4.83373	783397	−2.68232(07)	0.12
15	52.8289	1.68421	4.9196	631785	−2.43184(07)	0.22
30	30.6759	1.61608	5.03064	483437	−1.67366(07)	0.15
45	10.5936	1.54456	5.20307	238251	−2.54605(06)	0.14
60	5.06558	1.48035	5.16874	163450	712762	0.11
75	5.41102	1.44128	4.79253	129493	475096	0.18
90	3.81136	1.47879	4.67739	133112	563057	0.23

$r = 3.11092$ Å

θ_i (deg)	α_0^{i4}	α_1^{i4}	α_2^{i4}	α_3^{i4}	α_4^{i4}	σ
0	95.0364	1.72227	4.8365	1.01738(06)	−4.62372(07)	0.23
15	52.6268	1.63829	5.0485	538308	−2.49037(07)	0.40
30	32.0518	1.58379	5.11911	439688	−1.7527(07)	0.23
45	8.96255	1.51752	5.34	181856	199603	0.18
60	5.09916	1.45536	5.21437	146081	1.2812(06)	0.12
75	3.2397	1.41896	5.01772	125243	1.23178(06)	0.17
90	3.53312	1.45387	4.69037	145402	210545	0.12

[a] Distances are in angstroms and energies in cm^{-1}. Figures in parentheses are powers of 10.

$$V(R;\theta_i;r_k) = \alpha_0^{ik}(\exp(-2\alpha_1^{ik}(R-\alpha_2^{ik})) - 2\exp(-\alpha_1^{ik}(R-\alpha_2^{ik}))) - \frac{\alpha_3^{ik}}{R^6} - \frac{\alpha_4^{ik}}{R^8} \quad (2)$$

with parameters α_0^{ik}, α_1^{ik}, α_2^{ik}, α_3^{ik}, and α_4^{ik}, where $i = 1-7$ and $k = 1-4$. The resulting parameters, listed in Table 4, are obtained using a nonlinear least-squares fitting to the ab initio points. The model potential reproduces very well the ab initio values with a maximum standard deviation of 0.48 cm^{-1} and an average standard deviation of 0.17 cm^{-1} for all (r,R,θ) calculated values (see the last column of Table 4).

Figure 1 presents a two-dimensional contour plot of the $V(R,\theta;r_e = 2.666$ Å$)$ surface in the (θ,R) plane. The HeI_2 potential energy surface exhibits two minima. The global minimum with an energy of −43.52 cm^{-1} at $R = 4.89$ Å corresponds to a linear ($\theta = 0°$) configuration. The second minimum, with an energy of −37.32 cm^{-1}, at $R = 3.84$ Å corresponds to a T-shaped ($\theta = 90°$) configuration of the complex. The isomerization barrier between the two wells is found at an energy of −17.88 cm^{-1} (25.64 cm^{-1} above the global linear minimum), with $R = 4.93$ Å and $\theta \sim 51°$. These potential minima and the corresponding barrier are displayed in Figure 2, where the minimum energy path, V_m, and the

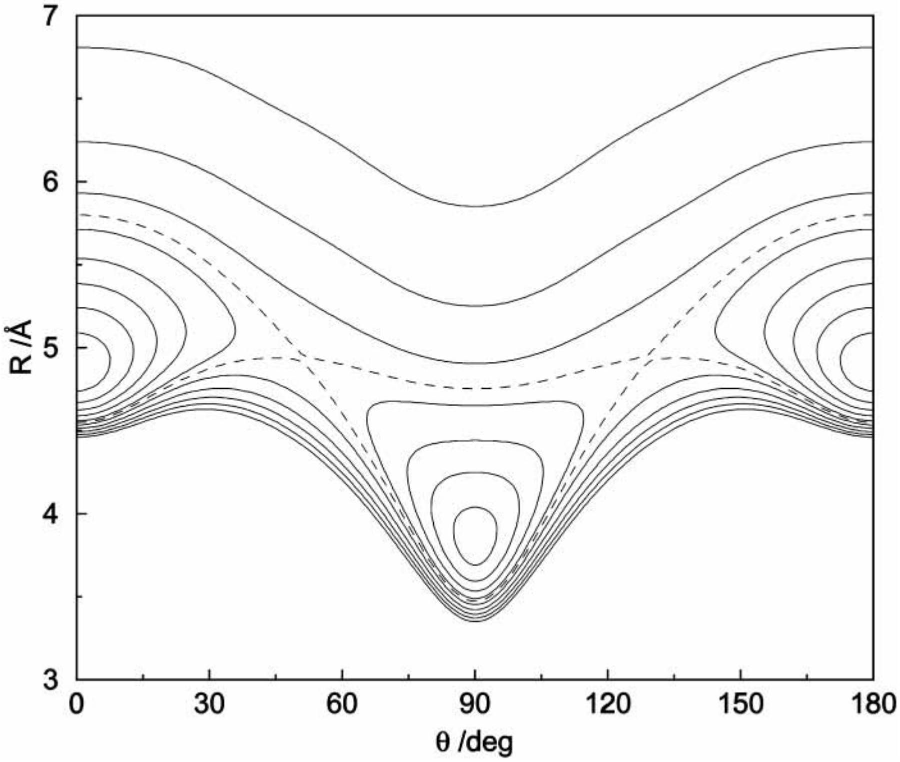

Figure 1. Contour plots of the HeI_2 potential energy surface, $V(R,\theta;r_e)$, in the (θ,R) plane. The I−I distance is fixed at $r_e = 2.666$ Å. Contour intervals (solid lines) are of 5 cm^{-1} and for energies from −40 to 5 cm^{-1}. The dashed line corresponds to the energy of the isomerization barrier.

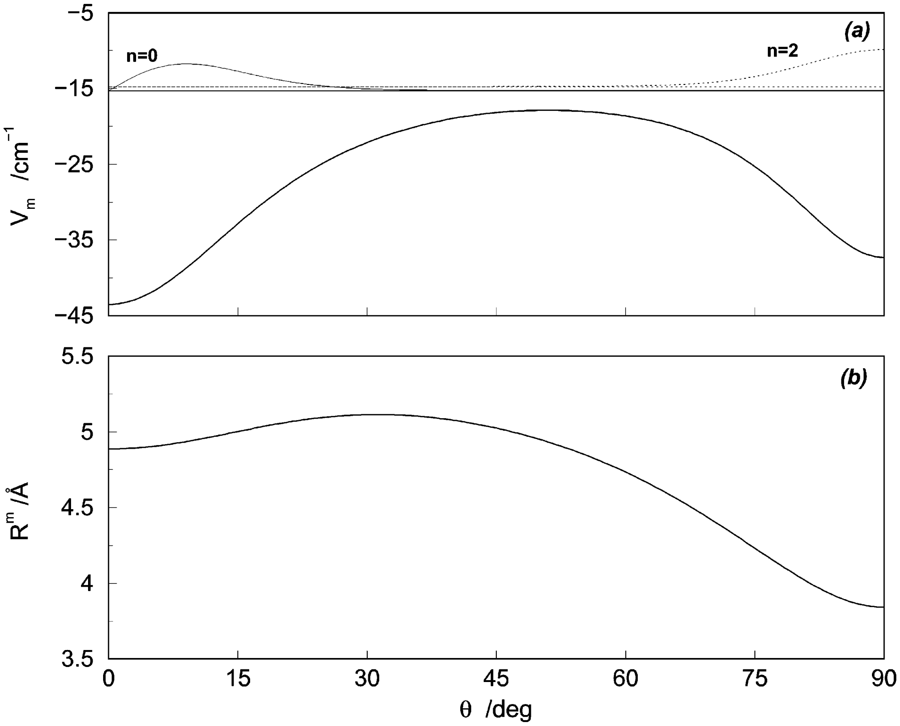

Figure 2. (a) Minimum energy, V_m, in cm^{-1} and (b) distance of minimum energy, R^m, as a function of θ. The energy levels and angular probability distributions for $J = 0$ of the $n = 0$ and $n = 2$ vibrational vdW states are also displayed.

distance, R^m, of the minimum energy are plotted as a function of the angle θ.

A previous ab initio calculation for the HeI_2 ground state potential at the MP2 and MP3 levels of theory has predicted[5] a significantly shallow well-depth for the T-shaped configuration of −6.94 and −6.29 cm^{-1}, respectively. Thus, a more reasonable semiempirical surface has been proposed by the authors[5] estimating a well-depth of 22.02 cm^{-1}, and they have suggested a larger estimate of the Morse range parameter than the one proposed by Levy and co-workers.[2] This later D_e value is very close to the experimental estimate of 21.6−22.7 cm^{-1} given by Levy and co-workers[2] for the perpendicular structure of HeI_2. Moreover, an earlier study on atom−diatomic molecule collinear collisions has predicted a well-depth of ground state HeI_2 of −52.10 cm^{-1}.[36] Unfortunately, no more theoretical attempts have been available in the literature.

TABLE 5: Experimental and Theoretical Binding Energies (D_e and D_0 in cm^{-1}), Equilibrium Distances (R_e and R_0 in angstroms), and Frequencies for the Linear and T-Shaped Isomers of the $He-I_2$ Complex[a]

	linear				T-shaped			
$He-I_2$	D_e	D_0	R_e/R_0	ω_e/ω_ex_e	D_e	D_0	R_e/R_0	ω_e/ω_ex_e
this work	43.52	15.38	4.89/5.34	8.12/nd	37.32	14.68	3.84/4.40	6.71/nd
1D CCSD(T) Morse	44.24	23.87	4.88/nd	46.97/12.47	37.82	21.40	3.84/nd	37.48/9.29
ab initio MP2/MP3[5]					6.29/6.94		4.45/nd	
semiempirical value[5]					22.02		4.05/nd	
semiempirical value[b] [36]	52.1	33.1	4.24/nd	42.22/8.55				
experimental value[1,2]					22.15 ± 0.55	18.8 ± 0.6	3.94/4.47	6.95−7.09/0.53−0.58
experimental value[4]						17.6 ± 1.0		

[a] nd = no data. [b] We assume that these potential parameters are for the $He-I_2$ linear structure, since they have been used to study atom−diatomic molecule collinear collisions.[36]

II.C. Bound State Calculations. The rovibrational Hamiltonian in the Jacobi coordinate system has the form

$$\hat{H} = -\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial R^2} + \frac{\hat{j}^2}{2\mu_2 r^2} + \frac{\hat{l}^2}{2\mu_1 R^2} + V(R,\theta,r) + \hat{H}_{I_2} \quad (3)$$

where

$$\hat{H}_{I_2} = -\frac{\hbar^2}{2\mu_2}\frac{\partial^2}{\partial r^2} + V_{I_2}(r)$$

is the vibrational Hamiltonian for a free I_2 molecule. $1/\mu_1 = (1/m_{He}) + (1/2m_I)$ and $1/\mu_2 = (1/m_I) + (1/m_I)$ are the reduced masses, $m_{He} = 4.00260$ and $m_I = 126.904473$ amu are the atomic masses of the ^4He and ^{127}I isotopes, $\hat{l}$ and $\hat{j}$ are the angular momentum operators associated with the vectors **R** and **r**, respectively, leading to a total angular momentum $\hat{J} = \hat{l} + \hat{j}$. Here all calculations are performed for $J = 0$. Starting from the $V(R,\theta;r_k)$ potential of eq 1, 1D cubic-spline interpolation is used to compute the value of $V(R,\theta,r)$ at 21 Gauss−Legendre points in the interval of $2.42249 < r < 3.11092$ Å. $V_{I_2}(r)$ is the one-dimensional I_2 ground state potential function, and a cubic-spline interpolation to CCSD(T) ab initio data (see Table 1) is used to reproduce the V_{I_2} potential at any r point. The eigenvalues and eigenfunctions of the diatomic $\hat{H}_{I_2}$ Hamiltonian are denoted as $E_{I_2}(v)$ and $\chi_v(r)$, respectively, and are evaluated by solving the 1D Schrödinger equation using a combined Truhlar−Numerov algorithm.[37] The vdW levels and corresponding wave functions are calculated variationally by diagonalizing the vibrationally averaged Hamiltonian

$$H_v = \langle\chi_v|\, H|\chi_v\rangle = -\frac{\hbar^2}{2\mu_1}\frac{\partial^2}{\partial R^2} + \frac{\hat{l}^2}{2\mu_1 R^2} + V_{v,v}(R,\theta) + E_{I_2}(v) + \frac{B_v\hat{j}^2}{\hbar^2} \quad (4)$$

where $V_{v,v}(R,\theta) = \langle\chi_v|\, V(R,\theta,r)|\chi_v\rangle$ is the intermolecular vdW potential of HeI_2 averaged over the I_2 $v = 0$ vibrational eigenfunction and B_v is the I_2 average rotational constant. The Hamiltonian is represented on a finite three-dimensional basis set. The $V_{v,v}$ potential matrix elements are calculated using Gaussian quadrature in the r coordinate, while for the angular coordinate we used orthonormalized Legendre polynomials $\{P_j(\cos\theta)\}$ as basis functions, with up to 40 values (even and odd) of the diatomic rotation j. For the radial R coordinate, a discrete variable representation (DVR) basis set is used based on the particle in a box eigenfunctions.[38] A basis set of 75 DVR functions over the range from $R = 1.75$ to 15 Å are used. In this way, a convergence of 0.000 05 cm^{-1} is achieved in bound state calculations.

In Table 5 we compare the results obtained with the present CCSD(T) surface with the previous theoretical and experimental data available. In addition, some semiempirical data are also available on the potential parameters for an interaction potential for the collinear collision of a He atom and a diatomic I_2 oscillator; thus, we compare these values with the ones corresponding to the present linear potential well (see Table 5).

The results of the bound state calculations for the HeI_2(X) potential show that the lowest three vdW vibrational levels ($n = 0, 1, 2$) are at energies of −15.3798 (even), −15.3796 (odd), and −14.6831 (even) cm^{-1}, and the associated wave functions correspond to linear configurations for the first two states and T-shaped configurations for the last one (see Figures 2 and 3). The next four vibrational states are found at energies of −7.9704 (odd), −7.2629 (even), −6.1173 (odd), and −4.3365 (even) cm^{-1} and as can be seen in Figure 3 are spreading all over θ values. All calculated vdW vibrational levels are located above the potential isomerization barrier (−17.88 cm^{-1}). The small energy difference between the $n = 0$ and $n = 2$ states (only 0.7 cm^{-1}) provides indications for the coexistence of the two isomers even at low temperatures. Vibrationally averaged structures with $R_0 = 5.34$ Å and $R_0 = 4.40$ Å are obtained for the linear and T-shaped isomers, respectively. Analysis of the rotational structure of the B ← X spectrum[1] indicated a perpendicular structure with $R_0 = 4.47 \pm 0.13$ Å for the X state, which is in very good accord with the T-shaped one predicted in the present work (see Table 5).

Direct experimental data are available only for the D_0 value of the B state and the spectral blue-shift value with respect to the corresponding band of the uncomplexed iodine molecule.[39] On the basis of these data, Levy and co-workers have presented[2] potential parameters and intermolecular stretching frequency values for the perpendicular ground state equilibrium geometry of $He-I_2$. According to their estimations, the intermolecular stretching frequency for the T-shaped well is between 6.95 and 7.09 cm^{-1}, while a semiempirical value of 42.22 cm^{-1} has been estimated[36] for the stretching frequency for the linear well. Later, Beswick and Delgado-Barrio[40] have suggested, using a sum of Morse pairwise potentials, that the first excited level of the B state corresponds to the excitation of the bending motion; thus, the range of the intermolecular frequencies given by the experimentalists[2] for the X state should also correspond to the bending mode excitation, as long as both electronic surfaces present similar topologies. Based now on our bound state calculations for the X state, the localization patterns of the corresponding wave functions ($n = 3$ and $n = 4$) did not allow us to assign the vdW levels to different normal modes and no direct way to compare with the experimental value exists. We should note that a direct comparison with experiment requires

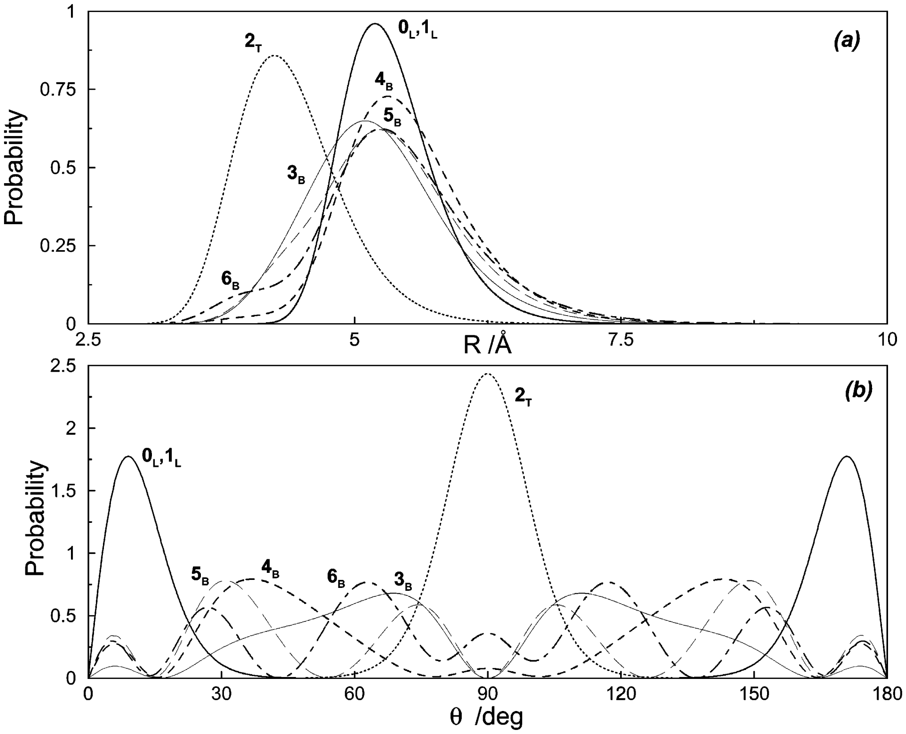

Figure 3. Radial and angular probability distributions (a,b) for the indicated n_C vdW levels, calculated using the $V(R,\theta,r)$ PES. L = linear, T = T-shaped, and B = bending configurations. Angular distributions contain the Jacobian sin θ volume element.

theoretical data for the B electronic state of the same quality[41] as the one presented here for the X state. Since such results are still not available, we choose to estimate the corresponding frequencies based partially on the probability distributions (see Figure 3). The calculated values are $E(n = 3) - E(n = 2) = 6.71$ and $E(n = 4) - E(n = 1) = 8.12$ cm^{-1} for the T-shaped and linear wells, respectively, which are close to the experimental T-shaped one and are mainly bending excitations. A direct comparison with semiempirical/experimental data is made by using one-dimensional Morse potentials fitted to the CCSD(T) data for $\theta = 0°$ and $\theta = 90°$ (see Table 5). In this way, values of 46.97 and 37.48 cm^{-1} are obtained, and their comparison with the experimental/bound state results indicates that, due to the high anharmonicity, a Morse potential could not be a sufficient representation of the intermolecular potential of the HeI$_2$ complex. We should mention that the Morse range parameters are 1.707 11 Å^{-1} for the linear well, which compares very well with the value of 1.41 Å^{-1} given by Secrest and Eastes,[36] and 1.473 37 Å^{-1} for the T-shaped well. This later parameter is larger than the value of 0.35−0.37 Å^{-1} predicted by Blazy et al.,[2] in accord with the estimation of the MP2/MP3 semiempirical surface.[5]

The experimental value for the binding energy of the X state of HeI$_2$ has been determined to be in the range between 18.2 and 19.4 cm^{-1}.[2] When Blazy et al.[2] reported the above values for D_0 they did not determine accurate values for the blue shifts of the HeI$_2$ B ← X excitation spectra for the high v levels. These shifts have been measured later by Sharfin et al., and a lower value (by 1.2 cm^{-1}) than the one used by Blazy et al. has been obtained for the $v = 62$ level. Thus, a revised value of 17.6 ± 1.0 cm^{-1} has been proposed for the D_0 of ground state HeI$_2$.[4] We should note that our prediction of 15.38 cm^{-1} for the D_0 binding energy is very close to the lower bound of the later experimental value (see Table 5). The present value, however, corresponds to a linear configuration, although we should stress that the support by the experiment for a nonlinear structure is based on a sampling of alternatives (see ref 11 of ref 1).

As we discussed above, our calculations indicate the coexistence of the two isomers in a supersonic beam, and given the difficulties of the previous experimental studies in determining equilibrium structures of different isomers, as well as the lack of recent direct experimental measurements on HeI$_2$, one should regard cautiously such assumptions. Further, it is clear that experimental studies similar to those reported recently[42] on the LIF spectra obtained from two different He−ICl (X, $v = 0$) isomers, in combination with theoretical simulations,[44] are invaluable for interpreting the intermolecular dynamics of such complexes (see also ref 43).

III. Conclusions

A three-dimensional potential energy surface is calculated for the HeI$_2$(X) complex at the CCSD(T) level of theory. As in other studies on such complexes, the existence of two relatively isolated minima is established.

Bound state calculations with $J = 0$ are carried out for the above CCSD(T) surface. The linear He−I−I structure is found to be the most stable isomer with a binding energy of $D_0 = 15.38$ cm^{-1}, while the T-shaped isomer is predicted to lie only 0.7 cm^{-1} above, indicating the coexistence of them even at low temperatures. The vibrationally averaged structures for these isomers are determined to be $R = 5.34$ Å, $\theta = 0°$ and $R = 4.40$ Å, $\theta = 90°$, respectively. The above values are in very good accordance with the experimental observations[1] available for the perpendicular structure. A good agreement is also obtained between the CCSD(T) results and the experimental estimates[2,4] concerning the D_0 value, although the linear He−I−I isomer is predicted here to be more stable than the T-shaped one.

These findings, in combination with the limited experimental information available on the system under study, demonstrate that CCSD(T) calculations provide an alternative way of constructing reliable potential surfaces for such complexes. Further, the above description of the atom−diatomic molecule interaction is of considerable importance in the study of the structure and bonding in larger systems $Rg_n{-}XY$,[45,46] where a diatomic molecule interacts with a solvent system of rare gas atoms, e.g., the relaxation dynamics of impurities embedded in He nanodroplets.[47] Whether the properties of the weak bonding in such systems can be predicted by the sum of atom−diatom interactions deserves further investigation.

Acknowledgment. The authors thank Centro de Calculo (IMAFF), CTI (CSIC), CESGA, and GSC (CIEMAT) for allocation of computer time. This work has been supported by CICYT, Spain, Grant No. BFM 2001-2179 and by a European TMR network, Grant No. HPRN-CT-1999-00005. R.P. acknowledges a contract from the Comunidad Autónoma de Madrid, Spain.

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