J. Phys. Chem. A **2006,** *110,* 13259−13263

The *p*-Difluorobenzene−Argon S_1 Excited State Intermolecular Potential Energy Surface

José Luis Cagide Fajín and Berta Fernández*

Department of Physical Chemistry, Faculty of Chemistry, University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain

Peter M. Felker

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569

Received: July 31, 2006; In Final Form: October 6, 2006

The first excited state (S_1) intermolecular potential energy surface for the *p*-difluorobenzene−Ar van der Waals complex is evaluated using the coupled-cluster method and the augmented correlation consistent polarized valence double-ζ basis set extended with a set of 3s3p2d1f1g midbond functions. In order to calculate the S_1 interaction energies we use the ground state surface evaluated with the same basis set and the coupled-cluster singles and doubles [CCSD] including connected triple excitations [CCSD(T)] model, and interaction and excitation energies evaluated at the CCSD level. The surface minima are characterized by the Ar atom located above and below the *p*-difluorobenzene center of mass at a distance of 3.4736 Å. The corresponding interaction energy is −435.233 cm^{-1}. The surface is used in the evaluation of the intermolecular level structure of the complex.

Introduction

Van der Waals complexes constituted by aromatic molecules and rare gas atoms have been studied intensely in the past.[1] In previous work (see ref 2 and references cited therein) we have evaluated highly accurate intermolecular potential energy surfaces (IPESs) for these complexes using the coupled-cluster singles and doubles (CCSD) model including connected triple corrections [CCSD(T)] and the aug-cc-pVDZ basis set extended with a set of 3s3p2d1f1g midbond functions (denoted 33211).[3,4] We also considered singlet and triplet excited states,[3,5,6] using the CCSD method to evaluate excitation energies. For all the studied complexes the vibrational levels obtained from the ground state IPESs agreed very well with the experimental data available and in several cases were able to correct some of the assignments. For the excited states considered[3,5,6] the results were also satisfactory.

The aim of the present study is the evaluation of an accurate intermolecular potential energy surface for the S_1 excited state of the *p*-difluorobenzene−Ar complex. This IPES has been requested in previous studies on the complex in order to be able to interpret the discordant experimental results from dispersed fluorescence and velocity map imaging, and corroborate the obtained conclusions (see below, ref 7 and references cited therein).

As a first step in order to get the S_1 IPES, we calculated an accurate *p*-difluorobenzene−Ar van der Waals complex ground state IPES.[2] We used the CCSD(T) method and the aug-cc-pVDZ-33211 basis set in the evaluation of the interaction energies, considering the good performance obtained with this method and basis set in previous studies. The ground state IPES displays two equivalent minima with an interaction energy of −398.856 cm^{-1}, and the Ar atom located above and below the *p*-difluorobenzene center of mass, at distances of ±3.5290 Å. We will evaluate the excited state interaction energies using those available for the ground state, CCSD intermolecular ground state interaction energies evaluated at the *p*-difluorobenzene excited-state geometry, and the corresponding chemical shifts. As usual the interaction energies are fitted to an analytical function, and the corresponding intermolecular level structure is evaluated. We compare our results to the experimental and theoretical data available.

There are many experimental studies for the S_1 excited state of the *p*-difluorobenzene−Ar complex but almost none theoretical. Recently Doyle et al.[8] obtained a potential curve for the displacement of the Ar atom on the C_2 axis perpendicular to the *p*-difluorobenzene plane with the CASPT2 method and the aug-cc-pVDZ basis set. They reported an equilibrium distance R_e equal to 3.52 Å and a dissociation energy D_e of 373 cm^{-1} for the S_1 excited state. A previous geometrical optimization of the *p*-difluorobenzene in its $1B_{2u}$ excited state was done using the CASSCF method.

Within the experimental work carried out on the complex, Su et al. (see ref 9 and references cited therein) were able to get the fluorescence excitation spectra of the complex and identify the $S_1 \leftarrow S_o$ absorption bands. The rotational band contours are consistent with a position of the argon atom on the axis that passes through the center of the *p*-difluorobenzene ring and is perpendicular to it, at 3.5 ± 0.5 Å from the ring in the S_0 state and with a reduction of 0.1 ± 0.04 Å in the S_1 state. The S_1 dissociation energy D_0' is estimated between 190 and 242 cm^{-1}. The value of the van der Waals stretching fundamental was estimated as 41 ± 2 cm^{-1} for the S_1 state.

Jacobson et al.,[10] using time-resolved two-color multiphoton ionization, measured the rates of vibrational predissociation from 12 vibrational levels of the S_1 state of the *p*-difluorobenzene−Ar complex.

In 1994 Sussmann et al.[11] studied the rotationally resolved UV spectra of two van der Waals vibronic transitions and the 0_0^0 ($S_1 \leftarrow S_0$) band of the complex. The band at 42 cm^{-1} corresponds to the stretching fundamental, and the band at 34 cm^{-1} was assigned to the Herzberg−Teller active $b_{y_0}^1$ band.

10.1021/jp064897j CCC: $33.50

Sussmann et al.[12] obtained the rovibronic spectrum of the complex and assigned the van der Waals vibronic bands up to 125 cm^{-1}. In previous work [13] they got a van der Waals bond length of 3.55(2) Å for the ground state and 0.06 Å less for the S_1 excited state, with the Ar atom on the C_2 axis perpendicular to the *p*-difluorobenzene plane.

Lembach et al.[14] used mass-analyzed threshold ionization spectroscopy to study the vibrationally induced predissociation of the *p*-difluorobenzene−Ar van der Waals cluster in the S_1 excited state. They basically confirmed the results obtained by Su et al.,[9] but they obtained larger upper and lower limits for the dissociation energy D_0, i.e. 410 and 280 cm^{-1}, respectively.

In a later work, Riehn et al.[15] studied the rotational coherence spectra of the *p*-difluorobenzene−Ar complex using time-resolved fluorescence depletion. They obtained the rotational constants $(A + B) = 2.2346 \pm 0.002$ GHz in excellent agreement with previous available results.[11]

Bellm et al.[16,17] studied the *p*-difluorobenzene−Ar complex with velocity map imaging techniques and determined D_0 as 367 ± 4 cm^{-1} in the S_1 excited state. This dissociation energy is inconsistent with the dispersed fluorescence spectra of ref 9. The authors concluded that the discrepancy between their results and the dispersed fluorescence results is solved by considering transitions of the van der Waals complex shifted such that they appear at the *p*-difluorobenzene wavelengths. In 2003, Bellm et al.[18] also studied the dissociation dynamics of this complex in the S_1 state.

Weichert et al.[19] have used time-resolved rotational spectroscopy to obtain an equilibrium *p*-difluorobenzene−Ar distance of 3.543 ± 0.017 Å in the ground state of the complex, with a change of -0.057 ± 0.009 Å in the S_1 excited state. They also reported the rotational constants.

Sampson et al.[20] studied the complex using the velocity- and mass-resolved resonance enhanced multiphoton ionization spectroscopy.

Recently, Moulds et al.[7] estimated the energetic barrier for the movement of the Ar atom around the *p*-difluorobenzene ring from one side of the *p*-difluorobenzene ring plane to the other in the S_1 state as ≤ 225 cm^{-1}. In order to do this, they used the barrier they evaluated for the ground state surface (with the MP2 method and the aug-cc-pVDZ basis set) and comparison between previous coupled-cluster S_0 and S_1 benzene−Ar results.[3,5,21] A band of the free *p*-difluorobenzene was observed in dispersed fluorescence from the 240 cm^{-1} level.[9] The authors of ref 7 formulated the hypothesis that this band could correspond to a state in which the argon atom orbits around the *p*-difluorobenzene molecule and not to the free *p*-difluorobenzene molecule. To check their MP2-CCSD(T) estimation the authors claimed that it is necessary to evaluate an accurate energetic barrier for the ring-plane crossing movement of the Ar atom.

Recently, Bellm et al.[22] have used the velocity map imaging technique to determine the distribution of translational energy released in the dissociation of the complex from seven states.

This paper is organized as follows: In section II we describe the computational details and analyze the IPES obtained, in section III the calculation of the intermolecular level structure, and in the last section we summarize and give our concluding remarks.

II. Intermolecular Potential Energy Surface

To generate the S_1 excited state potential energy surface of the *p*-difluorobenzene−Ar, the geometry of the *p*-difluorobenzene is kept fixed at that determined by Doyle et al.[8] This geometry is characterized by the bond lengths and angles given in Table 1.

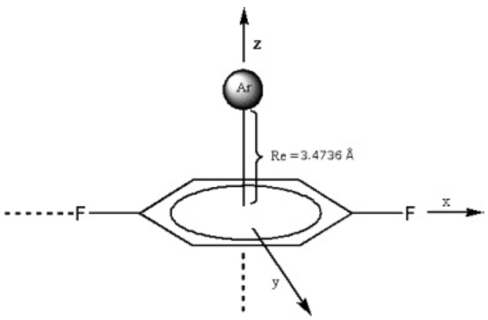

Figure 1. *p*-Difluorobenzene−Ar (S_1) intermolecular geometry ($R_e = \pm 3.4736$ Å).

TABLE 1: *p*-Difluorobenzene CASSCF/aug-cc-pVDZ Optimized Geometry[8]

length	value (Å)	angle	value (deg)
C(H)−C(H)	1.434	C(H)−C(H)−C(F)	118
C(H)−C(F)	1.426	C(H)−C(F)−C(H)	125
C−F	1.333	C(F)−C(H)−H	120
C−H	1.077		

As mentioned above, an accurate ground state IPES evaluated at the aug-cc-pVDZ-33211 CCSD(T) level is available for the complex.[2] The S_1 interaction energies are obtained as differences between ground state interaction energies and the corresponding frequency shifts.[5] We use the interaction energies obtained in ref 2, available for 176 intermolecular geometries, and evaluate for each geometry the corresponding chemical shift. For this, energies and excitation energies are calculated with the CCSD response code in the DALTON program[23] (see ref 5 for details). Considering the good performance we obtained in previous studies on similar complexes for excited states, to carry out these calculations we use the aug-cc-pVDZ basis set augmented with the additional set of 3s3p2d1f1g midbond functions centered in the middle of the van der Waals bond. The exponents of these functions are 0.90, 0.30, and 0.10 for the s and the p functions, 0.60 and 0.20 for the d functions, and 0.30 for the g and f functions. We correct for the basis set superposition error with the counterpoise method of Boys and Bernardi.[24]

The intermolecular geometries are described by the Cartesian coordinates (x, y, z) of the Ar position vector $\vec{r}$ with origin in the *p*-difluorobenzene center of mass. The two fluorine atoms are located on the X-axis, and the Z-axis is perpendicular to the *p*-difluorobenzene plane. The molecular orientation is shown in Figure 1.

The S_1 interaction energies can be obtained from the authors on request.

The S_1 IPES of the *p*-difluorobenzene−Ar complex is constructed from the ab initio single point results by fitting them to an analytic function $V(x,y,z)$. Similar expansions have been previously employed with excellent results.[2,6]

The function V includes the six terms V^C, V^F, V^H, V^{HF}, V^{HC}, and V^{CF}. V^C describes the interaction of the Ar with the carbon atoms and it is assumed in the form

$$V^C(\vec{r}) = V_0 + W_0^C\Big[\sum_k V_2^C(r_k) + \sum_{l<k} V_3^C(r_k,r_l) + \sum_{m<l<k} V_4^C(r_k,r_l,r_m)\Big] \quad (1)$$

where

$$r_k = [(x - X_k)^2 + (y - Y_k)^2 + b_z^C(z - Z_k)]^{1/2} \quad (2)$$

is a modified distance between Ar and the kth carbon atom placed at $R_k = (X_k,Y_k,Z_k)$.

TABLE 2: Parameters of the Analytic IPS Fitted to the Ab Initio Interaction Energies[a]

param	carbons	fluorines	hydrogens
r_0/Å	6.2560363	1.626770	1.9247817
a/Å^{-1}	0.5049684	1.132895	2.1276672
b_z/Å^{-2}	1.1109764	0.921807	0.84679139
V_0/cm^{-1}	−500.0637		
W_0/cm^{-1}	13.504613[b]	580.7716[c]	223.29962[d]

param	value	term
C_1	−11.17532	$W^3(r_k)$
C_2	−0.908461	$W^4(r_k)$
C_3	−0.111311	$W^5(r_k)$
C_4	−123.9289	$F^3(r_k)$
C_5	85.352496	$F^4(r_k)$
C_6	331.71587	$F^5(r_k)$
C_7	−402.93799	$F^6(r_k)$
C_8	126.00444	$F^7(r_k)$
C_9	−4.936211	$H^3(r_k)$
C_{10}	5.9700509	$W(r_k)\,W(r_l)$
C_{11}	−1.1712768	$W^2(r_k)\,W^2(r_l)$
C_{12}	3.1793631	$W(r_k)\,W^2(r_l) + W^2(r_k)\,W(r_l)$
C_{13}	0.72591951	$W(r_k)\,W^3(r_l) + W^3(r_k)\,W(r_l)$
C_{14}	0.009390304	$W^3(r_k)\,W^2(r_l) + W^2(r_k)\,W^3(r_l)$
C_{15}	0.70194543	$F(r_k)\,W(r_l)$
C_{16}	−1.2305639	$F^2(r_k)\,W(r_l)$
C_{17}	−3.3873091	$F(r_k)\,W^2(r_l)$
C_{18}	5.6110289	$F^2(r_k)\,W^2(r_l)$
C_{19}	−2.4944309	$F^3(r_k)\,W^2(r_l)$
C_{20}	0.04604993	$F^2(r_k)\,W^3(r_l)$
C_{21}	−31.837004	$H^6(r_k)\,F^{12}(r_l)$
C_{22}	−19.893314	$H^{12}(r_k)\,F^6(r_l)$
C_{23}	23.033471	$H^{12}(r_k)\,F^{12}(r_l)$
C_{24}	27.203147	$H^6(r_k)\,F^6(r_l)$
C_{25}	−0.8318037	$H^2(r_k)\,W^2(r_l)$
C_{26}	0.16378616	$H^4(r_k)\,W^4(r_l)$
C_{27}	0.01354004	$H^6(r_k)\,W^6(r_l)$
C_{28}	1.1834757	$H(r_k)\,W(r_l)\,F(r_m)$
C_{29}	−3.1259097	$W(r_k)\,W(r_l)\,W(r_m)$
C_{30}	−0.0693216	$F(r_k)\,W(r_l)\,W(r_m)$
C_{31}	0.00072624	$F^2(r_k)\,W^2(r_l)\,W^2(r_m)$

[a] $W(r_k)$ refers to the carbon, $F(r_k)$ to the fluorine, and $H(r_k)$ to the hydrogen atoms. [b] Used for terms including only $W^i(r_k)$. [c] Used for terms including $F^i(r_k)$ but not $H^i(r_k)$. [d] Used for all terms including $H^i(r_k)$.

The two-body potential term is represented by a Morse type expansion,

$$V_2^C(r_k) = W^2(r_k) + \sum_{i=3}^{5} C_i W^i(r_k) \tag{3}$$

where

$$W(r_k) = 1 - \exp(-a(r_k - r_0)) \tag{4}$$

The three- (four-) body potential term V_3^C (V_4^C) is the sum of the different 3- (4-) body terms given in Table 2 for the carbons (they are denoted by products of $W^i(r_k)$).

The V^F and V^H potentials represent the two-body interaction of the Ar atom with the fluorine and hydrogen atoms, respectively, and are defined by Morse-type functions analogous to that given in eq 3. They are denoted as $F^i(r_k)$ for the fluorine and $H^i(r_k)$ for the hydrogens.

The mixed terms V^{CF}, V^{HF}, and V^{HC} represent the three- and four-body interactions among the Ar, the carbons, the fluorine and the hydrogen atoms. The explicit forms of the properly selected three- and four-body terms for the V^{CF}, V^{HF}, and V^{HC} are collected in Table 2. The fitted values of the IPES parameters are also given in Table 2.

The determined IPES reproduces all the ab initio values with a standard error of 0.03 cm^{-1}. The maximum residual is of 1.6713 cm^{-1}, at the intermolecular geometry given by $(x,y,z) = (-2.227, 1.2856, 3.0642)$ Å and with an interaction energy of −190.131 cm^{-1}.

The absolute minima of the interaction energy between the Ar atom and the *p*-difluorobenzene molecule are located above and below the center of mass of the *p*-difluorobenzene in two equivalent positions at distances of ±3.4736 Å and with binding energies of −435.233 cm^{-1}. The complex equilibrium geometry is shown in Figure 1. Figure 2 panels a−d show the contour plots in the $y = 0$, $x = 0$, $z = Z_e$, and $z = 0$ planes, respectively.

In Table 3 we compare our IPES results to those previously available. We can see that the dissociation energy D_e is larger and the equilibrium distance shorter than the corresponding values determined for the S_1 state in ref 8.

When comparing the *p*-difluorobenzene−Ar S_1 IPES with that obtained for the fundamental state of the complex, using the CCSD(T) method and the aug-cc-pVDZ-33211 basis set,[2] we see that the general shapes of the IPESs are similar, but in the S_1 state the IPES global minimum is deeper and the equilibrium distance shorter than in the S_0 (36.377 cm^{-1} and 0.0554 Å, respectively), the interaction, therefore, being stronger in S_1. This increase in the interaction strength was also observed in the case of the benzene−Ar van der Waals complex.[3,5,21]

III. Calculation of the Intermolecular Level Structure

The calculation of the intermolecular level structure was carried out as described in our previous paper.[2] All the computational parameters are the same as in the case of the S_0 surface calculations, with the exception of the inertial parameters I_x, I_y, and I_z, considered in the S_1 surface calculations as 95.66, 352.38, and 447.83 amu-Å,[2] respectively, which are literature values obtained from high-resolution rovibronic spectroscopy.

The states were calculated in symmetry-specific fashion under the assumption that the G_4 molecular symmetry group (isomorphic to the point group C_{2v}) applies to the complex.[25] Such is the case when the crossing of the Ar atom from one side of the aromatic's ring plane to the other is taken as infeasible. Calculated states are labeled according to the G_4 irreducible representations (irrep) to which they correspond. The irrep labeling convention employed is the same as in refs 2 and 25. Thus, for example, translations of the Ar atom along the $\hat{x}$, $\hat{y}$, and $\hat{z}$ directions transform according to the B_1, B_2, and A_1 irreps, respectively.

In order to find the energy barrier for the crossing of the Ar atom from one side of the ring plane to the other, we searched numerically for fixed points in the IPES function. The ones found are similar in location (although not always in type) to those reported for the IPES of ref 7. In regard to ring-plane crossing, four symmetrically equivalent saddle points (transition states) in the y,z plane at (0, ±3.54, ±2.94 Å) determine the minimum-energy barrier. These occur at an energy 220.3 cm^{-1} above the IPES global minima.

The S_1 intermolecular vibrational levels ($J = 0$) up to 101.2 cm^{-1} are given in Table 4. As in ref 2, the assignments of the states given in the table are based on (a) the values of the root-mean-squared deviations in x, y, and z ($\langle\Delta x\rangle$, $\langle\Delta y\rangle$, and $\langle\Delta z\rangle$) for each eigenfunction and (b) the nodal structure of that eigenfunction. The assignments are given in terms of the numbers of quanta in each of the three intermolecular modes, such number of quanta denoted as n_x, n_y, and n_z, in conformity with the nomenclature of ref 25. These three modes correspond,

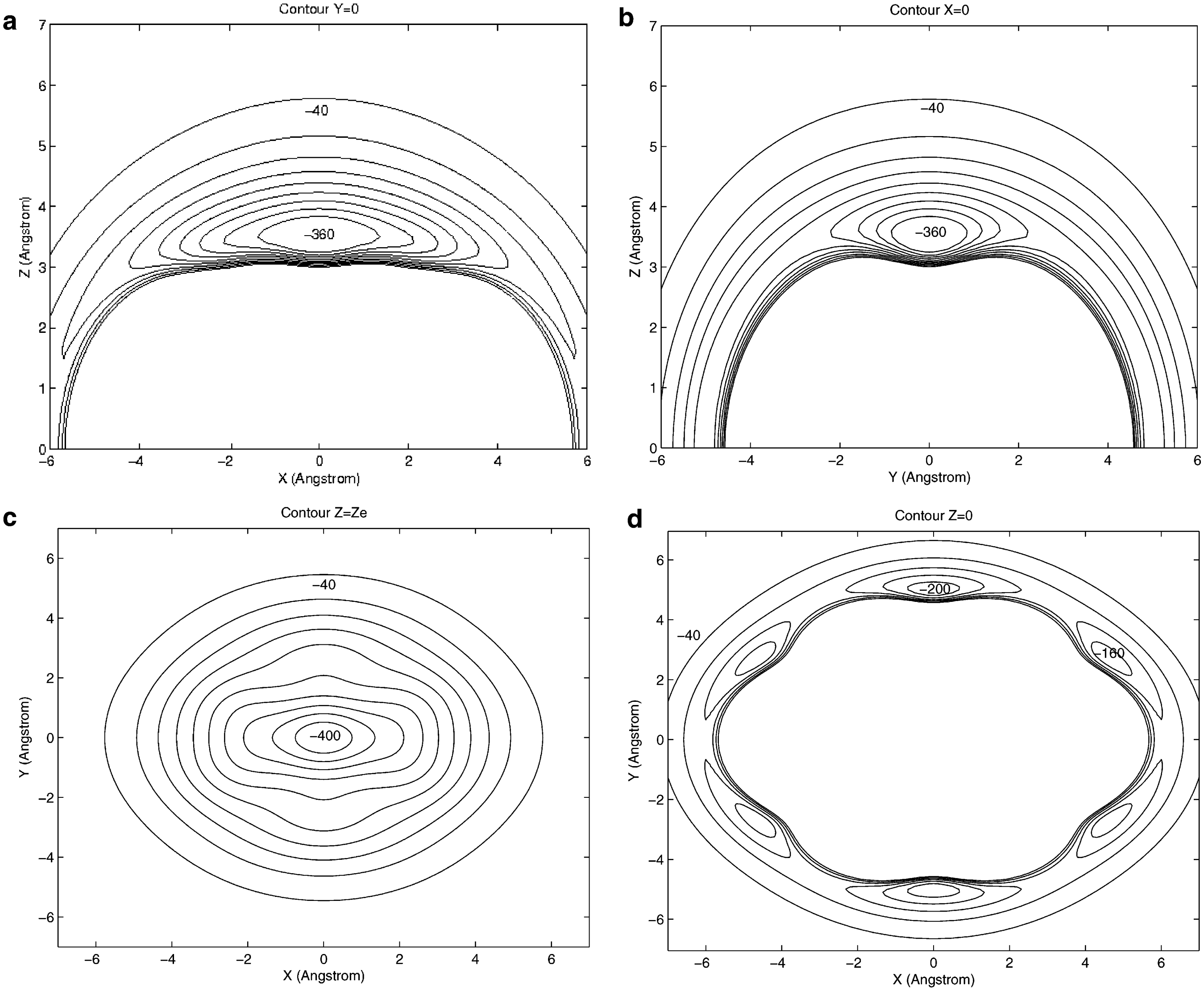

Figure 2. Contour plots of the IPES with the parameters specified in Table 3: in the *XZ* plane (a), in the *YZ* plane (b), in the *XY* plane at $z = z_e$ (c), and in the *XY* plane (d). The values of subsequent contours differ by 40 cm^{-1}.

TABLE 3: Equilibrium Distances (R_0 and R_e) (Å) and Dissociation Energies D_0 and D_e (cm^{-1})[a]

	R_0	R_e	D_0	D_e
S_0 (ref 2)		3.5290	348.57	398.856
S_1 CASPT2 (ref 8)		3.52		373
S_1 exp (ref 9)	3.4 ± 0.5		$190 \le D_0 \le 242$	
S_1 exp (ref 13)	3.49(2)			
S_1 exp (ref 14)	3.49		$280 \le D_0 \le 410$	
S_1 exp (refs 16, 17)			367 ± 4	
S_1 exp (ref 19)	3.486 ± 0.019			
S_1 (this work)		3.4736	384.527	435.233

[a] Comparison to previous results.

respectively, to relative translational motion of the Ar and *p*-difluorobenzene in the $\hat{x}$, $\hat{y}$, and $\hat{z}$ directions.

The stretching (42.575 cm^{-1}) and bending (35.543 cm^{-1}) fundamental frequencies are very close to those experimentally determined.[11]

TABLE 4: Intermolecular Vibrational Levels of the *p*-Difluorobenzene−Ar in the S_1 Excited State

N	Γ	ΔE^a	n_x,n_y,n_z	*N*	Γ	ΔE^a	n_x,n_y,n_z
1	A1	0.000	0,0,0	15	A2	76.782	3,1,0
2	B1	16.767	1,0,0	16	A1	77.218	6,0,0
3	A1	31.476	2,0,0	17	A1	82.843	0,0,2
4	B2	35.543	0,1,0	18	B1	83.809	1,2,0/7,0,0
5	A1	42.575	0,0,1	19	B1	84.677	7,0,0/1,2,0
6	B1	44.717	3,0,0	20	B2	87.485	4,1,0
7	A2	51.161	1,1,0	21	B1	87.939	3,0,1
8	A1	56.595	4,0,0	22	A2	90.034	1,1,1
9	B1	59.585	1,0,1	23	A1	92.940	8,0,0
10	B2	64.695	2,1,0	24	A1	96.522	2,2,0
11	B1	67.296	5,0,0	25	A2	96.991	5,1,0
12	A1	69.630	0,2,0	26	A1	99.104	4,0,1
13	A1	73.406	2,0,1	27	B1	99.934	1,0,2
14	B2	74.310	0,1,1	28	B1	101.203	9,0,0

[a] Energy in cm^{-1}, relative to the zero-point energy at $E_{(0,0,0)} = -384.527$ cm^{-1}.

The zero-point vibrational energy is very similar to that in the ground state (50.286 and 50.706 cm^{-1}, respectively). The S_1 D_0 dissociation energy is −384.527 cm^{-1}. This value is above the range experimentally determined in ref 9, a conclusion that was also reached in the case of the *p*-difluorobenzene−argon ground state potential surface. The agreement is better with the results of ref 14, our D_0 value being well within the $280 \le D_0 \le 410$ cm^{-1} experimentally determined range.

The rotational constants for the (0,0,0), (0,1,0), and (0,0,1) vibrational states are displayed in Table 5. The experimental values available[12,13] are also included. The agreement between the calculated and theoretical values is very good, the deviations

TABLE 5: Calculated Rotational Constants (in cm^{-1}) for Selected Intermolecular- Vibrational States of *p*-Difluorobenzene−Ar (S_1)

vibrational state	*A*	*B*	*C*
(0,0,0)	0.03783 (0.03765)[a]	0.03644 (0.03690)[a]	0.02337 (0.02355)[a]
(0,1,0)	0.03794	0.03572	0.02306
(0,0,1)	0.03788	0.03560	0.02299

[a] The experimental values are from ref 13.

being on the order of 1%. We would like to point out that the experimental data were obtained through two approximations: *A* for the complex was fixed to the value of *C* for the zero-point level of bare *p*-fluorobenzene; and additionally, to obtain *B* and *C* the complex was taken to be rigid (no vibrational averaging) with the Ar atom on the $\hat{z}$ axis.

IV. Summary and Conclusions

Following our previous study on the *p*-difluorobenzene−argon van der Waals complex, and using the coupled-cluster model together with the aug-cc-pVDZ-33211 basis set, we have evaluated an accurate IPES for the S_1 excited state. We calculated 176 interaction energies using the ground state surface results, and interaction and excitation energies evaluated at the CCSD level. The surface minima are characterized by the Ar atom located above and below the *p*-difluorobenzene center of mass at a distance of 3.4736 Å. The corresponding binding energy is -435.233 cm^{-1}.

When compared to the benzene− and fluorobenzene−Ar S_0 IPESs, we see that in the excited state the interaction is stronger, the dissociation energy being larger and the bond distance shorter.

The intermolecular level structure has been evaluated from the IPES, and good agreement is obtained with respect to the experimental results available. The energetic barrier for the movement of the Ar atom from one side of the *p*-difluorobenzene ring plane to the other is 220.3 cm^{-1}, a result that is in good agreement with the estimation of ref 7.

Acknowledgment. This work has been supported by the NANOQUANT RTN, Contract No. MRTN-CT-2003-506842, and by the Ministerio de Educación y Ciencia and FEDER (CTQ2005-01076 project). We acknowledge computer time from CESGA.

References and Notes

(1) Kukolich, S. G.; Shea, J. A. *J. Chem. Phys.* **1982**, *77*, 5242. Hobza, P.; Selzle, H. L.; Schlag, E. W. *Chem. Rev.* **1994**, *94*, 1767. Felker, P. M.; Maxton, P. M.; Schaeffer, M. W. *Chem. Rev.* **1994**, *94*, 1787. Klopper, W.; Lüthi, H. P.; Brupbacher, Th.; Bauder, A. *J. Chem. Phys.* **1994**, *101*, 9747. Sussmann, R.; Neuhausser, R.; Neusser, H. J. *J. Chem. Phys.* **1995**, *103*, 3315.

(2) Cagide Fajín, J. L.; Fernández, B.; Felker, P. M. *J. Phys. Chem. A* **2005**, *109*, 11602.

(3) Koch, H.; Fernández, B.; Christiansen, O. *J. Chem. Phys.* **1998**, *108*, 2784.

(4) Tao, F.; Pan, Y. *Mol. Phys.* **1994**, *81*, 507.

(5) Fernández, B.; Koch, H.; Makarewicz, J. *J. Chem. Phys.* **1999**, *111*, 5922.

(6) Cacheiro, J. L.; Fernández, B.; Koch, H.; Makarewicz, J.; Hald, K.; Jørgensen, P. *J. Chem. Phys.* **2003**, *119*, 4762.

(7) Moulds, R. J.; Buntine, M. A.; Lawrance, W. D. *J. Chem. Phys.* **2004**, *121*, 4635.

(8) Doyle, R. J.; Da Campo, R.; Taylor, P. R.; Mackenzie, S. R. *J. Chem. Phys.* **2004**, *121*, 835.

(9) Su, M. C.; O, H. −K.; Parmenter, C. S. *Chem. Phys.* **1991**, *156*, 261.

(10) Jacobson, B. A.; Humphrey, S.; Rice, S. A. *J. Chem. Phys.* **1988**, *89*, 5624.

(11) Sussmann, R.; Neuhauser, R.; Neusser, H. J. *Chem. Phys. Lett.* **1994**, *229*, 13.

(12) Sussmann, R.; Neusser, H. J. *J. Chem. Phys.* **1995**, *102*, 3055.

(13) Sussmann, R.; Neuhauser, R.; Neusser, H. J. *Can. J. Phys.* **1994**, *72*, 1179.

(14) Lembach, G.; Brutschy, B. *J. Phys. Chem. A* **1998**, *102*, 6068.

(15) Riehn, C.; Weichert, A.; Zimmermann, M.; Brutschy, B. *Chem. Phys. Lett.* **1999**, *299*, 103.

(16) Bellm, S. M.; Gascooke, J. R.; Lawrance, W. D. *Chem. Phys. Lett.* **2000**, *330*, 103.

(17) Bellm, S. M.; Moulds, R. J.; Lawrance, W. D. *J. Chem. Phys.* **2001**, *115*, 10709.

(18) Bellm, S. M.; Lawrance, W. D. *J. Chem. Phys.* **2002**, *118*, 2581.

(19) Weichert, A.; Riehn, C.; Matylitsky, V. V.; Jarzeba, W.; Brutschy, B. *J. Mol. Struct.* **2002**, *612*, 325.

(20) Sampson, R. K.; Bellm, S. M.; Gascooke, J. R.; Lawrance, W. D. *Chem. Phys. Lett.* **2003**, *372*, 307.

(21) Koch, H.; Fernández, B.; Makarewicz, J. *J. Chem. Phys.* **1999**, *111*, 198.

(22) Bellm, S. M.; Lawrance, W. D. *J. Chem. Phys.* **2005**, *122*, 104305.

(23) Helgaker, T.; Jensen, H. J. Aa.; Jørgensen, P.; Olsen, J.; Ruud, K.; Ågren, H.; Auer, A. A.; Bak, K. L.; Bakken, V.; Christiansen, O; Coriani, S.; Dahle, P.; Dalskov, E. K.; Enevoldsen, T.; Fernández, B.; Hättig, C.; Hald, K.; Halkier, A.; Heiberg, H.; Hettema, H.; Jonsson, D.; Kirpekar, S.; Kobayashi, R.; Koch, H.; Mikkelsen, K. V.; Norman, P.; Packer, M. J.; Pedersen, T. B.; Ruden, T. A.; Sánchez, A.; Saue, T.; Sauer, S. P. A.; Schimmelpfennig, B.; Sylvester-Hvid, K. O.; Taylor, P. R.; Vahtras, O.; *DALTON*−*an electronic structure program*, release 1.2; 2001.

(24) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553.

(25) Makarewicz, J. *J. Chem. Phys.* **2005,** *122*, 114312.