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# The Fluorobenzene−Argon $S_1$ Excited-State Intermolecular Potential Energy Surface

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We evaluate the first excited-state ($S_1$) intermolecular potential energy surface for the fluorobenzene−Ar van der Waals complex using the coupled cluster method and the augmented correlation-consistent polarized valence double-$\zeta$ basis set extended with a set of 3s3p2d1f1g midbond functions. To calculate the $S_1$ interaction energies, we use ground-state interaction energies 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 fluorobenzene ring at a distance of 3.5060 Å with respect to the fluorobenzene center of mass and at an angle of 5.89° with respect to the axis perpendicular to the fluorobenzene plane. The corresponding interaction energy is $-425.226$ cm$^{-1}$. The surface is used in the evaluation of the intermolecular level structure of the complex, and the results are compared to the experimental data available and to those found in previous theoretical papers on ground-state potentials for similar complexes.

## I. Introduction

van der Waals complexes comprised of 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).[2,3] We also considered singlet and triplet excited states[2,4] using the CCSD method to evaluate excitation energies. For all of 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, the results were also satisfactory. The aim of the present study is the evaluation of an accurate IPES for the $S_1$ excited state of the fluorobenzene−Ar complex.

Recently, we calculated an accurate fluorobenzene−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 $-391.1$ cm$^{-1}$ and the Ar atom located above and below the fluorobenzene center of mass, at distances of $\pm 3.562$ Å and at an angle of 6.33° with respect to the axis perpendicular to the fluorobenzene plane. We will evaluate the excited-state interaction energies using those available for the ground state, CCSD intermolecular ground-state interaction energies evaluated at the fluorobenzene 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 several studies of the complex ground-state IPES, and an overview of them has been given in ref 2. The $S_1$ excited state of the complex has been studied by Bieske et al. through one-color resonance-enhanced multiphoton ionization spectroscopy and time-of-flight mass spectroscopy.[5] Some of the van der Waals vibrational bands are assigned. When studying the ground-state IPES, we compared the van der Waals internal states with the experimental data available for $S_0$[6] and also with those corresponding to $S_1$[5] and concluded, considering that the IPES for both states should be quite similar, that there were some discrepancies between the theoretical assignments and those in the latter experimental work. For instance, the observed frequency of 33.5 cm$^{-1}$ should be ascribed to the fundamental frequency for the bending mode along the $x$ coordinate and not to the overtone. This conclusion had also been reached by Maxton et al. in their study of the ground-state IPES of the complex.[6]

Further discrepancies with respect to our ground-state IPES frequency assignment were found for two of the higher frequency states in a recent study carried out with the MP2 method and the aug-cc-pVDZ basis set and a smaller basis set derived from it.[7] To further check these problems, we thought it interesting to evaluate an accurate $S_1$ excited-state IPES.

Lembach and Brutschy used mass-analyzed threshold ionization spectroscopy and carried out several studies on the fragmentation energetics and dynamics of several fluorobenzene−argon clusters.[8] The dissociation energy in the $S_1$ state was estimated to be lower than 302 cm$^{-1}$, and the vibrational fundamentals were also given.

The rotational spectra of the complex have been investigated by Ford and Müller-Dethlefs,[9] and the $S_1$ rotational constants were determined. We will evaluate the constants and compare

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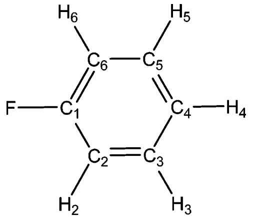


**Figure 1.** Atom numbering used in the fluorobenzene molecule.

**TABLE 1: Fluorobenzene Coordinates in Angstroms and Degrees (See Text for Details)**

| cartesian | *X* | *Y* | |
|---|---|---|---|
| $C_1$ | 0.000000 | −0.872273 | |
| $C_{2/6}$ | ±1.233211 | −0.203280 | |
| $C_{3/5}$ | ±1.225495 | 1.210134 | |
| $C_4$ | 0.000000 | 1.918773 | |
| F | 0.000000 | −2.208150 | |
| $H_{2/6}$ | ±2.148366 | −0.770677 | |
| $H_{3/5}$ | ±2.161976 | 1.745389 | |
| $H_4$ | 0.000000 | 2.997519 | |
| $R(C_1,C_2)$ | 1.4030 | $\Theta(C_2,C_1,C_6)$ | 123.042 |
| $R(C_1,F)$ | 1.3359 | $\Theta(C_2,C_1,F)$ | 118.479 |
| $R(C_2,C_3)$ | 1.4134 | $\Theta(C_1,C_2,C_3)$ | 118.166 |
| $R(C_2,H_2)$ | 1.0768 | $\Theta(C_1,C_2,H_2)$ | 119.722 |
| $R(C_3,C_4)$ | 1.4156 | $\Theta(C_3,C_2,H_2)$ | 122.112 |
| $R(C_3,H_3)$ | 1.0787 | $\Theta(C_2,C_3,C_4)$ | 120.351 |
| $R(C_4,H_4)$ | 1.0787 | $\Theta(C_2,C_3,H_3)$ | 119.438 |
| $R(C_1,F)$ | 1.3359 | $\Theta(C_4,C_3,H_3)$ | 120.211 |
| | | $\Theta(C_3,C_4,C_5)$ | 119.923 |
| | | $\Theta(C_3,C_4,H_4)$ | 120.039 |

with their results. From the rotational constants, the position of the Ar atom with respect to the aromatic ring was derived, resulting in a $z$ coordinate of 3.33 Å perpendicular to the ring center of mass and a displacement from the $Z$ axis in the direction opposite to the F atom of 0.78 Å.

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 is outlined, and in the last section, we summarize and give our concluding remarks.

## II. Intermolecular Potential Energy Surface

In order to evaluate the IPES, we fix the fluorobenzene $S_1$ geometry at the values given in Table 1, which have been evaluated with the SAC-CI method implemented in the Gaussian 03 program[10] and the cc-pVDZ basis set. The corresponding atom numbering is shown in Figure 1. We select 147 intermolecular geometries, described by the Cartesian coordinates $(x,y,z)$ (in Angstroms) of the Ar position vector $\vec{\mathbf{r}}$ with the origin in the fluorobenzene center of mass (see Figure 2).

For the evaluation of the interaction energies, we use the supermolecular model and correct for the BSSE by invoking the counterpoise (CP) method of Boys and Bernardi.[11] The BSSE is known to be essential in order to get accurate interaction energies for these systems.[2]

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.[12] We use the CCSD(T) interaction energies obtained in ref 2 in order to evaluate CCSD(T) corrections for the ground-state CCSD interaction energies that we calculate now at the fluorobenzene excited-state geometry; additionally, we evaluate the corresponding chemical shift for each intermolecular geometry. For this, energies and excitation energies are calculated with the CCSD response code in the DALTON program[13] (see ref 4 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 the f functions. The interaction energy is known to be highly stable with respect to the displacement of the functions from the midbond point. The interaction energy results can be obtained from ref 14.

Since we are interested in the evaluation of the rovibrational spectra of the complex, we select those interaction energies with

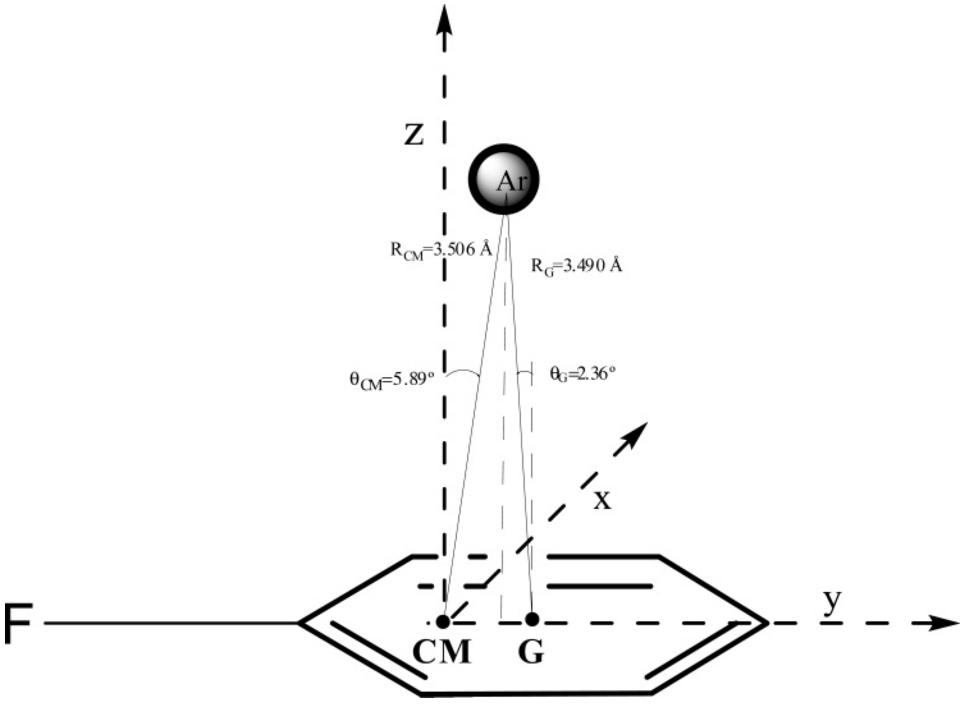


**Figure 2.** Fluorobenzene−Ar ($S_1$) intermolecular geometry.

**TABLE 2: Parameters of the Analytic IPES Fitted to the Ab Initio Interaction Energy Calculated for the $S_1$ Excited State of the Fluorobenzene−Ar**

| | potential | parameters | potential term |
|---|---|---|---|
| | Carbons | Fluorine | |
| $R_0$/Å | 3.33607252102 | 3.12013960582 | |
| $a$/Å$^{-1}$ | 0.55298942082 | 1.79525024913 | |
| $b_z$/Å$^{-2}$ | 1.15653820567 | 1.15450071783 | |
| $V_0$/cm$^{-1}$ | −423.70243980179 | | |
| $W_0$/cm$^{-1}$ | 3341.95695076083 | 3329.19631950643 | |
| $c_3$ | −1.58025388424 | −2.21828404944 | $w^3(r_k)$ |
| $\mathrm{c}_4$ | | 2.59131447667 | $w^4(r_k)$ |
| $c_5$ | −11.80024224250 | −1.31869259407 | $w^5(r_k)$ |
| $c_6$ | 10.35680250275 | | $w^6(r_k)$ |
| $c_7$ | −8.70652527508 | | $w^7(r_k)$ |
| $c_8$ | 2.95314457288 | 0.10777742984 | $w^8(r_k)$ |
| | Carbons | Potential Term | |
| $c_{11}$ | −0.79784486200 | $w(r_k)w(r_l)$[a] | |
| $c_{21}$ | 1.48914471384 | $w^2(r_k)w(r_l) + w(r_k)w^2(r_l)$ | |
| $c_{22}$ | −3.15832734878 | $w^2(r_k)w^2(r_l)$ | |
| $c_{31}$ | −0.36707680487 | $w^3(r_k)w(r_l) + w(r_k)w^3(r_l)$ | |
| $c_{41}$ | 10.21062773849 | $w^4(r_k)w(r_l) + w(r_k)w^4(r_l)$ | |
| $c_{32}$ | −3.67680745608 | $w^3(r_k)w^2(r_l) + w(r_k)^2w^3(r_l)$ | |
| $c_{33}$ | −5.29870695560 | $w^3(r_k)w^3(r_l)$ | |
| $C_{211}$ | −0.07459588016 | $w^2(r_k)w(r_l)w(r_m) + w(r_k)w^2(r_l)w(r_m) + w(r_k)w(r_l)w^2(r_m)$ | |
| $C_{311}$ | −8.29299023710 | $w^3(r_k)w(r_l)w(r_m) + w(r_k)w^3(r_l)w(r_m) + w(r_k)w(r_l)w^3(r_m)$ | |
| $C_{221}$ | 6.67000068354 | $w^2(r_k)w(r_l)^2w(r_m) + w(r_k)^2w(r_l)w^2(r_m) + w(r_k)w^2(r_l)w^2(r_m)$ | |
| $C_{222}$ | −21.00662452463 | $w^2(r_k)w^2(r_l)w^2(r_m)$ | |
| $C_{321}$ | 5.58188931263 | $w^3(r_k)w(r_l)w(r_m)(w(r_l) + w(r_m)) +$<br>$w(r_l)^3w(r_k)w(r_m)(w(r_k) + w(r_m)) +$<br>$w(r_m)^3w(r_k)w(r_l)(w(r_k) + w(r_l))$ | |
| $C_{411}$ | −3.20795480816 | $w^4(r_k)w(r_l)w(r_m) + w(r_k)w^4(r_l)w(r_m) + w(r_k)w(r_l)w^4(r_m)$ | |
| | Fluorine | Potential Term | |
| $c_{11}$ | −0.13388262344 | $w(r_k)$[b]$w(r_l)$ | |
| $c_{21}$ | 0.12665016984 | $w^2(r_k)w(r_l)$ | |
| $c_{13}$ | 0.29467859865 | $w(r_k)w^3(r_l)$ | |
| $c_{32}$ | 0.10593783353 | $w^3(r_k)w^2(r_l)$ | |
| $c_{23}$ | −0.39202160153 | $w^2(r_k)w^3(r_l)$ | |
| $c_{111}$ | −0.19443073174 | $w(r_k)w(r_l)w(r_m)$ | |
| $c_{121}$ | 0.11088049491 | $w(r_k)(w(r_l)^2w(r_m) + w(r_l)w(r_m)^2)$ | |

[a] The parameters $r_0$, $a$, and $b_z$ for all functions $w$ are taken from the second column for the carbons. [b] The parameters $r_0$, $a$, and $b_z$ for the functions $w(r_k)$ are taken from the third column for the fluorine, and $r_0$, $a$, and $b_z$ for the functions $w(r_l)$ and $w(r_m)$ are taken for the carbons.

an energy lower than 100 cm$^{-1}$ (141 points) for the fit. We use a potential function $V$ similar to that used in our previous studies,[2] which includes three terms $V^C$, $V^F$, and $V^{CF}$. The first term $V^C$ describes the interaction of the Ar atom with the carbon atoms, and it is assumed in the form

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

where

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

is a modified distance between the Ar and the $k$th carbon atom placed at $\vec{R}_k = (X_k, Y_k, Z_k)$. The effect of the hydrogen atoms is effectively included in the carbons.

The two-body potential term $V_2$ is represented by a Morse-type expansion

$$V_2(r_k) = w^2(r_k) + \sum_{i=3}^{8} c_i w^i(r_k) \qquad (3)$$

where

$$w(r_k) = 1 - \exp(-a(r_k - r_0)) \qquad (4)$$

The three- (four-) body potential term $V_3^C$ ($V_0^C$) is the sum of the different three- (four-) body terms given in Table 2 for the carbons (they are denoted as $W^i(r_k)$).

The potential $V^F$ represents a two-body interaction of the Ar atom with the fluorine atom, and it is defined by the Morse-type function analogous to that given in eq 3.

The mixed term $V^{CF}$ includes three- and four-body interaction terms among the Ar, the carbon atoms, and the fluorine. The explicit forms of the properly selected three- and four-body terms are collected in Table 2, together with the fitted values of the corresponding IPES parameters.

The fit is characterized by a standard error $\sigma$ of 0.1 cm$^{-1}$, the largest error being 3.8 cm$^{-1}$, located at the intermolecular geometry of (5.500, −1.000, 0.000) Å and with an energy of −130.94 cm$^{-1}$.

The IPES absolute minima are located at (0.000, 0.360, ±3.487) Å and have an energy of −425.23 cm$^{-1}$, with a distance from the Ar atom to the ring center of mass of 3.506 Å. These results show that the interaction in the $S_1$ state is stronger than that in the ground state,[2] a trend that was also found in the benzene−argon and the *para*-difluorobenzene−argon complexes.[15,16] The theoretical results give a larger equilibrium distance compared to the experimental determinations of ref 8 (0.086 Å larger).

## III. Calculation Of The Intermolecular States

The $J = 0$ intermolecular level structure of fluorobenzene−Ar was calculated variationally by using procedures described in detail elsewhere (see, e.g., ref 2). Briefly, the $J = 0$ intermolecular Hamiltonian ($\hat{H}_v$) in the rigid-monomer approximation was expressed in terms of the Cartesian components of $\vec{\mathbf{r}}$ referred to a body-fixed frame aligned with the principle inertial axes of the fluorobenzene moiety and having its origin at the center of mass of the complex. The molecular properties entering into $\hat{H}_v$ are the masses of Ar (39.948 amu) and fluorobenzene (96.038 amu), the principal moments of inertia of the latter ($I_x = 198.936$ amu·Å, $I_y = 94.867$ amu·Å, $I_z = 293.792$ amu·Å),[17] and the fitted IPES from the preceding section.

The basis employed was a three-dimensional discrete variable representation (DVR). The 3-D DVR consisted of products of one-dimensional Gauss−Hermite DVRs corresponding to the $x$, $y$, and $z$ components of $\vec{\mathbf{r}}$. The 1-D DVRs, each of which consisted of 40 functions, were individually scaled to cover the intermolecular geometries near the global minima of the IPES. Thus, the set of $x$ DVR quadrature points was centered at $x = 0$ and extended ±3.0 Å therefrom, the set of $y$ points was centered at $y = 0.36$ Å and extended ±3.0 Å, and the set of $z$ points was centered at $z = 4.0$ Å and extended ±1.1 Å. The $z$ DVR was chosen to cover only a single side of the fluorobenzene ring plane. Thus, we make the assumption that there is negligible tunneling due to ring-plane crossing of the Ar atom for the low-energy intermolecular states with which we are concerned. Calculations were also performed employing different basis set sizes (e.g., 30 × 30 × 30 and 50 × 50 × 50) and different ranges for the DVRs (e.g., ±2.5 Å in the $x$ and $y$ directions and ±1.2 Å in the $z$ direction). From the results of all of the calculations, we estimate that the eigenenergies quoted bellow are converged to within 0.01 $cm^{-1}$.

Diagonalization of $\hat{H}_v$ in the DVR basis was accomplished by filter diagonalization. Window basis functions[18] were accumulated by the Chebyshev filtering method[19] (2048 steps) at 50 energies between −375 and −265 $cm^{-1}$. The window functions were symmetrized so as to transform as one of the irreducible representations (irrep) of the $G_2$ molecular symmetry group (isomorphic with $C_s$) of single-sided fluorobenzene−Ar and were then orthogonalized. Finally, the matrix of $\hat{\mathbf{H}}_v$ in the symmetrized basis was diagonalized by standard numerical methods to yield irrep-specific eigenvalues and eigenvectors.

Table 3 presents the results of the $J = 0$ calculations for intermolecular states less than about 80 $cm^{-1}$ above the zero-point level, which is computed to be at −374.46 $cm^{-1}$. Included in the table are the relative energies, symmetries, and various geometrical properties of the calculated states. Also included are assignments of the states in terms of the number of quanta in each of the three van der Waals modes, the bending mode along the $x$-axis, the bending mode along the $y$-axis, and the stretching mode along the $z$-axis. The assignments were made based on the computed geometrical properties and on the nodal structure of the wave functions. Similar to the observations made in refs 2 and 7 relating to calculations on $S_0$ intermolecular eigenstates, we find evidence for significant mixing between the stretching mode and the $y$ bending mode. Such mixing is particularly pronounced for the $N = 8$ and 10 eigenstates but even shows up subtly in contour plots of the eigenfunctions of states like the stretching fundamental ($N = 4$), for example. Given the symmetry of the complex, wherein both $y$ and $z$ transform as A′, mixing of this sort is not surprising.

In comparing our results to experimental values, we note the existence of three sets of experimental results in the literature,[5,8,20] all obtained by resonant two-photon ionization spectroscopy on cold molecular beam samples. The $S_1$ intermolecular intervals reported in ref 5 are larger by one to several wavenumbers than those reported in refs 8 and 20. We take the latter data sets to be the more accurate ones because they are in agreement with each other and because wavelength calibration by a wavemeter was employed in the work of ref 8. We compare our results with the experimental frequencies in Table 4. One sees that agreement with the results of refs 8 and 20 is excellent. In addition, the assignments made in those two works match those made here. The only point of ambiguity in regard to assignments relates to the observed 64 $cm^{-1}$ interval.[20] Solely on the basis of this frequency in comparison with our computed frequencies, it could be reasonably attributed to the $S_1 \leftarrow S_0$ ($0_0$) band ending in $N = 7$, 8, or 9, or to the overlap of two or more of these bands.

**TABLE 3: Results of $J = 0$ Intermolecular State Calculations for Fluorobenzene−Ar**

| $N$ | irrep. | $\Delta E^a$ | $<z>^b$ | $\Delta z$ | $<y>$ | $\Delta y$ | $\Delta x$ | $n_x,n_y,n_z$ |
|---|---|---|---|---|---|---|---|---|
| 0 | A′ | 0.00 | 3.527 | 0.117 | 0.308 | 0.285 | 0.300 | 0,0,0 |
| 1 | A′ | 20.17 | 3.536 | 0.118 | 0.218 | 0.514 | 0.310 | 0,1,0 |
| 2 | A″ | 30.94 | 3.544 | 0.118 | 0.283 | 0.299 | 0.542 | 1,0,0 |
| 3 | A′ | 36.16 | 3.547 | 0.140 | 0.159 | 0.647 | 0.334 | 0,2,0 |
| 4 | A′ | 44.12 | 3.568 | 0.181 | 0.180 | 0.456 | 0.387 | 0,0,1 |
| 5 | A″ | 49.38 | 3.550 | 0.120 | 0.167 | 0.545 | 0.560 | 1,1,0 |
| 6 | A′ | 51.33 | 3.545 | 0.138 | 0.054 | 0.831 | 0.350 | 0,3,0 |
| 7 | A′ | 61.55 | 3.563 | 0.139 | 0.250 | 0.391 | 0.675 | 2,0,0 |
| 8 | A′ | 62.13 | 3.547 | 0.165 | −0.123 | 0.841 | 0.413 | 0,4,0<br>(0,1,1) |
| 9 | A″ | 63.59 | 3.556 | 0.139 | 0.079 | 0.699 | 0.601 | 1,2,0 |
| 10 | A′ | 66.86 | 3.566 | 0.165 | 0.110 | 0.782 | 0.418 | 0,1,1<br>(0,4,0) |
| 11 | A″ | 70.46 | 3.574 | 0.172 | 0.109 | 0.518 | 0.676 | 1,0,1 |
| 12 | A′ | 74.24 | 3.539 | 0.179 | −0.186 | 1.036 | 0.408 | 0,5,0 |
| 13 | A″ | 76.80 | 3.542 | 0.140 | −0.101 | 0.909 | 0.630 | 1,3,0 |
| 14 | A′ | 78.64 | 3.567 | 0.145 | 0.094 | 0.597 | 0.694 | 2,1,0 |
| 15 | A′ | 80.02 | 3.586 | 0.209 | 0.116 | 0.797 | 0.479 | − |

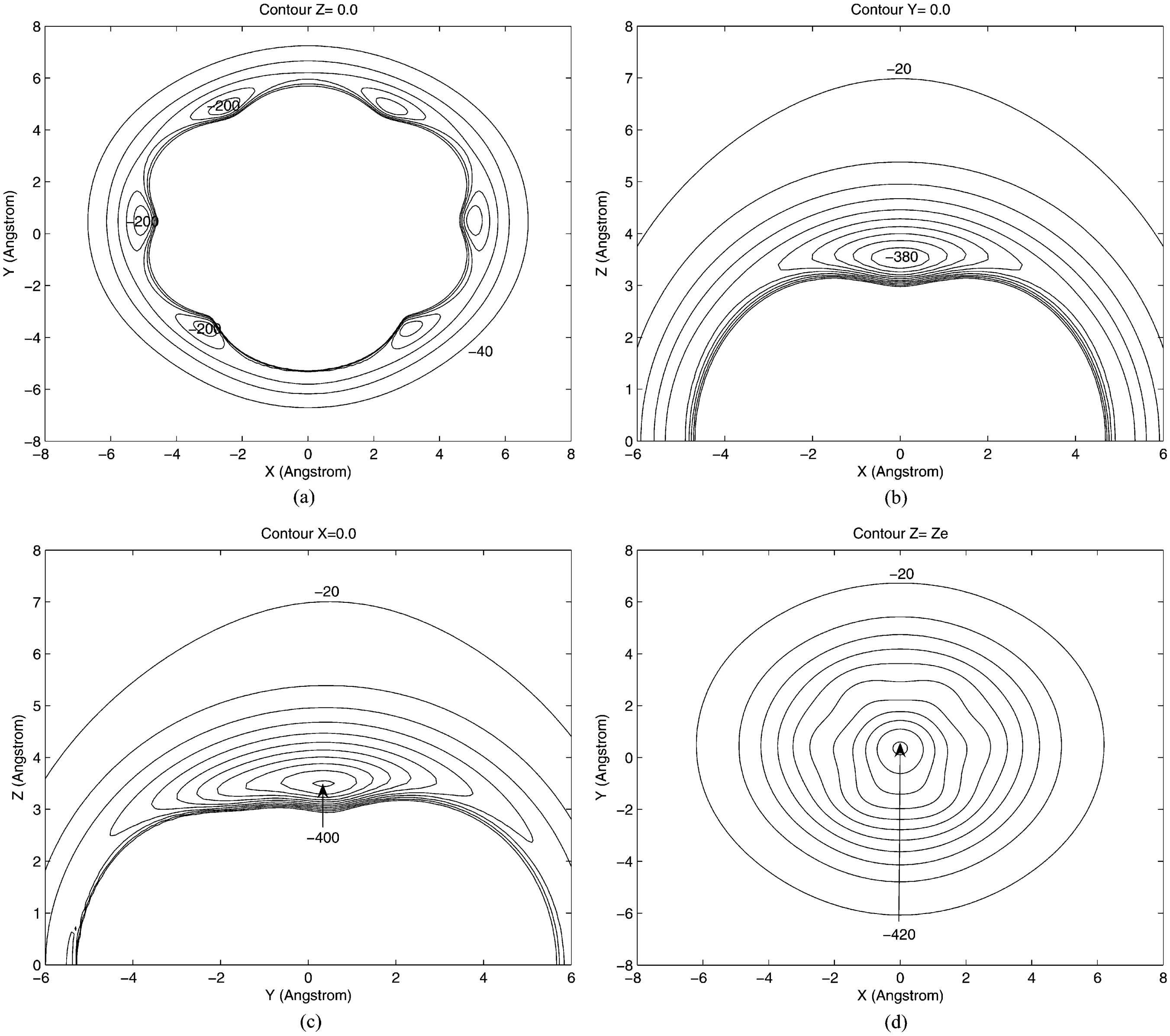
[a] Frequency shift in wavenumbers from the zero-point level at −374.46 $cm^{-1}$. [b] The $<z>$ and $<y>$ are the expectation values in angstroms of the $z$ and $y$ components of $\vec{\mathbf{r}}$, respectively; $\Delta x$, $\Delta y$, and $\Delta z$ are root-mean-squared values for the $x$, $y$, and $z$ components.

**TABLE 4: Comparison of Experimental and Computational Results for the $S_1$ Intermolecular Intervals in Fluorobenzene−Ar**

| final state assignment ($N$) | $\Delta E$(intensity)$^a$ | $\Delta E$(intensity)$^b$ | $\Delta E^c$ | $\Delta E$(intensity)$^d$ |
|---|---|---|---|---|
| 0 | 0 (100) | 0 (100) | 0 | 0 (100) |
| 1 | 20.17 (0.5) | 20 (1.7) | 20 | 21 (7) |
| 2 | 30.94 (0.4) | 32 (2.0) | | 34 (7) |
| 3 | 36.16 (1.3) | 35 (2.5) | | 38 (12) |
| 4 | 44.12 (4.9) | 44 (12) | 43 | 47 (22) |
| 6 | 51.33 (0.1) | | | 54 (1) |
| 7 | 61.55 (1.0) | 64 (2.0) | | 70 (3) |
| 8 | 62.13 (0.2) | | | |

[a] Calculated frequencies ($cm^{-1}$) and intensities (arbitrary units) from this work. [b] From ref 20. [c] From ref 8. [d] From ref 5.

One can get a firmer handle on the assignment of the observed $S_1 \leftarrow S_0\ X_0^n$ bands by computing their intensities relative to the $0_0^0$ band. (We use $X_0^n$ to denote a generic vibronic transition originating in the $0_0$ level of $S_0$ and ending in intermolecular vibrational state $X^n$ of $S_1$.) Relative intensities were computed by using the approach described in ref 21. Briefly, the intensities depend on the vibronic matrix elements of the electric dipole vector operator referred to the Eckart frame of the complex. Computation of these matrix elements is facilitated considerably by the fact that the $S_1 \leftarrow S_0$ transition in the fluorobenzene−Ar complex is essentially the fluorobenzene-localized $S_1 \leftarrow S_0$ transition (which is polarized along the fluorobenzene $x$-axis[17]).



(a) (b) (c) (d)

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

Given this, one can use eq 5.3 of ref 21 to find the transition dipole matrix elements. For the $X_0^n$ band, this requires the $S_1$ $J = 0$ eigenstate corresponding to $X^n$ (as computed above) and the $S_0$ $J = 0$ eigenstate corresponding to $0_0$. The latter was computed in the same way as the $S_1$ states were, except that the IPES used was that reported in ref 4 and the inertial parameters in $\hat{H}_v$ were those corresponding to the ground state of fluorobenzene.[22] The square of the transition dipole gives the relative intensity for a band. In cases where the final state corresponding to a given band has A′ vibrational symmetry, this approach is essentially the same as the usual Franck−Condon-type analysis. When the $X^n$ vibrational state is not totally symmetric, however, the computed band intensity can still be appreciable even though the Franck−Condon factor vanishes by symmetry.[6]

The results of the relative intensity calculations for the $S_1 \leftarrow S_0$ bands are also summarized in Table 4. Included in the table are only those final states from Table 3 that give rise to bands with computed relative intensities greater than $10^{-3}$ of the $0_0^0$ band. One sees that all of the bands observed experimentally also have appreciable calculated intensity. Indeed, the trend in calculated relative intensities matches quite well with the experimental trends reported in refs 5 and 20. (Ref 5 quotes intensities explicitly. Such are not quoted in ref 20; therefore, we have estimated them from peak heights in Figure 8 of that work.) This gives one further confidence in the assignments of Table 4, which mirror those of ref 20. We do note that the absolute values of our computed relative intensities differ consistently by about an order of magnitude from those of ref 5. On the other hand, the latter differ significantly from those characterizing the spectrum reported in ref 20, which are much closer to our computed values. In any case, if the experimental van der Waals band intensities are expressed relative to the intensity of the stretching fundamental at $S_1 + 44$ cm$^{-1}$ (reported at 47 cm$^{-1}$ in ref 5) rather than to that of the $0_0^0$ band, then agreement between calculated and experimental values is quite reasonable.

Finally, we have calculated the rotational constants of the $S_1$ zero-point level of the complex. The method used is the same as that described in ref 2 and is based on the “Eckart method” described in ref 23. We find $A = 1751$ MHz, $B = 1113$ MHz, and $C = 909$ MHz. These compare with experimental values of 1773.3, 1148.9, and 996.8 MHz, respectively, as obtained by the analysis of partially rotationally resolved zero-electron kinetic energy (ZEKE) spectra.[9] Clearly, there is less-than-perfect agreement between the calculated and experimental values, particularly in respect to the *C* constant. The discrepancies are reflected in the zero-point-averaged geometrical parameters from the calculations versus those derived from experiment (e.g., $<z> = 3.33 \pm 0.11$ Å from ref 9 compared to the calculated value of 3.527 Å). We are not sure of the reason for these rotational constant discrepancies. We would point out, though, that the 0.22 Å $S_0$-to-$S_1$ decrease in $<z>$ implied by the experimental results[9] is significantly larger than the analogous decreases in benzene and *p*-difluorobenzene. This suggests that, for example, the experimental $S_1$ *C* value for fluorobenzene−Ar might be too large. Given this and the disagreement with our computed values, a reanalysis of the experimental results seems warranted.

## IV. Summary And Conclusions

We evaluated an accurate IPES for the $S_1$ excited state of the fluorobenzene−Ar van der Waals complex. We used available ground-state interaction energies evaluated with the CCSD(T) and the aug-cc-pVDZ-33211 basis set. We selected 147 intermolecular geometries and, with the same basis set and the CCSD method, calculated the corresponding excitation energies and, from there, the $S_1$ interaction energies. The surface minima were characterized by the Ar atom located above and below the fluorobenzene ring at a distance of 3.506 Å with respect to the fluorobenzene center of mass and at an angle of 5.89° with respect to the axis perpendicular to the fluorobenzene plane. The corresponding interaction energy is $-425.226$ cm$^{-1}$. These results give a stronger interaction in the excited state compared to that of the ground state of the complex, with a larger dissociation energy and a shorter bond distance, a trend that was also found for the benzene− and *para*-difluorobenzene−Ar $S_1$ van der Waals complexes.

The intermolecular level structure has been evaluated from the IPES, and good agreement was obtained with respect to the experimental results available, after some of the experimental assignments have been corrected.

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**Supporting Information Available:** Coupled Cluster aug-cc-pVDZ-33211 fluorobenzene−argon $S_1$ excited-state interaction energies. This material is available free of charge via the Internet at http://pubs.acs.org.

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