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Theoretical Studies on the Pyridine−I_2 Charge-Transfer Complex. 1. Ab-Initio Calculations on I_2 and Pyridine−I_2

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We present results of comparative ab-initio calculations on the I_2 molecule and the pyridine−I_2 charge-transfer complex. Various basis sets are compared, including effective core potential and all-electron basis sets. Frequency calculations are performed, and the influence of a solvent, represented by a self-consistent reaction field, on the complex is investigated.

1. Introduction

Charge-transfer complexes are known to every chemist. The pyridine−iodine complex has been investigated spectroscopically in a number of instances, but only a few publications in the field of computations can be found in the literature.[1,2] Experimentally, a dipole moment in the range 4.5−6.3 D,[3−6] a binding energy of −7.4 to −8.6 kcal/mol,[7] and a net transfered charge from the pyridine to the I_2 of 0.2−0.3*e* have been found.[8−10] The geometry is not known for certain, a linear arrangement with the iodine in the ring plane, and a N−I distance in the range 2.2−2.8 Å[11,12] (see Figure 1) seems most probable and is usually accepted for the complex in the liquid phase. Similar values are found in crystals of iodine/4-methylpyridine.[13] In spectroscopic investigations, the vibrational frequencies of the I−I and N−I stretching modes can be observed. They are found to depend on the nature of the solvent.[14−20] Computationally, the complex was investigated using SCF-MS-Xα calculations based on experimental data.[1] A dipole moment of 8.1 D and a net charge transfer of 0.162*e* were calculated for the complex in vacuum.

Ab-initio calculations are nowadays performed in a more or less routine fashion on a vast variety of systems due to the availability of ever increasing computational power. It seems, however, that the number of works on complexes containing iodine remains limited. For atoms up to argon ab-initio calculations on complexes and the methods to be used are well established. The lack of ab-initio calculations for complexes containing heavier atoms may be due to the fact that the number of electrons, and therefore the computational effort for all-electron calculations, increases rapidly, especially when electron correlation has to be included. This is necessary for nonbonded interactions, a fact that should become even more important in the case of complexes containing iodine.

In the present study we investigate the usefulness and reliability of ab-initio calculations for the pyridine−iodine complex by using different basis sets. The results are compared with each other and also with experimental results. It is our ultimate goal to develop an interaction model for I_2−pyridine interactions from the present calculations and to study the dynamics of I_2 in this solvent[21] as well as mixed with a third, inert, solvent by molecular dynamics (MD) simulations.

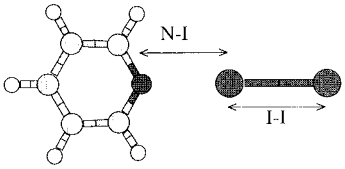

Figure 1. Geometry of the pyridine−iodine complex. Depicted are the iodine−iodine (R_{II}) and nitrogen−iodine (R_{NI}) distances. The iodine atom closest to the pyridine is referred to as I1 in the text.

TABLE 1: Basis Sets Used, with Their Number of Uncontracted/Contracted Basis Functions, the Resulting I−I Distance, and the Calculated Frequency, for an Isolated I_2 Molecule

basis set	number of basis functions	$r_{\mathrm{I-I}}$ [Å]	$\nu_{\mathrm{I-I}}$ [cm^{-1}]
SBKJC	40/16	2.7704	210.16
LANL1DZ	24/16	2.8172	198.98
LANL1DZ(*)	34/26	2.6794	231.90
LCRAE	64/34	2.8398	201.33
SV2P	170/78	2.7053	233.88
SV4P	206/78	2.6975	239.91
SV4PP	218/90	2.6943	235.28
expt.[54]		2.67	215.0

The paper is organized as follows: After this introduction, we present in section 2 the computational details of the methods that we used and a few selected results to establish their validity and limitations. Detailed results on the I_2−molecule and the I_2−pyridine complex are reported and discussed in section 3. The conclusions are presented in section 4.

2. Computational Details

2.1. Basis Sets. A variety of basis sets suitable for the pyridine−I_2 complex are available. One can choose between all-electron[22−27] and effective core potential (ecp) basis sets,[24,28−34] where the innermost core electrons are neglected, and hence the computational effort is reduced. In this work, we explore various basis sets and compare the results for the purpose of generating later on potential energy surfaces for molecular dynamics (MD) simulations with sufficient reliability and at acceptable computational costs.

The basis sets used in this work are presented together with a few characteristic results for the I_2 molecule in Table 1. The SBKJC basis set uses ecp's not only for iodine but also for carbon and nitrogen.[34−36] The LANL1DZ basis set consists of an ecp basis set for the iodine atoms and the D95[37] basis set for C, N, and H. The basis set LANL2DZ uses the same ecp

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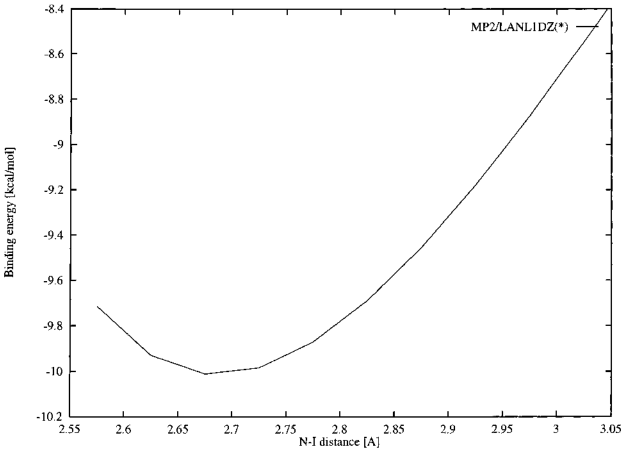

Figure 2. Binding energy of the pyridine−I_2 complex versus the N−I distance. The energy was calculated using MP2/LANL1DZ(*) (see text).

basis for iodine but uses the basis set D95V[37] instead of D95 for C, N, and H (thus only results for LANL1DZ appear in Table 1). All three basis sets, LANL2DZ, LANL1DZ, and SBKJC, are of double-ζ quality in the valence region.

To further improve the quality of the LANL1DZ basis set, a set of d-functions developed by Höllwarth et al.[38] was used. The notation LANL1DZ(*) describes a basis set were these d-functions were added for iodine only, whereas the notation LANL1DZ* denotes a basis set where d-functions were added to all heavy atoms. This addition of d-functions improves the LANL1DZ basis set to triple-ζ quality in the valence region.

A further ecp basis set was developed by LaJohn et al.;[28] it is denoted here LCRAE. This basis set was used with uncontracted p- and s-functions, as reported by Tonokura et al.,[39] and is thus of near quad-ζ quality for the valence region.

Among the all-electron basis sets published we investigated only the series of split valence (SV) basis sets developed by Anzelm et al.[26] for iodine, namely, SV2P, SV4, and SV4P. Nevertheless, the limits of our computational resources were quickly reached with these basis sets. For subsequent calculations on the pyridine−I_2 complex we constructed an all electron basis set consisting of the SV2P and the 6-31G*[40−43] basis set. This basis set is denoted as BIG.

2.2. Calculations. All calculations were performed using the Gaussian92[44] program on two IBM RS6000 workstations, an SNI S400/40, a Cray C94, and a Cray C98. Energies and geometries were computed at the Hartree−Fock (HF) level and using Møller−Plesset second-order perturbation theory (MP2) for the inclusion of electron correlation.[45] One calculation using fourth-order Møller−Plesset perturbation theory was performed in order to investigate the effects of higher perturbation terms. For all ecp basis sets complete geometry optimizations were performed. For the geometry optimizations of the complex with the SV2P basis set, the internal degrees of freedom of pyridine were kept fixed.

2.2.1. Geometry Optimizations. All geometries were optimized using the standard convergence criteria of the Gaussian92 program. For two basis sets, geometries corrected for the basis set superposition error (for short: BSSE-corrected geometries) at the MP2 level were computed for the pyridine−I_2 complex in the following manner: The iodine−nitrogen distance was varied in steps of 0.05 Å, and for a given distance the rest of the geometry was relaxed. For this resulting geometry, the BSSE-corrected dimer formation energy was calculated, using the counterpoise method developed by Boys and Bernardi.[46] A curve "binding energy versus N−I distance" resulting from this procedure is seen in Figure 2.

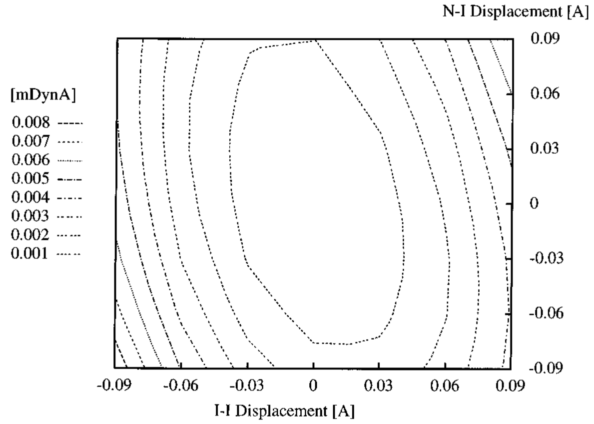

Figure 3. Contour plot of the bond stretching energy, in mdyn Å.

2.2.2. Frequency Calculations. Frequencies were calculated in two ways: firstly, by calculating complete ab-initio spectra, resulting in normal modes frequencies, harmonic force constants, and intensity information. For some of the methods applied to the pyridine−I_2 complex, however, ab-initio frequency calculations are not possible within Gaussian92 (e.g. in self-consistent reaction field (SCRF) calculations), or geometries are only partly relaxed, or complete frequency calculations are too costly (e.g. with the SV2P basis set). Here a different approach based on a stepwise variation of the N−I and I−I internal degrees of freedom was chosen: Both distances were varied in steps of 0.03 Å, from $r_0 - 0.06$ Å to $r_0 + 0.06$ Å (5 points for each coordinate), with r_0 being the equilibrium distance. All combinations of the two coordinates were calculated, leading to 25 single-point calculations. The result is an energy surface, depicted in Figure 3, to which a simple force field of the form

$$V = \frac{k_{\mathrm{I-I}}}{2}(\Delta r_{\mathrm{I-I}})^2 + \frac{k_{\mathrm{N-I}}}{2}(\Delta r_{\mathrm{N-I}})^2 + \frac{k_{\mathrm{coup}}}{2}\Delta r_{\mathrm{I-I}}\Delta r_{\mathrm{N-I}} \quad (1)$$

with $\Delta r_{\mathrm{I-I}} = r_{\mathrm{I-I}} - r^{\mathrm{e}}_{\mathrm{I-I}}$, $\Delta r_{\mathrm{N-I}} = r_{\mathrm{N-I}} - r^{\mathrm{e}}_{\mathrm{N-I}}$, and r^{e} referring to the equilibrium values, was fitted. With this force field, the normal modes of a three-body model-molecule with the masses of Py, I, and I, and the appropriate geometry, were calculated. It is assumed here that the internal modes of pyridine can be decoupled from the low-frequency ones discussed. The validity of this approximation can be gauged in Figure 4 and Table 2. The figure shows that the modification of the character of the ring breathing mode, chosen as an example, due to the complexation, is indeed small. The frequency of this mode in pyridine is 669 cm^{-1} and in the complex 687 cm^{-1}; see also Table 2, where all frequencies are compared for one basis set. All modes were identified visually to make sure that the frequencies of modes of the same character are compared. The vibrational frequencies associated with the pyridine are typically shifted up by 10−20 cm^{-1} upon complexation with the I_2. The character of the vibrational motions of the ring is very little affected.

Frequencies obtained directly from the ab-initio program and from the described fitting procedure are compared in Table 3. In this table and subsequent tables, unscaled frequencies are presented, while in Figures 5 and 6, where theoretical and experimental spectra for the LANL1DZ basis set are compared, the ab-initio frequencies were scaled by a factor of 0.897.

2.2.3. Self-Consistent Reaction Field (SCRF) Calculations. In order to approximate crudely the effect of a polar solvent (in the experiments: pyridine) on the properties of the complex, we used an Onsager model, where the molecule to be investigated is placed inside a cavity surrounded by the solvent treated as a continuum.[47−50] Two parameters, namely, the dielectric

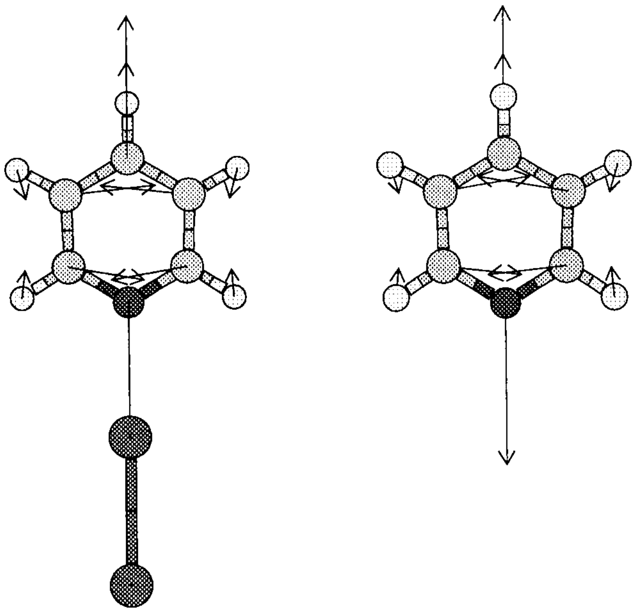

Figure 4. Comparison of the in-plane ring deformation modes of Pyr−I_2 and pyridine (left to right).

TABLE 2: Comparison of the Frequencies, in cm^{-1}, for the Isolated Pyridine Molecule and the Isolated Pyridine−I_2 Complex, Calculated with HF/LANL1DZ

pyridine	pyridine−I_2	pyridine	pyridine−I_2
	35.71	1156.51	1160.87
	37.31	1160.58	1169.96
	86.07	1177.85	1178.43
	117.14	1244.62	1249.22
	142.08	1327.78	1333.59
	173.12	1346.39	1347.92
444.98	445.99	1509.11	1512.58
475.28	485.53	1594.28	1599.10
669.33	687.03	1637.62	1643.93
725.06	722.82	1765.26	1768.77
802.45	796.73	1769.61	1778.31
853.16	862.85	3399.76	3411.08
1011.00	1010.12	3405.20	3415.97
1074.36	1084.14	3416.84	3427.93
1080.69	1098.47	3425.73	3435.03
1124.24	1133.43	3439.29	3447.48
1139.02	1143.29		

TABLE 3: Normal-Mode Frequencies, in cm^{-1}, Obtained from the Gaussian92 Program (Columns 2 and 3) and from a Fitting Procedure (Columns 4 and 5) Described in the Text, Force Constants, in mdyn/Å, and Coupling constants, in mdyn/Å (Columns 6−8), for the Py−I_2 Complex in Vacuum, Calculated Using Different Basis Sets. Experimental Values Are Given for Comparison

			fitted				
basis set	frequency		frequency		$k_{\mathrm{I-I}}$	$k_{\mathrm{N-I}}$	k_{coup}
HF/LANL1DZ	173	86	173	89	1.254	0.292	0.200
MP2/LANL1DZ	163	118					
HF/BIG			220	65	1.892	0.155	0.111
MP2/BIG			191	111	1.476	0.437	0.212
experiment[a]	170	118					
experiment[b]	184	95					

[a] Measured in 0.2 M I_2 in pyridine;[55] see also ref 17. [b] Measured in ternary mixture, 0.05 M I_2 and 0.38 M pyridine in heptane.[55]

constant ϵ assumed for the solvent and the radius of the cavity, a_0, influence the result of such self-consistent reaction field (SCRF) calculations. The experimental value ϵ_0[51] for pyridine was used here. Usually, a_0 is obtained by calculating the volume of the complex according to some definition and determining the radius of a sphere with the same volume. Here, however, the complex is far from being spherical. Since the shape of the cavity is not easily modified in the program we used, a larger spherical cavity ($a_0 = 6.63$ Å) was employed, so that the entire complex resides inside the cavity. This is expected to lead to a roughly adequate representation of the solvent effect in the direction of the N−I−I axis of the complex, which should be mainly responsible for the modifications of the bond lengths and frequencies.

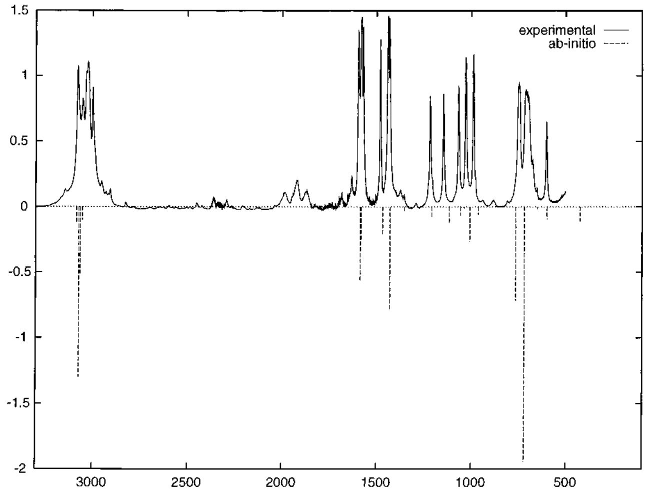

Figure 5. Experimental and scaled (factor 0.897) ab-initio spectra, frequencies, in cm^{-1}, for pyridine.

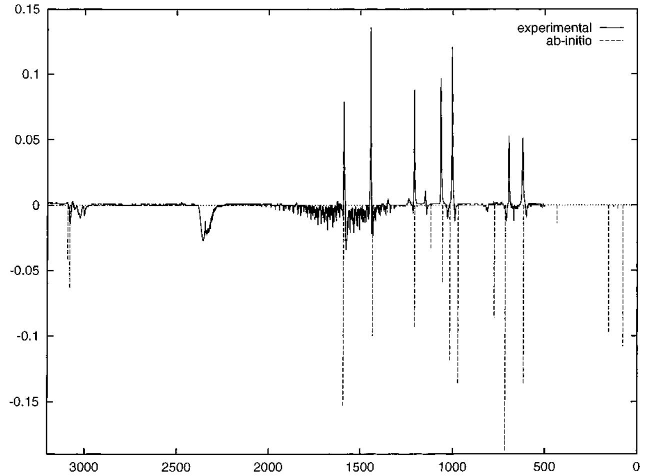

Figure 6. Experimental mid-infrared and scaled (factor 0.897) ab-initio spectra, frequencies in cm^{-1}, for Py−I_2. (experiments: diluted in apolar solvent (CCl_4), from original experimental data used in ref 55).

2.2.4. Determination of Partial Charges. Partial charges on the atoms are useful to rationalize intermolecular interactions, e.g. for computer simulations. They were determined here in two different ways; either with a Mulliken population analysis or as electrostatic potential (esp) derived charges, using the CHELPG scheme and the Breneman atomic radii for C, N, and H.[52,53] The atomic radius for iodine, which is needed for this procedure, was determined by fitting the dipole moment calculated using the esp charges to the ab-initio dipole moment. The resulting radius is 2.2 Å. Charges were calculated using both the HF and the MP2 densities.

3. Results

3.1. The I_2 Molecule. The basis sets, the resulting numbers of basis functions for the I_2 molecule, and the results of geometry optimizations and frequency calculations at the HF level are presented in Table 1 and are compared with experimental values.

TABLE 4: Results of the Geometry Optimizations of the Pyridine−Iodine Complex with Different Basis Sets: Nitrogen−Iodine and Iodine−Iodine Distances, and Normal Mode Vibrational Frequencies Related to These Degrees of Freedom, from ab-Initio Geometry Optimizations at the HF Level[a]

basis set	r_{N-I} [Å]	r_{I-I} [Å]	ν_{Py-I} [cm^{-1}]	ν_{I-I} [cm^{-1}]	number of basis functions
LANL2DZ	2.4218	2.9457 (0.1285)	112.3	131.6	129/51
SBKJC	2.6356	2.8429 (0.0725)	86.4	177.7	151/74
LANL1DZ	2.6307	2.8929 (0.0757)	86.1	173.7	194/80
LANL1DZ(*)	2.8158	2.7145 (0.0351)	70.1	211.3	204/90
LANL1DZ*	2.9856	2.7000 (0.0206)	56.5	219.8	234/120
BIG	2.9207	2.7303 (0.0250)	[65]	[220]	358/178

[a] The numbers in parentheses denote the change in the I−I distance upon formation of the complex compared to the free iodine molecule calculated with the same basis set. In the case of the BIG basis only a geometry optimization with rigid pyridine was carried out; the frequencies were calculated as outlined in section 2.2.2. Experimental frequencies are given in Table 3.

All basis sets overestimate the I−I distance in the I_2 molecule, the ecp basis sets more than the all-electron basis sets, with deviations of up to 0.17 Å compared with the experimental data. The addition of d-functions to the LANL1DZ basis set drastically improves the results. The I−I distances in the SV series decrease smoothly to the experimental value. But the best value of the SV4PP basis set still shows a larger deviation from experimental results than the one from the LANL1DZ(*) basis. The results obtained with the ecp basis sets, however, do not converge smoothly to the "true" result: The LCRAE basis set, the ecp basis set with the largest number of basis functions, delivers the worst agreement with experiment.

For the ecp basis sets the calculated frequencies have a tendency to be too low compared with the experimental value of 215 cm^{-1}.[54] The results obtained with the largest ecp basis set, LCRAE, are of average quality. The LANL1DZ(*) basis set seems again to give results of better quality compared with the LANL1DZ basis. The frequency calculated using the LANL1DZ(*) basis set is too high, a result one would expect from an ab-initio frequency calculation. The scaling factor to obtain the experimental frequency is 0.927, in the expected range. All results of frequency calculations using all-electron basis sets are too high. The scaling factors here are in the range 0.915−0.945.

3.2. The Pyridine−I_2 Complex. *3.2.1. HF and MP2 Geometries and Frequencies.* The results of the geometry optimizations and of the frequency calculations at the HF level for the pyridine−I_2 complex using various basis sets are presented in Table 4. The total number of basis functions in each set is also given for comparison.

With the smallest basis set, LANL2DZ, a N−I distance of 2.42 Å and an I−I distance of 2.95 Å are computed; that is, the I−I distance is enlarged by 0.13 Å compared with the isolated molecule treated with the same basis (LANL1DZ, Table 1). This basis also leads to a drastic change in the frequency of the I−I mode, a reduction by about 35%, compared to the free molecule. All values computed with this basis set are extreme values, far out of the variations obtained from other basis sets, and therefore seem to be unreliable.

The basis sets SBKJC and LANL1DZ, both ecp basis sets of comparable sizes, deliver comparable results. I−I distances of 2.89 and 2.84 Å are computed; an N−I distance of 2.63 Å and frequencies of 86 and 174−177 cm^{-1} are computed. The difference in the I−I distance in the complex of 0.05 Å between the two basis sets is the same as the one determined for the free I_2 molecule. An augmentation of the LANL1DZ basis set with d-functions on iodine (LANL1DZ(*)) and on iodine, carbon, and nitrogen (LANL1DZ*) systematically changes the results: The N−I distance increases (2.63 → 2.82 → 2.99 Å); the I−I distance decreases (2.89 → 2.71 → 2.70 Å). As a consequence of the weakening Py−I_2 interaction, and hence the less perturbed I−I bond, the frequencies of the Py−I_2 mode lowers, and the I−I frequency rises. For the all electron basis set composed of the basis sets SV2P for iodine and 6−31G* for pyridine (BIG), the results are similar to the LANL1DZ* basis set: The N−I distance is 0.06 Å smaller, and the I−I distance is 0.03 Å larger.

TABLE 5: Effect of Correlation on the Geometry of the Pyridine−Iodine Complex; For All Basis Sets Except BIG, a Complete Geometry Optimization Was Performed; in the Latter Case the Internal Degrees of Freedom of Pyridine Were Kept Fixed

calculation	r_{N-I} [Å]	r_{I-I} [Å]
HF/LANL2DZ	2.4218	2.9457
MP2/LANL2DZ	2.4096	3.0222
HF/SBKJC	2.6356	2.8429
MP2/SBKJC	2.5091	2.9481
HF/LANL1DZ	2.6307	2.8929
MP2/LANL1DZ	2.4991	2.9871
HF/LANL1DZ(*)	2.8158	2.7145
MP2/LANL1DZ(*)	2.5746	2.7747
MP2/LANL1DZ(*) BSSE	2.675	2.7585
HF/LANL1DZ*	2.9856	2.7000
MP2/LANL1DZ*	2.6114	2.7624
HF/BIG	2.9207	2.7303
MP2/BIG	2.5806	2.7952
MP2/BIG BSSE	2.705	2.7784

These findings are partly only repetitions of the ones already made for the I_2 molecule. The addition of iodine d-functions to the LANL1DZ basis set leads to a shortening of the I−I distance, both in the complex and in the free I_2 molecule. We note that the deviations in the bond lengths between the free iodine molecule and the complex fall roughly into two groups: 0.06−0.12 and 0.02−0.03 Å; see Table 4. The trend of shortening I−I distances upon addition of polarization functions is also reflected in the frequencies.

Geometry optimizations at the MP2 level were performed to investigate the effect of electron correlation on the geometry. The results are presented in Table 5 (see also Figure 2 and the discussion in section 2.2.1). The effect of electron correlation is the same for all basis sets: The N−I distance shortens, and the I−I distance increases. The longer the N−I distance at the HF level, the larger the effect of the MP2 treatment on the geometry. The smallest variation appears for the LANL2DZ basis set. The short N−I distance of 2.4218 Å computed at the HF level is shortened by merely 0.02 Å. The change is the largest, 0.37 Å, for the LANL1DZ* basis set. This effect may be due to the increasing number of basis functions and thus the increasing MP2 effect by sheer basis set size. This is, however, only partly true: The basis sets LANL1DZ(*) and BIG, of different absolute sizes and of different quality in the valence region of the atoms, show nearly identical contractions of the N−I distance, 0.37 and 0.34 Å, respectively, while the LANL2DZ and LANL1DZ sets, both of similar quality in the valence region, strongly differ in the effect of MP2 on the geometry. Frequencies at the MP2 level were calculated using the basis sets LANL1DZ and BIG; results are found in Table 3. For both basis sets, the inclusion of electron correlation leads to a rise of the N−I mode frequency and to a lowering of the I−I mode frequency. As for the geometries, the effect of MP2 on the frequencies is larger for the BIG basis set.

The effect of BSSE on the MP2 geometries was investigated by computing BSSE-corrected geometries with the method

TABLE 6: Counterpoise-Corrected Interaction Energies for the I$_2$−Pyridine Complex, Calculated at the HF and MP2 Levels, Using Various Basis Sets and Geometries; Energies Computed without BSSE Correction Are Given in Parentheses for Comparison

basis set for the energy calculation//method/basis set for the geometry calculation	energy [kcal/mol]	
	HF	MP2
SBKJC//HF/SBKJC	−6.02 (−7.01)	−10.32 (−14.21)
SBKJC//MP2/SBKJC	−5.85 (−7.20)	−9.94 (−14.56)
LANL1DZ//HF/LANL1DZ	−6.30 (−7.41)	−10.63 (−14.64)
LANL1DZ//MP2/LANL1DZ	−6.09 (−7.50)	−10.02 (−15.01)
LANL1DZ(*)//HF/LANL1DZ(*)	−6.36 (−6.80)	−9.80 (−12.58)
LANL1DZ(*)//MP2/LANL1DZ(*)	−5.52 (−6.15)	−9.71 (−13.57)
LANL1DZ(*)//MP2/LANL1DZ(*) BSSE	−6.28 (−6.80)	−10.01 (−13.32)
LANL1DZ*//HF/LANL1DZ*	−4.35 (−4.69)	−7.76 (−9.72)
LANL1DZ*//MP2/LANL1DZ*	−2.36 (−2.89)	−8.26 (−11.64)
BIG//HF/BIG	−4.38 (−5.92)	−8.65 (−11.68)
BIG//MP2/BIG	−1.62 (−4.06)	−8.93 (−13.77)
BIG//MP2/BIG BSSE	−3.10 (−5.18)	−9.26 (−13.30)

TABLE 7: Effect of Electron Correlation, As Determined by MP Perturbation Treatment of Increasing Order, on the Binding Energy of the Py−I$_2$ Complex, Computed Using the LANL1DZ(*) Basis Set on an MP2/BSSE-Corrected Geometry (SDTQ = Single/Doubles/Triples/Quadruples)

perturbation	energy [kcal/mol]
HF	−6.28
MP2	−10.01
MP3	−6.86
MP4(SDTQ)	−9.19

described above. This was done for the basis sets LANL1DZ(*) and BIG, with the same result for both: The trends in geometries observed at the MP2 level are partly due to the BSSE. After BSSE correction the values obtained are intermediate between the uncorrected HF and MP2 values.

3.2.2. Interaction Energy. Counterpoise-corrected energies of the pyridine−I$_2$ complex are presented in Table 6. These energies were computed at the HF and MP2 levels, with and without BSSE, based on the HF-, MP2-, and MP2(BSSE)-derived geometries. The non-BSSE-corrected values are given in parentheses.

The effect of the MP2 perturbation treatment is significant in all cases. The contributions by MP2 are in the range 4−7 kcal/mol. With increasing basis set size, the contributions of MP2 become more and more important, the HF interaction energies decline. This effect is, however, often nearly compensated by the MP2 contributions. Thus, the HF energies vary between −1.62 and −6.36 kcal/mol, the MP2 energies only between −7.76 and −10.63 kcal/mol. As already known from calculations of other nonbonded interactions, the BSSE of the MP2 calculations is larger than that of the HF calculations. The larger the contribution of MP2, the larger the BSSE. The computed interactions energies at the MP2 level are all lower than, or at the lower limit of, the range of experimental binding energies (−7.4 to −8.6 kcal/mol), but with increasing quality of the basis set, the results are approaching the experimental values. The energies computed at the HF level are all of smaller magnitude than the experimental values and decrease with increasing basis set quality, so the already well-known importance of electron correlation for nonbonded interactions is once more stressed.

In order to investigate the role of higher terms in perturbation theory, the interaction energy was calculated with MP3 and MP4, using the LANL1DZ(*) basis set, with the MP2 BSSE-corrected geometry. The result is listed in Table 7. The contributed change in energy is slowly converging (HF → MP2 −3.72 kcal/mol; MP2 → MP3 3.15 kcal/mol; MP3 → MP4 −2.33 kcal/mol) for the individual terms. The difference between MP2- and MP4-computed energy is below 1 kcal/mol.

3.2.3. Comparison of Experimental and Theoretical Spectra. The complete spectra for the free pyridine molecule and the pyridine−I$_2$ complex, calculated at the HF level, are presented in Table 2. They are compared in Figures 5 and 6 with experimental spectra. In both figures the same scaling factor, 0.897, was applied to the ab-initio data; it was obtained as the ratio of experimental and computed H−C stretching modes' frequencies. The frequencies calculated using the LANL1DZ basis set at the HF level are shown.

Here one problem of this basis becomes apparent: Whereas the internal frequencies of pyridine are calculated too high, as expected for ab-initio results, the frequencies of the N−I and I−I modes are, without scaling, already in the range of the experimental values; see Table 3. This might be explained as follows: The LANL1DZ basis set is a combination of an ecp basis set on the iodine and the D95 basis set for pyridine. In the calculations of the free I$_2$ molecule the frequencies were also calculated as too low. The calculations of the free pyridine molecule using the D95 basis set, on the other hand, result in frequencies that are too high. The combination of these basis sets should now result in too high frequencies for the modes of pyridine, which are unaffected by the ecp basis set, and too low, or lowered, for the modes where the influence of the ecp basis set on iodine is important, namely, the I−I and N−I modes.

The addition of d-functions to the basis set does not improve the situation, since now the basis sets LANL1DZ(*), LANL1DZ*, and also the all-electron basis set underestimate the binding energy at the HF level. Therefore, the frequencies of I−I and N−I were calculated with the BIG basis set at the HF and MP2 level (see Table 3). The frequencies at the HF level are due to the weak interaction of pyridine and I$_2$ computed at the HF level: The I−I mode frequency is just 11 cm^{-1} below the value of the free I$_2$, and the N−I mode frequency is too low compared with experiment. At the MP2 level, the I−I mode frequency has shifted by 42 cm^{-1}, still above the experimental value, and the N−I mode frequency is higher than the experimental one. If now a scaling based on the ratio experimental/ab-initio value for the free iodine is applied (scaling 0.9442), the scaled values are close to the experimental results (I−I 180 cm^{-1}; N−I 104 cm^{-1}).

3.2.4. Dipole Moment and Charge Transfer. The dipole moment and Mulliken charges of the two iodine atoms in the complex, calculated at the HF level, are presented in Table 8. I1 denotes the iodine atom closer to the pyridine.

A clear trend can be seen: The dipole moment and transferred charge decrease with increasing basis set size. The dipole moment tends to be somewhat larger than the experimental estimates, the "best" values being within the range of experi-

TABLE 8: Mulliken Charges on the Two Iodine Atoms, Net Charge Transferred, and Total Dipole Moment, in Debyes, of the Py−I$_2$ Complex, Calculated Using the HF Densities and the HF-Derived Geometries with Each Basis Set

basis set	q_{I1} au	q_{I2} au	Δq au	dipole [D]
LANL2DZ	0.13	−0.42	−0.29	13.37
SBKJC	0.09	−0.18	−0.09	8.56
LANL1DZ	0.09	−0.20	−0.11	8.67
LANL1DZ(*)	0.09	−0.14	−0.05	6.37
LANL1DZ*	0.06	−0.10	−0.04	5.00
BIG	0.06	−0.12	−0.06	5.50

TABLE 9: Comparison of Mulliken and esp-Derived Charges for the Pyridine−I$_2$ Complex Using the LANL1DZ Basis Set. In the Last Two Rows the Results for the SCRF Calculations with an ϵ of 13.26 Are Presented

geometry	density	method	q_{I1} [au]	q_{I2} [au]	δq [au]	dipole moment [D]
HF	HF	Mulliken	0.09	−0.20	−0.11	8.67
HF	HF	ESP	−0.02	−0.21	−0.23	8.56
HF	MP2	Mulliken	0.04	−0.18	−0.14	8.78
HF	MP2	ESP	−0.07	−0.18	−0.25	8.67
MP2	HF	Mulliken	0.13	−0.26	−0.13	10.55
MP2	HF	ESP	−0.02	−0.27	−0.29	10.44
MP2	MP2	Mulliken	0.05	−0.22	−0.17	10.27
MP2	MP2	ESP	−0.09	−0.23	−0.32	10.18
HF$_{SCRF}$	HF	Mulliken	0.15	−0.29	−0.14	11.29
HF$_{SCRF}$	HF	ESP	0.01	−0.31	−0.30	11.06

TABLE 10: Distances in Py−I$_2$ from the SCRF Calculations with the LANL1DZ Basis Set and a Cavity Radius of a_0 = 6.63 Å

ϵ	r_{N-I}	r_{I-I}
4	2.54	2.92
7	2.53	2.92
13	2.51	2.93
vacuum	2.63	2.89

mental values (4.5−6.3 D).[3−6] The net transferred charge is somewhat smaller than the experimental estimates.

A comparison between Mulliken and esp-derived charges for the LANL1DZ basis set is made in Table 9. The transferred charge is generally smaller with the Mulliken analysis. The differences between Mulliken charges and esp charges mainly originate from the I1 atom; the I2 atom shows nearly identical charges in both cases. The esp charges calculated with the different geometries and densities vary in the range 0.23−0.32*e*. It must be noted, however, that the basis set used here, LANL1DZ, overestimates the dipole moment.

3.2.5. Calculations with Self-Consistent Reaction Field. SCRF calculations of the pyridine−I$_2$ complex in a cavity with a radius a_0 = 6.63 Å were performed using the LANL1DZ basis set. The experimental value of the dielectric constant ϵ_0 of pyridine is 13.26.[51] First, geometry optimizations were performed with values of ϵ of 4, 7, and 13. The effect on the I−I and N−I distance is shown in Table 10. It can be seen that, due to the electric field of the solvent, the N−I distance slowly contracts and the I−I distance expands. The effect on the frequency can be seen in Table 11. The frequencies were computed at the HF level, using the fit procedure described above. While the I−I mode lowers, the frequency of the N−I mode rises. Due to the solvent, the coupling (k_{coup}) between the two modes increases. The dipole moment and charge transferred (see Table 9) are clearly increased in comparison to the same calculation in vacuum. The charge separation between I1 and I2 is also increased by the external field.

TABLE 11: Frequencies, in cm^{-1}, Force Constants, in mdyn/Å, and Coupling Constants, also in mdyn/Å for Py−I$_2$ in Vacuum and in a Continuum with a Dielectric Constant of ϵ = 13.26, Calculated Using the Fit Procedure Described in the Text

	fitted				
	freq		k_{I-I}	k_{N-I}	k_{coup}
vacuum	173	89	1.25	0.29	0.200
ϵ = 13.26	158	106	1.10	0.41	0.280

4. Conclusion and Outlook

We have explored the potentialities and limitations of ab-initio calculations on charge-transfer complexes of pyridine and iodine. Our results and conclusions can be summarized as follows.

Such calculations can be performed both with all-electron and with effective core bases.

The results of ab-initio calculations with ecp basis sets have to be interpreted with knowledge of the qualities and properties of such basis sets. We found comparisons between the results of calculations on free iodine/free pyridine and on the pyridine−I$_2$ complex inevitable for a reliable interpretation of the results.

We could not perform a "final" ab-initio calculation with the accuracy one would like to achieve. Both the effects of effective core potentials and the size of all electron basis sets limit the accuracy of ab-initio calculations on these types of systems. Nevertheless, the calculations allow conclusion about relative changes due to complex formation.

The inclusion of electron correlation is important, not only for the binding energy but also for the frequencies (obtained with the "bigger" basis sets) and the charge transfer.

The smaller basis sets LANL1DZ and SBKJC fail on accurate calculations of properties directly connected to iodine (I−I and N−I mode, I−I distance) due to effects of the effective core potential used. But if these effects are known, they allow relatively reliable "routine" calculations with only little computer resources.

The experimentally observed shifts of frequency in polar solvents can be explained qualitatively on the basis of dielectric effect.

For the bigger ecp and the all-electron basis sets, the inclusion of MP2 becomes important. Without the inclusion of MP2 the results suggest only a weak binding in the complex.

Due to cancellation of errors for the LANL1DZ basis set, it is possible to obtain binding energies at the MP2 level that deviate by below 1 kcal/mol from our best. The major drawback of this basis set is the overestimated "softness" of the I atom, which leads to deviations in frequencies and geometries.

Taking into account these conclusions, the results of our study suggest that the I$_2$ −pyridine complex has an N−I distance of 2.6−2.7 Å. Due to the formation of the complex, the I−I distance is increased by about 0.05−0.07 Å. The charge transfer is between 0.2*e* and 0.3*e*, and the binding energy is about 9 kcal/mol. We have now developed a first version of a simple interaction model from the present calculations and further ab-initio work on I$_2$−pyridine$_2$ supermolecules[56] and have tested it in molecular dynamics (MD) simulations of one I$_2$ molecule in liquid pyridine.[21] The essential spectroscopic features seem to be reasonably well reproduced by this ansatz.

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