

Theoretical Study of the Electronic Spectrum of Imidazole[†]

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The complete active space (CAS) self-consistent field (SCF) method and multireference second-order perturbation theory (CASPT2) have been used to study the electronic spectrum of imidazole and the imidazolium ion. The calculations comprise a large number of, both singlet and triplet, valence and Rydberg excited states. A newly developed continuum model has been used to compute solvatochromic shifts. In the gas phase the first and second $\pi \rightarrow \pi^*$ excited singlet valence states of imidazole are computed at 6.72 and 7.15 eV, and they shift to 6.32 and 6.53 eV upon solvation. The gas-phase values are somewhat too large (≈ 0.3 eV) due to an erroneous valence–Rydberg mixing in the CASSCF wave function. The first and second $\pi \rightarrow \pi^*$ excited singlet valence states of the imidazolium ion are computed at 5.72 and 6.94 eV in the gas phase and shifted to 5.86 and 6.83 eV in aqueous solutions. The present results are in agreement with the observed absorption band maxima in aqueous solution, 6.0 and 6.5 eV for imidazole and 6.0 and 6.9 eV for the imidazolium ion. The computed intensities suggest another possible (but less probable) interpretation of the solution spectrum, where both species are simultaneously present. In this case the lowest band at 6.0 eV is assigned to a transition to the 2^1A_1 state in protonated imidazole, while the second band observed in neutral solution at 6.5 eV corresponds to excitation to the $3^1A'$ state in imidazole.

1. Introduction

Imidazole is the active, functional group of histidine, one of the 20 naturally occurring amino acids residues. Histidine can act as a proton donor and acceptor, and, because of its low pK, ≈ 6.2 , it is partially protonated at neutral pH. Histidine is frequently found as a ligand in metalloprotein complexes such as carboxypeptidase A, azurin, myoglobin, and others. It also often assumes a catalytic role such as the charge-transfer relay system found in α -chymotrypsin and other serine proteases.¹ To elucidate structure and function relationships is an important and difficult problem in biomolecular sciences, and reliable data concerning the physical, chemical properties of the individual amino acid residues are needed. For these reasons we have undertaken a project aiming at the determination of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ excitation energies and transition moments of the chromophores in proteins.² In this paper we report on the spectroscopic properties of imidazole in the protonated and deprotonated form in the gas phase as well as in solution. The latter system has been added in order to investigate the possibility that some of the experimental spectra show features from both the neutral molecule and the protonated form.

The absorption spectra of imidazole in ethanol and aqueous solutions exhibit two broad bands with maxima around 207 nm (6.00 eV) and 187–178 nm (6.63–6.97 eV).^{3–9} They are, in general, assigned to $\pi \rightarrow \pi^*$ transitions. With use of ultraviolet resonance Raman spectroscopy in aqueous solutions and by analysis of the band envelopes, Caswell and Spiro⁵ suggested that the band at 207 nm is composite and includes two overlapping peaks at approximately 218 nm (5.69 eV) and 204 nm (6.08 eV). More recent UV Raman excitation studies,^{9,10} however, could not confirm Caswell and Spiro's observations.

Convincing experimental evidence for $n \rightarrow \pi^*$ transitions has not been given. Mason¹¹ described a weak feature in the vicinity of 265 nm (4.68 eV) in aqueous solutions of imidazole, and Braude¹² reported a band near 250 nm (4.96 eV). No gas-phase spectroscopy has to our knowledge been reported for imidazole.

Theoretical investigations on the electronic spectrum of imidazole are scarce. Semiempirical calculations^{4,13,14} have not been able to clarify the structure of the spectrum. On the other hand, only two *ab initio* calculations have been performed: the CI study by Bigot and Roux¹⁵ using minimal basis sets, and, more recently, the MRCI study by Machado and Davidson,¹⁶ which reported valence excited and Rydberg states of imidazole.

In the present paper we have applied the complete active space (CAS) self-consistent field (SCF) method¹⁷ and multi-reference second-order perturbation theory^{18,19} to predict excitation energies and oscillator strengths. The advantages and accuracy of the CASSCF/CASPT2 method in predicting electronic spectra have been reviewed recently.^{2,20} In general, the results were in qualitative and quantitative agreement with experiment and allowed conclusive assignments to be made for valence excited and Rydberg states. In order to predict shifts in band positions upon solvation, the self-consistent reaction field (SCRF) method as it is implemented in the MOLCAS program package has been used.^{21–24}

Two interpretations are possible on the basis of the results of the present study. The spectrum of imidazole in aqueous solution could be considered as a superposition of two similar spectra, imidazole and imidazolium, each with two reasonably intense bands, where vibrational coupling leads to an enhancement of the weak transitions. In contrast, the experimental data may also be interpreted as the superposition of two spectra, each including a single strong peak. The experimental information at hand does not allow exclusion of one or the other interpretation.

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2. Methods and Calculation Details

2.1. Geometries and Basis Sets. The ground-state geometry of imidazole in the gas phase, as measured by microwave spectroscopy,²⁵ was employed in the calculations. Because no such data are available for the imidazolium ion, the geometry of the ground state has been optimized at the MP2 level using 6-31G* basis sets. The molecules belong to the C_s and C_{2v} point groups, respectively. Both molecules are placed in the yz -plane.

Generally contracted basis sets of atomic natural orbital (ANO) type²⁶ were used and contracted as follows: C,N 2s1p/H 1s (BS1) and C,N 4s3p1d/H 2s1p (BS2). In addition, BS2 was supplemented with a set of 1s, 1p, and 1d Rydberg functions, which were obtained following the procedure described elsewhere²⁰ and placed at the charge centroid of the $2A''$ cation. This approach has proven to yield a good description of Rydberg states which only weakly interact with other states²⁷ and therefore helps to minimize spurious interaction between Rydberg and valence states. Experience also shows^{2,20} that the BS2 + 1s1p1d basis set is flexible enough for a proper description of valence excited states of medium-sized organic molecules while keeping the balance between size and accuracy.²⁸

2.2. Wave Functions. The CASSCF method was employed to describe the ground- and excited-state wave functions of imidazole and its protonated ion. Multireference second-order perturbation theory, the CASPT2 method, has been used to estimate dynamic correlation effects for the excitation energies. For detailed reviews of the methods the interested reader is referred to refs 2 and 17.

The application of multiconfigurational methods critically relies on a proper selection of the reference function, i.e., the active space in CASSCF method. In general, the active space should include all orbitals with occupation numbers appreciably different from 2 or 0 in any of the excited states under consideration. All near-degeneracy effects are then included in the CASSCF reference function, and there will be no large terms in the perturbation expansion. The imidazole molecule has three occupied molecular orbitals of relatively high energy, $2a''$, $3a''$, and $15a'$. The latter represents the lone pair at the pyridine-type nitrogen atom. Therefore, and in analogy to pyrrole, the electronic spectrum resulting from this orbital structure should be composed of four valence $\pi \rightarrow \pi^*$ excited states and also include up to three Rydberg series. Also two $n \rightarrow \pi^*$ excited states should be expected. Preliminary calculations showed that the $1a''$ orbital, located at the pyrrole-type nitrogen atom, remains almost doubly occupied for all states of interest, and the weight of configuration state functions with singly occupied or empty $1a''$ is less than 0.3%. Therefore this orbital was not included in the active space for the final calculations.

As the imidazole molecule belongs to the C_s point group, all states of interest are obtained in two irreducible representations only. This puts some limitations on the number of states that can be obtained using a single common active space, and different choices for states of different characters have to be made. The n and π, π^* valence orbitals should be present in all of the active spaces. In addition, the diffuse orbitals of the appropriate symmetry must be included to compute the Rydberg states. Therefore, the states of A' symmetry are computed with the orbitals $15a'$, $2a''$, $3a''$, $4a''$, and $5a''$ active. For convenience we shall label this active space (1,4), indicating the number of σ - and π -orbitals in the active space. In order to describe the Rydberg states lowest in energy and of the same symmetry, four more orbitals are needed: $3s$, $3p_x$, $3d_{xz}$, and $3d_{xy}$. This

space is labeled (2,7). Moreover, to minimize the intruder state problem, the active space was enlarged by two or more orbitals leading to the final size (2,9). Most of the Rydberg states obtained with this active space correspond to excitations out of the HOMO orbital $3a''$. The $3s$ orbital has been added in order to compute the onset of the Rydberg series generated by excitations out of the lone-pair orbital $15a'$.

The calculation of the valence states in a system with low symmetry such as the imidazole molecule requires special attention, in particular for states belonging to symmetries simultaneously including valence and Rydberg states. The difference in dynamic correlation effects for the valence and Rydberg excited states may lead to unphysical mixing of Rydberg character into some of the valence excited states. A proper procedure to avoid these mixings is to perform a preliminary-state average CASSCF calculation, which gives a set of optimized Rydberg orbitals. They are then deleted from the molecular orbital space, and the calculations are repeated but now only include valence excited states. The same procedure has been successfully used in earlier applications.^{29,30}

The low symmetry of imidazole combined with the high energy of the lowest $n \rightarrow \pi^*$ transition makes it difficult to define a balanced active space for all states of A'' symmetry. The natural choice is (7,4), which includes both the valence and the corresponding Rydberg orbitals. However, as the Rydberg states of A'' symmetry are comparable in energy to the valence states, we find that a large number of roots was required to reach the $n \rightarrow \pi^*$ transitions within the A'' symmetry. To avoid such large CASSCF calculations, we compute the reference functions of the valence excited $n \rightarrow \pi^*$ states by employing the minimal (1,4) active space. Of course, all relative energies are computed using a ground-state energy calculated with the appropriate active space.

The selection of the active space for the imidazolium ion is simpler since there are no $n \rightarrow \pi^*$ transitions. In this case we are only interested in the valence $\pi \rightarrow \pi^*$ excited states. Because of delocalization all six π -electrons and correspondingly six π -orbitals have to be considered. Here, too, we added Rydberg orbitals. Thus, the size of the final active space was (0,9). The calculations for imidazolium were in practice performed within the C_{2v} framework.

The CAS state interaction method (CASSI) has been used to compute transition properties.³¹ Intensities were obtained by combining the CASSCF transition moments with CASPT2 evaluated excitation energies. This approach has in a number of previous applications proven to give accurate results.^{2,20}

2.3. Solvent Effects. To calculate solvatochromic shifts, we used a modified version of the self-consistent reaction field method described earlier,²¹⁻²⁴ which is a generalization of the classical dielectric cavity model originally due to Onsager and Kirkwood. The solute is described as a series of multipolar moments centered at the origin of a spherical cavity and surrounded by a homogeneous, polarizable dielectric with dielectric constant ϵ . The present formulation differs from similar methods in that it includes a repulsive potential representing the exchange repulsion between the solute and solvent.

Dielectric cavity models, in general, assume equilibrium between the electronic state of the solute and the reaction field. This condition is not fulfilled for an electronic excitation. Therefore, the present model introduces the time dependence for partitioning the reaction field factor into two parts, which give a slow and a fast component, respectively, of the reaction field. The fast component can be considered as the instantaneous electronic polarization that follows the absorption of a

TABLE 1: Calculated Excitation Energies (eV), Oscillator Strengths, Dipole Moments μ (D), and Orbital Extensions $\langle r^2 \rangle$ (au) in Gas-phase Imidazole

state	excitation energies			μ	$\langle r^2 \rangle$	oscillator strength	
	CAS	PT2	MRCI ^a			this work	MRCI ^a
singlet states							
1 ¹ A'				3.70	64		
1 ¹ A'' (3a''→3s)	5.91	5.71	5.87	8.79	151	4 × 10 ⁻⁶	0.001
2 ¹ A'' (3a''→3p)	6.47	6.38	6.34	5.62	140	1 × 10 ⁻⁸	0.037
2 ¹ A' (3a''→3p)	6.70	6.49		1.17	134	0.079	
3 ¹ A'' (val,nπ*)	7.02	6.52		0.22	63	0.011	
4 ¹ A'' (3a''→3p)	6.73	6.62	6.64	5.05	166	2 × 10 ⁻⁹	6 × 10 ⁻⁵
3 ¹ A' (val,ππ*)	7.51	6.72	7.71	4.61	65	0.126	0.080
5 ¹ A'' (2a''→3s)	8.36	7.10		10.19	142	2 × 10 ⁻¹¹	
4 ¹ A' (15a'(n)→3s)	7.00	7.10	7.37	7.17	160	0.018	0.044
6 ¹ A'' (3a''→3d)	7.25	7.11	7.23	1.40	146	3 × 10 ⁻⁶	0.005
5 ¹ A' (val,ππ*)	8.43	7.15	8.18	3.00	87	0.143	0.070
7 ¹ A'' (3a''→3d)	7.36	7.26	7.57	4.30	154	6 × 10 ⁻⁹	0.003
6 ¹ A' (3a''→3d)	8.14	7.40	6.77	2.94	128	0.060	0.088
8 ¹ A'' (val,nπ*)	8.42	7.56		2.79	64	0.013	
7 ¹ A' (3a''→3d)	7.77	7.60	7.65	0.91	158	0.015	0.004
9 ¹ A'' (3a''→3d)	7.59	7.67	7.81	6.30	189	0.011	0.005
8 ¹ A' (val,ππ*)	10.06	8.51		3.85	84	0.594	
triplet states							
1 ³ A' (val,ππ*)	5.04	4.49	4.53	3.17	68		
2 ³ A' (val,ππ*)	6.15	5.47	6.95	4.03	70		
1 ³ A'' (3a''→3s)	5.88	5.68	5.59	8.22	150		
2 ³ A'' (val,nπ*)	6.52	6.07		1.38	62		
3 ³ A'' (3a''→3p)	6.43	6.33	6.36	4.98	130		
3 ³ A' (val,ππ*)	7.63	6.53	7.22	4.68	69		
4 ³ A' (3a''→3p)	6.70	6.57	5.47	1.51	136		
4 ³ A'' (3a''→3p)	6.70	6.58	6.69	3.83	159		
5 ³ A'' (3a''→3d)	7.16	7.00	6.99	0.78	123		
6 ³ A'' (2a''→3s)	8.34	7.07		10.01	140		
5 ³ A' (val,ππ*)	9.08	7.08	7.67	3.32	73		
7 ³ A'' (val,nπ*)	7.99	7.15		6.19	64		
6 ³ A' (15a'(n)→3s)	6.84	7.19		10.91	137		
8 ³ A'' (3a''→3d)	7.33	7.22	7.35	4.24	152		
7 ³ A' (3a''→3d)	7.63	7.42	7.18	0.75	145		
8 ³ A' (3a''→3d)	8.09	7.43		2.60	121		
9 ³ A'' (3a''→3d)	7.54	7.66	7.98	8.23	191		

^a CIR6 calculations from Machado and Davidson.¹⁶

photon. For excited states, the reaction field thus obtains both components and the strength of the fast component is proportional to the square of the refractive index, while the slow component is held fixed from the ground-state calculation.

In condensed phase, solute–solvent interactions will prohibit transitions to Rydberg states. This also applies to the present model, and therefore we do not explicitly include in the basis sets the Rydberg-type functions. Moreover, due to the repulsive potential there will be no spurious interaction between diffuse and valence states. Consequently, the intruder-state problem will be strongly reduced, and we can use the minimal active space for these calculations—(1,4) in the case of imidazole and (0,6) for the imidazolium ion.

The calculations have been performed with the MOLCAS-3³² program package on IBM RS/6000 workstations. The MP2 geometry optimization was performed using the MULLIKEN program.³³

3. Results and Discussion

3.1. Gas-Phase Spectrum of Imidazole. The UV spectrum of imidazole is characterized by a strong and two somewhat weaker $\pi \rightarrow \pi^*$ singlet transitions with calculated energies at 8.51, 7.15, and 6.72 eV, respectively. The computed oscillator strengths are 0.594, 0.143, and 0.126, respectively. The present excitation energies are ≈ 1 eV lower than those reported by Machado and Davidson, and we predict oscillator strengths about twice as large. The MRCI calculations by Machado and Davidson¹⁶ obtained the valence A' states with strong mixtures

among valence and Rydberg configurations, and it is difficult to identify them. Therefore, the excitation energy to the lowest $\pi\pi^*$ valence state oscillates from 6.66 to 7.71 eV, depending on the choice of the molecular orbital basis set and the number of computed roots. Table 1 compiles the computed gas-phase excitation energies, oscillator strengths, dipole, and total second electric moments. In addition, Table 1 also contains the MRCI results reported previously by Machado and Davidson.¹⁶

Vertical excitations from the lone pair localized at the deprotonated nitrogen atom into the π -orbitals are calculated to occur at 6.52 and 7.56 eV, respectively, and characterized by low oscillator strengths, ≈ 0.01 . The first member of the singlet Rydberg series with $n = 3$ is predicted at 5.71 eV. Similar values were found for cyclopentadiene, furan, and thiophene (5.65, 5.92, and 5.93 eV), while it is somewhat higher than in pyrrole (5.08 eV).^{27,34} The onsets of the next two singlet Rydberg series have been computed at 7.10 eV for both 2a'' \rightarrow 3s and 15a'(n) \rightarrow 3s. The energy of the excitations compared to the other cycloienes and the identical values of the 2a'' and 15a'(n) series onsets are in agreement with the assignments of the ionization potentials based on photoelectron spectroscopy. The first ionization potential in imidazole is intermediate between cyclopentadiene and furan and thiophene values, while it is 0.5 eV higher than the ionization potential for pyrrole. On the other hand, two levels were found to be degenerate for the second band in imidazole and presented a unique ionization potential band.^{35,36} There is a general agreement with the MRCI results¹⁶ for the Rydberg A'' states but not for the A' states.

The singlet state computed at 6.77 eV was assigned as a $3a'' \rightarrow 3d$ state in their CI6R calculations, while no 3p Rydberg state was found in this symmetry. The CI2R calculations¹⁶ placed, however, the 3p state at 6.35 eV. The agreement for the states of the 3d series is better.

Comparing the spectrum of triplet excited with singlet excited states, we observe that the excitation energies of Rydberg states are hardly affected by the different spin couplings. The valence $n \rightarrow \pi^*$ states are shifted ≈ 0.4 eV to lower energies. The valence $\pi \rightarrow \pi^*$ states are predicted to occur at low energies, starting at 4.49 eV, and the relative state separations also change drastically. Finally, we notice that these changes are in accord with the five-membered heterocyclic compounds studied earlier.^{27,34} Comparison with the MRCI results reported by Machado and Davidson¹⁶ for the valence $\pi \rightarrow \pi^*$ triplet states shows agreement for the low-lying state: 4.49 eV at the CASPT2 level and 4.53 eV at the MRCI level. The results for the second state in their CI6R (CI six roots) calculations are not in agreement with the present result. The computed MRCI value at 5.47 eV apparently corresponds to a diffuse state ($\langle r^2 \rangle = 115.7 \text{ au}^2$) and is assigned as the $3a'' \rightarrow 3p$ state, while the three expected $\pi \rightarrow \pi^*$ valence states are computed higher in energy: 6.95, 7.22, and 7.67 eV. The result is modified when using a larger multireference space leading to a $2^3A'$ state with valence character at 5.81 eV.

It is difficult to relate the theoretical data to experiment since all measurements have been performed in solution at energies below 6.9 eV. Two bands have been clearly described in ethanol and water at 6.0³⁻⁹ and 6.5^{5,8} and have been assigned to $\pi \rightarrow \pi^*$ transitions. The interpretation has, however, been questioned by Caswell and Spiro. These authors analyzed the excitation profile of the strongest vibrational band at 6.0 eV in aqueous solutions of imidazole using ultraviolet resonance Raman spectroscopy and observed two overlapping peaks at approximately 5.7 and 6.1 eV. The frequency difference between both features is larger than any of the imidazole vibrational ring frequencies, and therefore they assigned the bands to two different $\pi \rightarrow \pi^*$ transitions. More recent UV Raman studies^{9,10} could not confirm Caswell and Spiro's observations. Moreover, Grebow and Hooker⁸ pointed out that, regardless of the experimental conditions, the first absorption maximum remains at about 207 nm, whereas the second transition shifts from 6.63 to 6.97 eV when the pH is lowered from 7 to 2. The origin of the pH-dependent spectral changes is not established yet. Experimental data on $n \rightarrow \pi^*$ transitions are scarce. Mason¹¹ reported a very weak band to occur at 4.67 eV in aqueous solutions of imidazole. Moreover, Braude¹² observed a transition at 4.96 eV in ethanol.

Semiempirical calculations^{4,13,14} predict the two $n \rightarrow \pi^*$ transitions lowest in energy to occur at 4.3–4.7 and 5.8 eV. The excitation energies of the first two $\pi \rightarrow \pi^*$ excited singlet states range from 5.0–5.9 and 5.6–6.5 eV, respectively. The calculations of Bernarducci *et al.*⁴ at the INDO/S level are of particular interest. These authors computed the spectra of a number of methylated derivatives of imidazole and showed that substituent effects may lead to a red shift up to 0.4 eV. In fact, Caswell and Spiro knew about the calculations of Bernarducci *et al.* and used their data as arguments in favor of two low-energy and overlapping $\pi \rightarrow \pi^*$ transitions. The semiempirical calculations further suggest that the low-energy transitions observed independently by Mason and Braude are $n \rightarrow \pi^*$ type in origin.

The presence of two low-lying valence $\pi \rightarrow \pi^*$ states is confirmed both by the semiempirical and the CASPT2 results, although the question to answer is if the transitions to these

states appear overlapped in the 6.0 eV band or they form two different bands around 6.0 and 6.5 eV in solution. In contrast to predictions at the semiempirical level, the present calculations on the isolated imidazole molecule show, in accord with the MRCI results reported by Machado and Davidson, that no valence excited singlet state can be expected at energies below 5.7 eV. Thus, no $n \rightarrow \pi^*$ transitions should be expected at the low energies predicted by the semiempirical calculations. Usually, but not always, the $n \rightarrow \pi^*$ excitation gives rise to the lowest energy singlet–singlet transition. Table 2 shows the orbital energy differences related to excitations from the $15a'$ -(n) orbital of the pyridine-type nitrogen, as well as excitations within the π -orbital space. These energy differences show that we cannot expect $n \rightarrow \pi^*$ states with energies below the $\pi \rightarrow \pi^*$ states. The equivalent $n \rightarrow \pi^*$ transitions observed at low energies in the six-membered ring molecules such as pyridine³⁷ appear when the five-membered ring is annelated, such as in 9-methylpurine,¹¹ but not in the free ring. Transitions of the $n \rightarrow \pi^*$ type involve the addition of an electron to the π -system in the excited state, and in five-membered ring heteroaromatic molecules with an average of 1.2 π -electrons per ring atom, such transitions will be of high energy. Thus, the weak low-energy features observed by Mason and Braude appear to be due to transitions to the $1^3A'$ and $2^3A'$ states, although these transitions are in principle spin-forbidden in absorption measurements. Further support for this interpretation is due to the fact that Braude's excitation energies for the equivalent states in pyrrole (5.17 eV) and furan (4.96 eV) match perfectly with the CASSCF/CASPT2 excitation energy for the second $\pi \rightarrow \pi^*$ excited triplet valence state reported earlier.³⁴ Because there are no gas-phase data on the electronic spectrum of imidazole available, we shall abandon from discussing in more detail the valence gas-phase spectrum. Instead, in the next subsection we shall discuss the present data on the basis of the model of two interacting double bonds such as in *cis*-butadiene and compare the results with other five-membered heterocyclic compounds.

3.2. Nature of the Valence States. As pointed out above, the electronic structure of imidazole resembles the five-membered heterocyclic ring systems studied earlier by the CASSCF/CASPT2 method. To discuss qualitatively the excited states, it is useful to consider *cis*-butadiene³⁸ as the model for two interacting double bond systems. Within the π -subspace, four singly excited states can be formed, two of $1A_1$ and two of $1B_2$ symmetry. The two $1A_1$ states are degenerate and mix to yield the $1A_1^+$ and $1A_1^-$ states. There may also be significant contribution from doubly excited configurations, predominantly to the $1A_1$ and 2^1B_2 states. Table 2 presents the analysis for imidazole of the electronic structure of the $\pi \rightarrow \pi^*$ singlet valence states at the CASSCF level of approximation. Results obtained with both basis sets are given. For the sake of comparison, results of pyrrole³⁴ are also included.

The upper half of Table 2 shows orbital energies and orbital energy differences for imidazole and pyrrole. We notice that improving the basis set leads to considerable changes in the orbital energies and also brings the orbital energy differences closer to the situation found in pyrrole. However, we also note for BSI that the pattern of orbital energy differences is more similar to pyrrole than for BS2. This similarity is also reflected in the structure of the wave function, lower half of Table 2. The $3^1A'$ state is dominated by the $3a'' \rightarrow 4a''$ excitation and corresponds to the 1^1B_2 state in pyrrole, whereas the $2^1A'$ and $4^1A'$ states exhibit strong mixing of the $3a'' \rightarrow 5a''$ and $2a'' \rightarrow 4a''$ excitations and resemble the $1A_1^-$ and $1A_1^+$ states in pyrrole. The structure of the wave function in pyrrole is more restricted, due to the higher symmetry, and therefore more

TABLE 2: SCF Orbital Energies and Orbital Energy Differences for Imidazole and Pyrrole Using Different Basis Sets and Active Spaces^a Also including CASSCF Wave Functions and Natural Occupations, PT2 Excitation Energies (eV), and Oscillator Strengths for the Valence $\pi \rightarrow \pi^*$ States of Both Systems

	imidazole		pyrrole								
	<i>E</i> (BS1)	<i>E</i> (BS2)	<i>E</i> (BS2)								
SCF Orbital Energies (eV)											
1a''(n)	−14.64	−16.29	1b ₁ (n)	−15.39							
15a'(n)	−13.99	−11.98									
2a''(π)	−13.41	−10.91	2b ₁ (π)	−9.46							
3a''(π)	−11.89	−8.80	1a ₂ (π)	−8.05							
4a''(π*)	2.77	3.46	3b ₁ (π*)	3.68							
5a''(π*)	4.84	4.53	2a ₂ (π*)	5.78							
Orbital Energy Differences (eV)											
(1) 3a'' → 4a''	14.7	12.3	1a ₂ → 3b ₁	11.7							
(2) 3a'' → 5a''	16.7	13.3	1a ₂ → 2a ₂	13.8							
(3) 2a'' → 4a''	16.2	14.4	2b ₁ → 3b ₁	13.2							
(4) 2a'' → 5a''	18.3	15.4	2b ₁ → 2a ₂	15.2							
(5) 15a' → 4a''	16.8	15.4									
(6) 15a' → 5a''	18.8	16.5									
weights in the CASSCF wave function											
state	(1)	(2)	(3)	(4) ^b	high ^c	2a''	3a''	4a''	5a''	PT2	oscillator strength
Imidazole BS1											
2 ¹ A'	0.01	0.30	0.40	≤0.01	≈0.29	1.32	1.46	0.69	0.54	6.84	0.005
3 ¹ A'	0.90	0.02	≤0.01	0.02	≈0.08	1.94	1.09	0.91	0.06	8.49	0.297
4 ¹ A'	0.02	0.28	0.34	0.16	≈0.20	1.33	1.53	0.43	0.72	9.42	0.627
5 ¹ A'	0.01	0.05	0.07	0.74	≈0.13	1.08	1.83	0.15	0.96	10.20	0.404
Imidazole BS2											
2 ¹ A'	0.37	0.25	0.23	0.01	≈0.14	1.78	1.15	0.83	0.21	6.72	0.126
3 ¹ A'	0.53	0.24	0.12	0.03	≈0.08	1.85	1.10	0.87	0.15	7.15	0.143
4 ¹ A'	0.01	0.37	0.50	0.01	≈0.11	1.43	1.53	0.56	0.45	8.51	0.594
Pyrrole BS2 ^d											
2 ¹ A ₁		0.28	0.46		≈0.26	1.32	1.48	0.71	0.47	5.92	0.020
1 ¹ B ₂	0.64			0.08	≈0.26	1.80	1.15	0.85	0.17	6.00	0.130
3 ¹ A ₁		0.15	0.21		≈0.63	1.49	1.23	0.86	0.32	7.46	0.330

^a BS1 calculations used an active space (1,4) and BS2 the space (2,9), also including the Rydberg orbitals. See text. ^b The numbers refer to the single excitations defined above. ^c Includes higher (mainly doubly) and other singly excited configurations. ^d Reference 34. The pyrrole orbitals change the labels to C_{2v} symmetry. See above.

independent of the basis set. This is not the case in imidazole. When BS2 and a larger active space are used, the states 2¹A' and 3¹A' are composed of three major contributions: 3a'' \rightarrow 4a'', 3a'' \rightarrow 5a'', and 2a'' \rightarrow 4a''. This result may be expected on the basis of the orbital energy differences, which are all about equal. The 3a'' \rightarrow 4a'' does not, however, contribute to the 4¹A' state and correlates with the 1A₁⁺ (3¹A₁) state in pyrrole, as can also be seen from the oscillator strength.

In the earlier study,²⁷ we have compared a number of five-membered heterocycles to each other with respect to their electronic structure and spectral properties. It was found that *cis*-butadiene (cB), cyclopentadiene (CP), and furan represented systems with a weak interaction between the double bonds, while pyrrole and thiophene had a more aromatic character with a smaller gap between the HOMO-1 and HOMO orbitals and between LUMO and LUMO+1. The largest energy for the 2¹A₁ state, 6.31 eV, was found in CP. The energies for the 1¹B₂ state varied between 5.27 eV (CP) and 6.04 eV (furan). The energies are higher in imidazole, due to the presence of a CN instead of a CC double bond. Apart from that, the electronic structure looks similar to that of pyrrole. A detailed comparison is not possible, due to the strong mixing that occurs between the lowest singly excited configurations because of the lowered symmetry. As a result, the A and B character of the excited states is lost and the two lowest states appear with similar intensities. It is also interesting to notice the small contribution of double excitations to the state energies of imidazole in contrast to pyrrole and other pentacyclic dienes.

3.3. Electronic Spectrum of Imidazole in Solution. As pointed out above, all experimental information on the electronic

spectrum of imidazole stems from measurements in liquids. The electronic spectrum of a chromophore in the condensed phase, in general, differs from the gas-phase spectrum due to solute-solvent interactions. For instance, Rydberg states are normally not observed in the condensed phase. The SCRF method has been applied in order to study the solvatochromic shifts in imidazole. The presence of the repulsive terms representing the exchange interaction between the solute and the environment allows computation of the cavity radius by energy minimization at cavity sizes larger than the molecular size. Therefore, we have selected the position and radius of the cavity to give the lowest value for the absolute energy of the ground state of the molecule at the CASSCF level of calculation. As discussed previously,²¹ the size of the cavity, 7 au, is large and the distance between the dielectric interface and the closest hydrogen atom is 2.4 au. This is necessary in order to keep the electron density of the molecule within the cavity. A consequence is that the solvatochromic shifts are normally somewhat underestimated. Table 3 lists the computed results together with the experimental data. The lowest $\pi \rightarrow \pi^*$ valence excited singlet state undergoes a red shift of 0.40 eV, and the oscillator strength reduces drastically from 0.126 in the gas phase to 0.024 in water. The bathochromic effect is even larger for the second and third $\pi \rightarrow \pi^*$ singlet states. Moreover, we observe that the oscillator strength of the highest state remains almost constant. The red shift is not caused by changes in the dipole interaction with the solute, since the dipole moments of the three electronic states are similar. As a matter of fact, so large and unpredictable solvent effects without large dipole moment differences do not agree with previous experience.

TABLE 3: Calculated and Experimental Excitation Energies (eV) and Oscillator Strengths f for the Valence Singlet State of Imidazole in the Gas Phase, Ethanol, and Water^a

state	gas phase		expt ^c	ethanol ^b		water ^b	
	PT2	f		PT2	f	PT2	f
1 ¹ A' (1) ^d							
2 ¹ A' (3)	6.72	0.126	6.0	6.32	0.036	6.32	0.024
3 ¹ A' (5)	7.15	0.143	6.5	6.53	0.307	6.53	0.275
4 ¹ A' (8)	8.51	0.594		7.48	0.600	7.48	0.561

^a The gas-phase results used a basis set supplemented with a set of diffuse 1s1p1d functions on the 2A'' cation charge centroid. The calculations in solvent phase used a valence 4s3p1d/2s1p basis set. See text. ^b Ethanol, $\epsilon = 24.3$, $\eta = 1.36$; water, $\epsilon = 80.0$, $\eta = 1.33$ ^c Similar positions for bands in water and ethanol.^{5,8,9} ^d In brackets the order of the state into the 1A' symmetry in Table 1.

By comparing the results for ethanol and water, we notice that the excitation energies are identical. The oscillator strengths change on an absolute scale no more than 0.04 but as much as 35% on a relative scale. The relative error is expected to be specially significant for small oscillator strengths.

It is also interesting to note that the strong configuration mixing characteristic for the CASSCF wave function for imidazole in the gas phase is strongly reduced in "solution" and resembles more the pattern found for pyrrole in the gas phase: The 2¹A' state is composed to 0.03, 12, and 70% of the 3a'' \rightarrow 4a'', 3a'' \rightarrow 5a'', and 2a'' \rightarrow 4a'' singly excited states, respectively. The 3¹A' state is dominated (86%) by the 3a'' \rightarrow 4a'' singly excited state and corresponds to the B state in pyrrole. This is mainly a consequence of the type of basis set used in the calculations in the cavity.

The computed excitation energies in aqueous solutions, 6.32 and 6.53 eV, are in accord with the experimental data, ≈ 6.0 and ≈ 6.4 eV. The present model has been shown, in general, to underestimate somewhat the effect of solute-solvent interactions, which is maybe the source of the somewhat too large excitation energy for the lowest state. On the other hand, the predicted oscillator strengths rather seem to suggest that the first transition cannot be seen in aqueous solutions unless its intensity is strongly enhanced by vibronic coupling. We shall return to this point when discussing the spectrum of the imidazolium ion.

The main question still remains. Why do so large bathochromic shifts appear for the valence $\pi \rightarrow \pi^*$ states of imidazole? The change of basis sets and active spaces (see Methods and Calculation Details) in going from gas-phase to solvated calculations is not a sufficient explanation. In the gas phase, the presence of proper Rydberg functions guarantee in most of the cases an adequate simultaneous treatment of valence and Rydberg states. In the solvent phase, the Rydberg states are pushed up in energy and the presence of diffuse orbitals is unnecessary. The only explanation we find for these apparent large shifts is that the gas-phase energies are too high due to an erroneous treatment of the valence-Rydberg mixing. Within

the present CASSCF/CASPT2 methodology, some $\pi \rightarrow \pi^*$ states are computed too high in energy in the gas phase. Examples are the 1B_u states in ethene and *trans*-1,3-butadiene.³⁹ An improper treatment of the valence-Rydberg mixing at the CASSCF level was responsible for the observed deviations of 0.3–0.4 eV from the experimental values. As no experiment in the gas phase is available, we cannot completely confirm this point. Some test calculations have however been performed to compare the results in *trans*-1,3-butadiene, imidazole, and imidazolium. Table 4 compiles the CASPT2 energies for the lowest valence $\pi \rightarrow \pi^*$ singlet excited state in the molecules *trans*-1,3-butadiene and imidazole and the second excited state in imidazolium. Inclusion or exclusion of the diffuse functions and the solvent effects in the calculations give some insights regarding the characteristics and quality of the calculations. The *trans*-1,3-butadiene is an apolar molecule. The computed bathochromic shift of 0.25 eV from the gas-phase value is therefore too large. The same holds true for imidazole, since there are no large differences in the dipole moment values for the different states. The results are however different from imidazolium, where only a small shift of 0.1 eV is computed. Imidazolium is an electron deficient species, and such species are known not to present Rydberg states in the low-energy part of the spectrum.² Therefore the mixing between valence and Rydberg orbitals and states does not occur, and the gas-phase value can be considered correct. We conclude that in imidazole the same phenomenon as in ethene and butadiene occurs, and about 0.3 eV too high energy can be expected for the 1A' states in the gas phase. Only a model that explicitly includes dynamic correlation effects in the wave function can solve this problem.

3.4. Imidazolium Ion. Table 5 compiles the present results for the protonated imidazole in gas phase and aqueous solution. For the isolated molecule, we predict the first two $\pi \rightarrow \pi^*$ transitions to occur at 5.75 and 6.94 eV with oscillator strengths of 0.107 and 0.096. Upon solvation we compute a blue shift for the 2¹A₁ state to 5.89 eV and an increase of the oscillator strength to 0.167. In contrast, the 1¹B₂ state loses intensity and undergoes a red shift to 6.83 eV. On inspection of the CASSCF wave functions of imidazolium, we find that the HOMO and LUMO are strongly localized with the HOMO, including the carbon centers and the LUMO the nitrogen atoms. The HOMO \rightarrow LUMO singly excited state contributes 70% to the wave function of the 2¹A₁ state. In contrast, the 1¹B₂ and 2¹B₂ states are characterized by the symmetric and antisymmetric combinations of HOMO-1 \rightarrow LUMO and HOMO \rightarrow LUMO + 1 excitations. Unlike the imidazole molecule, the description of the wave function does not strongly differ when the imidazolium is embedded in the cavity. The effect of solute-solvent interactions on the excitation energies is substantially smaller in the protonated form, partly due to the larger delocalization of the charge, but mainly because of the accuracy of the gas-phase results. Test calculations using C_s symmetry on the imidazolium ion proved that asymmetric charge localization or symmetry breaking does not occur.

TABLE 4: Computed CASPT2 Excitation Energies (eV) and Oscillator Strengths f for the Lowest $\pi \rightarrow \pi^*$ Valence Singlet Excited State in *trans*-1,3-Butadiene (1¹B_u), Imidazole (2¹A'), and Imidazolium (1¹B₂)^a in the Gas Phase and Water as Solvent

basis set		butadiene		imidazole		imidazolium	
		PT2	f	PT2	f	PT2	f
4s3p1d/2s1p+1s1p1d	gas phase	6.32	0.804	6.72	0.126	6.94	0.097
4s3p1d/2s1p	solvent ^b	6.07	0.569	6.32	0.024	6.83	0.019
		Experimental Results ^c					
		gas phase		6.0 eV		6.9 eV	
		water					

^a In imidazolium the 1¹B₂ state is the second $\pi \rightarrow \pi^*$ singlet valence state. ^b Cavity size: 7 au. $\epsilon = 80.0$. ^c See text.

TABLE 5: Calculated and Experimental Valence $\pi \rightarrow \pi^*$ Singlet States of the Imidazolium Ion in the Gas Phase and Water

state	gas phase		water		
	PT2	<i>f</i>	PT2	expt ^a	<i>f</i>
1^1A_1					
2^1A_1	5.75	0.107	5.89	6.0	0.167
1^1B_2	6.94	0.096	6.83	6.9	0.019
2^1B_2	8.38	0.550	7.75		0.556

^a Experiments from refs 5, 8, and 9.

For imidazole, the difference between the calculated excitation energy in solution and the experimental band locations was of the order of 0.3 eV for the lowest excited singlet states. Keeping this in mind, we may claim that the computed excitation energies match with the measured band maxima. Also, in imidazolium, we observe that the predicted distribution of the oscillator strengths would make a direct observation of the upper state rather unlikely.

As pointed out in the Introduction, the *pK* of imidazole is ≈ 6.2 , and therefore it is partially protonated in aqueous solution and neutral pH. In fact, Grebow and Hooker⁸ noted that in the energy region from 6.5 to 7.0 eV the spectrum is pH sensitive, which indicates that close to neutral pH a superposition of two spectra is observed. These authors also show that the band at 6.5 eV is dominant in ethanolic solutions of imidazole. In acid aqueous solution (pH 2) the 6.5 eV band is pushed up in energy near 6.9 eV. The computed transition energies and oscillator strengths are compatible with such an interpretation, which would lead to the following assignments: The band maximum at 6.0 eV is characteristic of the 2^1A_1 state of the imidazolium ion, while the band centered around the 6.5 eV is due to transition to the $3^1A'$ state in neutral imidazole. Although this model reduces the difference between the calculated and measured position of the band maxima to a fortunate 0.1 eV, it does not allow one to fully resolve the conflict with the experimental data presented by Caswell and Spiro⁵ but rather seems to support the viewpoint of the Asher and Majoube.^{9,10} These authors claim that the 6.0 eV band is mostly due to one single electronic state, while Caswell and Spiro⁵ used the results of the semiempirical calculations to suggest that two different states are responsible for the 6.0 eV band. It is also possible that the features reported by Caswell and Spiro⁵ belong to two different species. The intensity patterns should be in this case weighted with the abundance of each system in the medium.

Taking into account the above explained deviations expected for the gas-phase energies in imidazole and that more sophisticated treatments, which include dynamic correlation effects in the wave functions, are needed for the $^1A'$ states in imidazole, we cannot expect a perfect match among the experimental and theoretical values. The interpretation where the two bands observed in basic and neutral aqueous solutions at 6.0 and 6.5 eV correspond to transitions to the two low-lying imidazole valence singlet $\pi \rightarrow \pi^*$ states while the bands at 6.0 and 6.9 in acid solutions correspond to the two low-lying valence singlet $\pi \rightarrow \pi^*$ states of imidazolium seems the most reliable explanation of the observed spectrum.

4. Summary and Conclusions

The lowest valence and Rydberg excited states of the imidazole molecule have been studied using the CASSCF/CASPT2 method. The model is a two-step procedure with static correlation effects included in the first step, where both the molecular orbitals and coefficients of the multiconfigurational expansion of the wave function are optimized. Remaining

correlation effects are computed in the second step using a second-order perturbation approach. Solvation effects are considered within a simple cavity model in which the solute is placed at the center of a spherical cavity surrounded by a homogeneous, polarizable dielectric medium.

The first two $\pi \rightarrow \pi^*$ excited singlet valence states of imidazole are computed at 6.72 and 7.15 eV. To the authors' knowledge, there has been no reported UV spectrum of imidazole in the gas phase. Because of that, the structure of the wave functions is compared to related five-membered heterocyclic compounds pyrrole, cyclopentadiene, furan, and thiophene. Although the basic patterns are similar, the low symmetry of the imidazole allows more configurations to contribute to the wave function of a given state. In particular, we observe a strong mixing of the pyrrole-like B state with the A' state. In summary, one obtains a consistent picture, although the energies for the $^1A'$ states are higher than expected. In addition, large bathochromic shifts are predicted for imidazole in aqueous solution, e.g., the $2^1A'$ valence state is lowered in energy by 0.4 eV. In contrast, the 2^1A_1 state of the protonated imidazole shows a small, 0.15 eV, hypsochromic shift in aqueous solutions and is found at 5.89 eV. We have found that the apparent large red shifts computed in the imidazole states are a consequence of the too high excitation energies computed for the gas-phase $\pi \rightarrow \pi^*$ $^1A'$ states. This could be the effect of an erroneous valence–Rydberg mixing obtained at the CASSCF level of calculation which caused deviations of 0.3 and 0.4 eV in previous calculations on butadiene and ethene.³⁹ The inclusion of the solvent avoids the mixing by pushing the Rydberg states up and therefore the results in the solvent for imidazole can be considered more accurate than the gas-phase values. The extent of the solvatochromic shifts in imidazole are expected to be similar to imidazolium, where no problems with Rydberg states appear due to its cationic character.

The present results put forward two possible interpretations of the observed experimental spectrum. In one case each of the observed absorption band maxima in aqueous solutions, 6.0 and 6.5 eV, represent a single electronic transition in two different systems. The lowest band is assigned to a transition to the 2^1A_1 state in protonated imidazole, whereas the second band is due to excitation to the $3^1A'$ state in the neutral form. Assuming somewhat larger errors in the computed positions of the band maxima and oscillator strengths, the experimental data may, however, also be interpreted as a superposition of two similar spectra, each with two bands. In the imidazole molecule they occur at 6.0 and 6.5 eV and correspond to transitions to two different electronic states. The corresponding band maxima in the imidazolium ion appear at approximately 6.0 and 6.9 eV. The experimental results at hand do not allow a conclusive assignment, although the latter model seems to be more consistent with the reported imidazole spectrum in basic solutions (pH 9),⁸ where the concentration of the protonated system is expected to be small.

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