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A theoretical study of the electronic spectra of pyridine and phosphabenzene

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Abstract. The electronic excitation spectra of pyridine and phosphabenzene have been studied using theoretical methods. The electronic states are described by wave functions derived from second-order perturbation theory based on multiconfigurational reference functions. The study includes singlet and triplet valences excited states as well as a number of Rydberg states. For both molecules the transition energies to the two lowest $\pi \rightarrow \pi^*$ excited singlet states are known from experiment and reproduced with an accuracy of 0.15 eV or better, while the $n \rightarrow \pi^*$ transition energies are predicted with a somewhat uncertain error of about 0.2 eV. The calculations suggest the lowest $n \rightarrow \pi^*$ transition detected experimentally in pyridine corresponds to an adiabatic transition. 43 electronic states have been determined in each of the molecules.

Key words: Pyridine and phosphabenzene – Electronic excitation spectra – CASSCF/CASPT2 method

Introduction

Heterocyclic derivatives of benzene containing a single N, P, As, Sb or Bi atom have been investigated by various spectroscopic techniques [1–4]. This interest arises from the importance of these molecules in understanding the electronic structure of heterocyclic compounds, their close relation to benzene, and, specifically, from the ordering of the orbital levels. It is now well established, except for pyridine, that the highest occupied π-orbital is of b_1 symmetry and destabilized as compared to benzene. In contrast, the next to the highest π-orbital is of a_1 symmetry and stabilized relative to the e_{1g} orbital in benzene. For pyridine the situation is reversed.

In spite of the difference in electronic structure, the absorption and MCD spectra of pyridine, phosphabenzene, arsabenzene and stibabenzene are similar at qualitative level [1]. Using the PPP method combined with parameters derived from experimental IP and EA values as well as INDO/S calculations, Waluk et al. [1] concluded that the first broad absorption band of phosphabenzene, arsabenzene and stibabenzene are composed of three electronic transitions, $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, and $\pi \rightarrow \pi^*$ in origin and in this order. In pyridine, however, only two excited states are observed in this range. The authors explained the difference, following arguments given earlier by Burrow et al. [4], where the basic cause of the shifted orbital ordering is assumed to be due to the large increase in the carbon to heteroatom distance when proceeding from pyridine to the heavier heterocycles.

The available experimental data [1] on the electronic spectrum of phosphabenzene, arsabenzene and stibabenzene extend only to 5.5 eV and thus allow only for a limited comparison of the spectrum in relation to pyridine and benzene. One potential means of getting insight into the correlations among spectral and structural data is through theoretical calculations. However, to predict excited states from first principles, both qualitatively and quantitatively, is a demanding task for several reasons:

- The electronic structure of excited states is often of complex nature. The strong configurational mixing and near degeneracy effects (static correlation effects), common to many excited states, need to be described properly by multiconfigurational wave functions.
- Since dynamic correlation effects – especially the dynamic polarization of the σ-electrons – may differ substantially for states of different character, quantitative agreement with experiment can only be achieved when all valence electrons are treated at the correlated level.
- A complete study of the electronic spectrum in the energy region above 6 eV must also include a number of Rydberg states. As a consequence the basis sets must be able to describe equally well compact covalent, diffuse ionic, and Rydberg states. They should be large enough to avoid contamination of the results due to basis set deficiencies.
- CI-methods, such as the MRCI technique, which have been applied very successfully to small molecules are not suitable to describe the wave functions of larger systems because of the very rapid increase of the computational effort with growing size of the basis sets and number of electrons. In general, the n^4 dependence of the integral calculation or the n^5 dependence of the integral transformation is not the crucial step. It is instead the treatment of electron correlation effects that will decide which size of basis set a given method can handle. It is therefore imperative to use methods for larger molecules, where the complexity grows as slowly as possible with the size of the system.

Due to its inherent flexibility the complete active space (CAS) SCF [5] method has proven to be particularly suited to cope with situations where the electronic structure varies strongly. A convenient way to include dynamic correlation effects is to use a second-order perturbation treatment, the so-called CASPT2 method [6, 7] (for a recent review see [8]), where the CASSCF wave function is taken as a reference state. The CASPT2 equations are written in terms of density matrices. Therefore, the computational effort depends primarily on the number of active orbitals included in the CASSCF reference state and thus allows to use high-quality basis sets. It has been shown in numerous applications [9]–[18] that the CASSCF/CASPT2 method is able to reproduce the position of band maxima in electron absorption spectra with high accuracy (for a recent review of CASPT2 applications in spectroscopy, see Ref. [19]).

The present paper reports the results of theoretical calculations on vertical excited electronic states of pyridine and phosphabenzene using the CASSCF/CASPT2 method. To enable comparisons on an equal footing we repeated our earlier calculations on the pyridine molecule. The present study includes for each molecule a total of 16 vertically excited singlet or triplet valence states. We were also able to predict the position of numerous Rydberg states arising from excitations out of the a_1-,a_2- and b_1-orbitals highest in energy. Finally, to establish the position of the lowest $n \rightarrow \pi^*$ bands in pyridine, we also report adiabatic transition energies to these excited states.

The valence excited spectrum of phosphabenzene can be interpreted as a perturbed benzene spectrum and closely resembles the spectrum of pyridine. We find the $\pi \rightarrow \pi^*$ valence excited spectrum of phosphabenzene, on the average, to be shifted by 1.07 eV to lower energies as compared to the pyridine spectrum. For both molecules the $\pi \rightarrow \pi^*$ valence excited states correlating with the 1^1B_{2u} and 1^1B_{1u} states in benzene are reproduced with an accuracy of 0.15 eV and better. These observations lead to the conclusion that the accuracy of the present results is comparable for both molecules.

Details of the calculations

Geometry and basis sets

All calculations on the electronic spectra have been performed at the ground state geometries in gas phase as measured by microwave spectroscopy [2, 20]. The molecules were placed in the *xy*-plane and were assumed to possess C_{2v} symmetry. The computations have been carried out on IBM RS/6000 workstations using the MOLCAS version 2 [21] quantum chemistry software.

Generally contracted basis sets of atomic natural orbital (ANO)-type [22, 23] are used. These have been obtained from a (17*s* 12*p* 5*d*), (14*s* 9*p* 4*d*) and (8*s* 4*p*) primitive sets [24] for phosphorous, carbon and nitrogen, and hydrogen, respectively. They were contracted to: (5*s* 4*p* 2*d*), (4*s* 3*p* 1*d*) and (2*s* 1*p*), respectively. These basis sets are constructed to treat optimally correlation and polarization effects in the valence shells, and have been shown [9, 25] to yield good results for valence excited states. Since the aim here is to describe both valence excited states and Rydberg states, the original basis sets was supplemented with an adequate single center set of contracted functions describing the 3*s*, 3*p* and 3*d* Rydberg orbitals. These were placed at the charge centroid of the cation lowest in energy and obtained in the following way: The wave function for the cation state was first computed including the uncontracted (8 primitives per shell) set [26]. The contraction coefficients for the final functions were then obtained by diagonalizing a density matrix constructed from the lowest virtual orbitals of Rydberg type only and applying rotational averaging [23].

CASSCF and CASSI calculations

Multiconfigurational wave functions were determined at the CASSCF level of approximation [5] with the atomic core orbitals frozen in the form determined by the ground state SCF wave function. It has been shown [9, 10], that the active space, which adequately describes the $\pi \rightarrow \pi^*$ valence excited states of the azabenzenes correlating with those of the benzene molecule, needs to include the 6π-electrons and preferably 12π-orbitals, which can be reduced to 6π-orbitals in the calculation of $n \rightarrow \pi^*$ states. In an ideal situation these rules should be extended to include an extra orbital for each angular function of Rydberg type. Although the total number of configurations state functions is drastically reduced by spatial symmetry, the calculations on the $\pi \rightarrow \pi^*$ valence excited states would not be feasible (6 electrons in 21 orbitals). The alternative is to select one active space for each type of excitation, thus following the general rule that the active space should consist of orbitals having occupation numbers, which differs sizably from zero or two. It is a general experience with the CASPT2 method that extensions of the active space to include orbitals with small occupation numbers will change the CASPT2 energy very little and thus not affect results for relative energies (such as excitation energies). For convenience we shall label the active spaces (k, l, m, n) where the indices give the number of orbitals in the four irreducible representations a_1, b_2, b_1, and a_2.

$\pi \rightarrow \pi^*$ valence excited states: To compute the $\pi \rightarrow \pi^*$ valence excited states we first run for each symmetry a state average calculation using the smaller active π-space, (0, 0, 4, 2), extended to include the Rydberg orbitals. In a second step the active space was enlarged to include 12 π-orbitals, (0, 0, 8, 4), with the well-characterized Rydberg orbitals deleted from the molecular orbital basis. Thus, valence-Rydberg state interactions are minimized in the first step and neglected in the second. Instead, the extra valence orbitals in the active space will be correlation orbitals for the π-electrons.

$n \rightarrow \pi^*$, $n \rightarrow$ Rydberg and $\pi \rightarrow$ Rydberg excited states: All calculations on the $n \rightarrow \pi^*$, $n \rightarrow$ Rydberg and $\pi \rightarrow$ Rydberg excited states are performed with the small (0, 0, 4, 2) active space. Extra orbitals are then added to allow for specific excitations. As an example, consider the Rydberg states of $^1A_1$ symmetry. The selected active space is (5, 0, 4, 2) and thus allows to propagate, e.g., one electron from the σ-HOMO (the lone-pair orbital) to four Rydberg orbitals of symmetry a_1: ($3s$, $3p_x$, $3d_{z^2}$, and $3d_{x^2-y^2}$). The active space for the other symmetries of the $n \rightarrow$ Rydberg states have been constructed in an equivalent way, and the same is true for the $\pi \rightarrow$ Rydberg excited states of $^1B_1$ and $^1A_2$ symmetry. The corresponding active space for the $\pi \rightarrow$ Rydberg states of $^1A_1$ and $^1B_2$ symmetry would be (0, 0, 6, 3). Here it was, however, necessary to enlarge the space further due to the appearance of intruder states in the CASPT2 treatment [19], and the active space finally used was the same as for the valence excited $\pi \rightarrow \pi^*$ states, (0, 0, 8, 4). The different active spaces used in the current study are described in Table 1. All excitation energies are computed with respect to a ground state using the same active space as applied in the calculation of the excited states.

The CASSCF state interaction (CASSI) method [27], developed to compute transition matrix elements for nonorthogonal state functions, is used here to compute transition dipole moments. It has been shown that the transition dipole moments are sensitive to the details of the one-electron density of the two states, which is normally well described at the CASSCF level of approximation, but far less sensitive to dynamic correlation effects. In contrast, the state energy differences needed to compute the oscillator strength are strongly effected by dynamic correlation effects, and therefore we used the CASPT2 energy differences to compute the oscillator strengths.

The CASPT2 method

The CASPT2 method [6, 7] computes the first-order wave function and the second-order energy in the full CI space without any further approximation, with a CASSCF wave function constituting the reference function. The zeroth-order Hamiltonian is defined as a Fock-type one-electron operator and is constructed

Table 1. CASSCF wave functions used for the different excited states of pyridine and phosphabenzene

Symmetry	Active orbitals[a]	Acitve electrons[c]	No. of CSFs[b]
$\pi \rightarrow \pi^*$ excited states			
$^1A_1$	(0,0,8,4)	6	7954
$^1B_2$	(0,0,8,4)	6	7776
$n \rightarrow \pi^*$ and $n \rightarrow R$ excited states			
$^1A_1$	(5,0,4,2)	8	8482
$^1B_2$	(1,2,4,2)	8	1380
$^1B_1$	(1,0,6,2)	8	1204
$^1A_2$	(1,0,4,3)	8	392
$\pi \rightarrow R$ excited states			
$^1A_1$	(0,0,8,4)	6	7954
$^1B_2$	(0,0,8,4)	6	7776
$^1B_1$	(4,2,4,2)	6	3932
$^1A_2$	(4,2,4,2)	6	3888

[a] Within parentheses the number of active electorns in symmetries a_1, b_2, b_1, and a_2, respectively

[b] Number of configurations in the CASSCF wave function

[c] Number of active electrons in the CASSCF wave function

such that a Möller–Plesset type perturbation theory is obtained in the closed shell single determinant case. Two different formulations of the zeroth-order Hamiltonian are possible: one which includes only the diagonal part of the Fock matrix (called PT2D) and one, which includes also the nondiagonal elements (PT2F). It is only the PT2F approach that leaves the zeroth-order Hamiltonian invariant with respect to rotations among the molecular orbitals. Earlier studies have shown that this invariance is important in describing Rydberg states. We shall, therefore, only present the PT2F results. The CASPT2 program also computes the weight, ω, of the CASSCF reference in the first-order wave function. It is a measure of how large a fraction of the wave function is treated variationally. Normally, one requires ω to be about the same for all states in order for a calculation to be balanced with respect to the electron correlation.

Geometry optimizations

To compute the adiabatic excitation energy of the lowest $n \rightarrow \pi^*$ states the geometry of the pyridine molecule was allowed to relax for both the ground and the excited states. To reduce the computational costs, we insisted on C_{2v} symmetry and the structure optimizations were performed using Dunning's [28] DZP basis sets. These calculations were carried out using the small active space.

Results and discussion

Ionization potentials

The assignment of the first three ionization potentials of pyridine as seen by photoelectron spectroscopy (PES) [29–32] led to a number of disputes and has been summarized by von Niessen et al, [33]. At present, it is generally accepted that the highest occupied MO is of n-type and close in energy to the highest occupied π-orbital. The line splitting amounts to approximately 0.15 eV. The first broad band seen (onset at 9.26 eV) in the PES, thus, contains signals due to the two lowest ionic states (1^2A_1 and 1^2A_2) and the second band is related to the 1^2B_1 state.

For phosphabenzene the PES has also been recorded [3]. In contrast to the situation observed for pyridine the first band, located at 9.2 eV, corresponds to excitation out of the π-orbital $3b_1$. The second band in the PES is, however, composite and includes signals due to propagating an electron out of the highest occupied a_2 and a_1 orbitals. The two orbitals are within 0.2 eV in energy.

The computed ionization potentials of pyridine and phosphabenzene are collected in Table 2 along with experimental data and some representative, earlier calculations. The predicted values are in close agreement with experiment: For pyridine, the measured values are underestimated by $\approx$0.15 eV, and 0.2–0.4 eV for phosphabenzene. The computed ionization potentials are also virtually identical to the values reported in earlier theoretical studies [32–36]. For pyridine the order of the states matches the current interpretation of the experimental data. Our results on the 1^2A_1 and 1^2A_2 states of phosphabenzene are, however, in conflict with earlier assignments, i.e., they are predicted in reversed order. The available data, both experimental and theoretical, are not accurate enough to draw final conclusions.

Singlet excited valence states

The vacuum UV spectrum of pyridine presented by Bolovinos et al. [37] shows three $\pi \rightarrow \pi^*$ absorption band systems located at 4.99, 6.38 and 7.22 eV. Recently, these findings were fully confirmed by Walker et al. [34]. The peak at 7.22 eV is a composite band due to transitions to the near degenerate 3^1A_1 and 2^1B_2 states. States correlating with the degenerate $^1E_{2g}$ state in benzene were not assigned.

Table 3 displays our results for pyridine for the lowest $\pi \rightarrow \pi^*$ valence excited singlet states. The computed transition energy for the lowest 1^1B_2 state, 4.84 eV, is

Table 2. Ionization potentials, IP, in eV

	IP calc.					IP exp.		
	This work	Ref. [33]	Ref. [34]	Ref. [35]	Ref. [36]	Ref. [29]	Ref. [30]	Ref. [31]
Pyridine								
1^2A_1	9.54	9.59	8.96	8.84	9.6	9.6	9.66	9.7
1^2A_2	9.65	9.57	9.38	9.53	9.5	9.8	9.80	9.7
1^2B_1	10.37	10.24	9.95	10.13	10.4	10.6	10.64	10.5
Phosphabenzene								
	This work	Ref. [32]				Ref. [3]		
Pyridine								
1^2B_1	9.03	8.74				9.2		
1^2A_1	9.42	9.44				9.8–10.0		
1^2A_2	9.52	9.20						

Table 3. Pyridine, singlet excited valence states

State	ΔE^a exp.	ΔE^b calc.	E^c_{corr}	$\langle r^2 \rangle^d$	$\langle \mu \rangle^e$	f^f
$\pi \to \pi^*$ excited states						
$1^1B_2(1B_{2u})$	4.99	4.84	− 0.20	84.34	2.03	0.018
$2^1A_1(^1B_{1u})$	6.38	6.42	− 1.09	80.64	3.28	0.005
$4^1A_1(^1E_{1u})$	7.22	7.23	− 1.73	82.17	2.67	0.82
$3^1B_2(^1E_{1u})$		7.48	− 1.43	79.82	1.83	0.64
$3^1A_1(^1E_{2g})$		7.96	− 0.40	79.39	1.30	0.03
$2^1B_2(^1E_{2g})$		7.95	− 0.20	78.21	2.57	0.158
$n \to \pi^*$ excited states						
1^1B_1	4.59	4.91	− 0.35	76.79	− 0.40	0.009
1^1A_2	5.43	5.17	− 0.79	77.36	− 0.93	–

[a] Experimental excitation energies in eV
[b] Calculated excitation energies in eV
[c] Dynamic correlation energy contribution in eV ($E_{corr} = \Delta E_{CASPT2} - \Delta E_{CASSCF}$)
[d] Second electric moment in atomic units
[e] Dipole moment in Debye
[f] Oscillator strength

in excellent agreement with the experimental data. Similarly, the predicted excitation energy for the second singlet excited $\pi \to \pi^*$ valence state, 6.42 eV, is virtually identical to the measured band position. The calculated excitation energies of the nearly degenerate states corresponding to the $^1E_{1u}$ state in benzene are 7.23 and 7.48 eV respectively. The lower falls right on the top of the experimental band maximum and the second is 0.25 eV higher in energy. The second pair of near degenerate states are predicted to be located at 7.95 and 7.96 eV.

The theoretical literature on the absorption spectrum of pyridine includes several reports of *ab initio* calculations. In general, the MRDCI calculations by Walker and Palmer [34] and the SAC-CI results presented by Kitao and Nakatsuji [35] are in qualitative agreement with experiment. In contrast, Foresman et al. [38] failed to reproduce the experimental state ordering and the computed excitation energies are spread over a wide range. It is also worth noting that the present results for the high-energy states differ somewhat from those obtained in our previous calculations [9] which was carried out together with some other azabenzenes. The energy splitting of the nearly degenerate states, 3^1A_1 and 2^1B_2, respectively, was predicted to be larger, 0.65 eV. Preference is, however, to be given to the present results for the following reasons: The predicted splitting appears to be small enough to explain the experimental difficulties in separating the bands. Moreover, the calculations reported here are performed using superior basis sets with respect to the description of Rydberg states which might have contaminated our earlier calculations as indicated by the weight, ω of the reference states. They are almost identical for the present wave functions, 0.76 and 0.75, but differed substantially in our previous attempts. The second pair of degenerate states are shifted by $\approx$0.2 eV to larger energies than those computed earlier.

The band positions and assignments of the $n \to \pi^*$ valence excited singlet states of pyridine are, unfortunately, not as well defined as for the $\pi \to \pi^*$

transitions. Goodman [39] and Doering and Moore [40] report an excitation energy of 4.59 and 4.3 eV for the singlet–singlet states lowest in energy, respectively. The lower value was also found in MCD spectra of solutions [41, 42] and seem to be compatible with the spectra observed by Villa et al. [43] for jet cooled S_1 pyridine, $E_{max} = 4.44$ eV. Furthermore, Walker et al. [34] have been able to locate a second $n \rightarrow \pi^*$ transition, 1^1A_2, which is seen as a weak inelastic feature in the electron energy loss spectrum at 5.43 eV.

The two lowest singlet excited $n \rightarrow \pi^*$ valence states are predicted to have excitation energies 4.91 and 5.17 eV. These results are identical to those we reported earlier. Depending on the specific experiment, the result for the 1^1B_1 state is between 0.32 and 0.47 eV above the measured location of the transition. This unusual large discrepancy is due to the fact that only the region of the band origin is observed for the $n \rightarrow \pi^*$ state. The vertical peak is buried under the stronger $^1B_2$ state. Also, the small dipole moment of the 1^1B_1 state as compared to the ground state is expected to lead to a blue shift in solution.

To verify the effect of the structure on the excitation energy we performed additional calculations allowing the geometry of pyridine to relax in both the ground and the two $n \rightarrow \pi^*$ excited states. A planar C_{2v} symmetry was assumed for all three states. The possibility of a nonplanar structure in the excited state has thus not been considered. However, it is believed that even if this should be the case, the energy gain is small and will not grossly affect the adiabatic excitation energy. The results are collected in Table 4.

From Table 4 it is seen that the C–N–C angle opens 10–20° in the excited state. In addition, we also observe a concomitant change in the bond distances up to ≈ 50 pm. Although the basis sets used in these calculations are substantially smaller than for all others the computed vertical excitation energies are virtually identical. In contrast, the adiabatic excitation energies for the $^1B_1$ and $^1A_2$ states become almost identical and closely agree with the bands reported by Doering and Moore [40]. The large difference between the adiabatic and vertical transition energies shows that the bands are very broad. The exact location of the band maxima will depend on the vibrational intensities and is difficult to predict from these calculations only. However, the band observed by Goodman [39] is more likely to be close to the vertical transition. Assuming that the feature detected at 5.43 eV by Walker et al. [34] really corresponds to the second $n \rightarrow \pi^*$ excited state, the calculations underestimate its energy by 0.24 eV.

UV/VIS and MCD solution spectra were published for phosphabenzene by Waluk et al. [1]. These spectra extend from 4 to 5.5 eV. Within this region three transitions can be identified and are located at 4.2, 4.7 and 5.1 eV. The computed

Table 4. Pyridine. Vertical and adiabatic excitaiton energies. Excited state geometries

State	ΔE^a vert.	ΔE^b adia.	R(N–C1)^c	R(C1–C2)	R(C2–C3)	θ(C1–N–C1)^d	θ(C2–C3–C2)	θ(C1–C2–C3)
1^1A_1			1.327	1.399	1.397	117.9	118.1	118.2
1^1B_1	4.95	4.37	1.373	1.367	1.443	128.1	118.7	120.1
1^1A_2	5.19	4.36	1.325	1.460	1.398	135.0	123.4	117.4

[a] Vertical excitation energies in eV

[b] Adiabatic excitaiton nergies in eV

[c] Bond distance in Ångström

[d] Bond angles in degrees

Table 5. Phosphabenzene, singlet excited valence states[a]

State	ΔE exp.	ΔE calc.	E_{corr}	$\langle r^2 \rangle$	$\langle \mu \rangle$	f
$\pi \rightarrow \pi^*$ *excited states*						
$1^1B_2(^1B_{2u})$	4.2	4.10	-0.11	96.96	1.94	0.002
$2^1A_1(^1B_{1u})$	5.1	5.32	-0.94	99.46	3.30	0.17
$2^1B_2(^1E_{1u})$		5.85	-1.77	99.94	2.44	0.63
$3^1A_1(^1E_{1u})$		6.30	-1.39	99.48	3.43	0.72
$6^1A_1(^1E_{2g})$		6.67	-0.14	97.83	2.83	0.004
$5^1B_2(^1E_{2g})$		7.21	-0.09	96.73	1.77	0.001
$n \rightarrow \pi^*$ *excited states*						
1^1B_1	4.7	4.44	-1.45	90.11	0.78	0.06
1^1A_2		4.63	-1.65	89.01	-1.93	–

[a] See legend of Table 3

excitation energies are shown in Table 5. By matching energies the results can be brought into agreement with the experimental data, i.e., the first band is due to transitions to the 1^1B_2 state. By the same token the second and third band may be assigned to the 1^1B_1 and 2^1A_1 state, respectively. Thus, in accord with experimental observations [1], the following state ordering with respect to the electronic origin is obtained: $\pi \rightarrow \pi^*, n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$.

By comparing the computed energies of $\pi \rightarrow \pi^*$ valence excited states we find that the spectrum of phosphabenzene is shifted on the average by 1.07 eV to lower energies relative to pyridine and the relative state separations are similar in both molecules. As could be expected, the splitting of the states corresponding to the degenerate E-states in benzene is somewhat larger for phosphabenzene. It is also interesting to note that the dynamic correlation contributions to the lower excited states, also for the very ionic "E_u"-states, hardly changes. Moreover, the strong similarities of the predicted spectra combined with the few experimental data at hand lead to the conclusion that comparable accuracies are obtained for pyridine and phosphabenzene.

Triplet excited valence states

The assignment of the lowest triplet states of pyridine is a long standing, yet unresolved, problem. Doering and Moore [40] observed in the ion and electron impact spectra a peak at 4.1 eV. These authors however, did not attempt to assign it to a particular transition. Walker et al. [34] recently confirmed the 4.1 eV transition and assigned it to a singlet–triplet transition. In addition, they observed one more optically forbidden band at 4.84 eV, for which they failed to make conclusive assignments.

The computed energies and properties for a few of the lowest triplet states of pyridine are presented in Table 6. The 1^3A_1 state is clearly lowest in energy, and the computed excitation energy is in agreement with the observed peak. Based on our calculations, we then may assign the structures observed by Walker et al. at 4.83 eV to one of three states: 1^3B_2, 2^3A_1 or 1^3B_1. The first two choices are consistent with the MRCI calculations presented by these authors, but conflict with their

Table 6. Pyridine, triplet excited valence states[a]

State	ΔE exp.	ΔE calc.	E_{corr}	$\langle r^2 \rangle$	$\langle \mu \rangle$
$\pi \rightarrow \pi^*$ excited states					
1^3A_1	4.10	4.05	0.08	77.83	2.13
1^3B_2	4.84	4.56	− 0.24	78.44	2.03
2^3A_1		4.73	− 0.20	78.46	2.41
2^3B_2		6.02	− 0.86	79.18	3.79
3^3A_1		7.34	0.03	78.81	1.73
3^3B_2		7.28	− 0.25	78.93	1.04
$n \rightarrow \pi^*$ excited states					
1^3B_1		4.41	− 0.41	76.39	− 0.51
1^3A_2		5.10	− 1.70	73.53	− 0.15

[a] See legend of Table 3

Table 7. Phosphabenzene, triplet excited valence states[a]

State	ΔE exp.	ΔE calc.	E_{corr}	$\langle r^2 \rangle$	$\langle \mu \rangle$
$\pi \rightarrow \pi^*$ excited states					
1^3A_1		3.21	− 0.12	96.20	2.11
1^3B_2		3.94	− 0.14	96.15	2.17
2^3A_1		4.13	− 0.08	96.20	1.77
2^3B_2		4.85	− 0.86	97.19	2.96
3^3A_1		6.29	− 0.06	97.06	2.80
3^3B_2		6.44	− 0.01	96.29	1.93
$n \rightarrow \pi^*$ excited states					
1^3B_1		3.62	− 1.08	90.11	0.78
1^3A_2		4.68	− 1.44	89.02	− 1.93

[a] See legend of Table 3

assignment of the 1^3B_1 state which was predicted to be lower in energy than 1^3A_1 state. On the other hand, the SAC-CI calculations of Kitao [35] support our results, although their excitation energies are somewhat higher: 4.34(1^3A_1), 4.49(1^3B_1), 5.09(1^3B_2) and 5.32(2^3A_1) eV. Assuming, that the observed transitions are due to states of different symmetry, it appears likely that the 1^3B_2 state is responsible for the 4.84 eV maximum in the electron energy loss spectrum. The resulting errors in the computed excitation energies would then amount to 0.05 and 0.28 eV, respectively.

The triplet states of phosphabenzene seem to be unknown. The computed excitation energies are shown in Table 7. Similar to the situation noted for the singlet excited states the spectra, the triplet states of phosphabenzene are lower in energy than those of pyridine. The structure of the spectra, i.e. the relative state separations, however, differ substantially and we find for phosphabenzene one more low energy ($<$ 6.0 eV) state than in pyridine.

Rydberg series ($N = 3$)

The excitations energies for transitions from the highest occupied π-orbital (of b_1 symmetry) to the 3*s*, 3*p* and 3*d* Rydberg states have been computed to lie in the range 6.2–7.2 eV for phosphabenzene and 7.4–8.8 eV for pyridine. All energies and states splittings are smaller for phosphabenzene. In contrast, Rydberg states arising from excitations out of the highest occupied lone-pair orbital (of a_1 symmetry) are almost identical in energy for both molecules. In between these two "extreme" situations we find the third series, including excitations out of the highest occupied π-orbital of a_2 symmetry, which appears to be shifted ≈0.2 eV to lower energies for phosphabenzene, whereas the relative state separations are roughly maintained. As noted previously [17] the dynamic correlation contributions are, in general, small, in some cases even negative. The details are shown in Tables 8 and 9.

Table 8. Pyridine, Rydberg states ($R_{n,l}$, $n = 3, l = 0, 1,2$)[a]

State	ΔE exp.	ΔE calc.	E_{corr}	$\langle r^2 \rangle$	$\langle \mu \rangle$	n_{eff}[b]	f
$b_1 \rightarrow R_{n,l}$ *excited states*							
$2^1B_1(3s)$		7.39	0.12	148.396	−4.15	2.14	0.001
$5^1A_2(3p_x)$		8.03	0.10	169.762	−1.49	2.41	–
$4^1B_1(3p_y)$		8.16	0.27	167.350	1.53	2.48	0.006
$2^1A_1(3p_z)$		8.05	0.24	172.731	−0.59	2.42	0.032
$5^1B_1(3d_{z^2})$		8.71	0.33	207.721	0.73	2.86	0.004
$6^1B_1(3d_{x^2-y^2})$		8.86	0.36	215.761	8.29	3.00	0.009
$6^1A_2(3d_{xy})$		8.72	0.19	217.966	3.32	2.87	–
$4^1A_1(3d_{yz})$		8.64	0.19	208.895	2.19	2.80	0.020
$4^1B_2(3d_{xz})$		8.77	0.24	218.995	0.39	2.92	0.012
$a_2 \rightarrow R_{n,l}$ *excited states*							
$1^1A_2(3s)$		6.75	0.15	144.028	−3.47	2.17	–
$1^1B_1(3p_x)$	6.93	7.25	0.11	161.454	−2.23	2.39	0.039
$2^1A_2(3p_y)$	–	7.52	0.28	170.527	−1.21	2.53	–
$2^1B_2(3p_z)$		7.41	0.29	160.110	−1.12	2.47	0.030
$3^1A_2(3d_{z^2})$		7.98	0.33	206.097	0.13	2.86	–
$4^1A_2(3d_{x^2-y^2})$		8.17	0.35	216.200	5.50	3.04	–
$3^1B_1(3d_{xy})$		8.03	0.20	217.800	0.65	2.91	0.001
$3^1B_2(3d_{yz})$		8.18	0.38	220.152	0.62	3.05	0.001
$3^1A_1(3d_{xz})$		8.09	0.25	210.918	−1.11	2.96	0.002
$a_1 \rightarrow R_{n,l}$ *excited states*							
$2^1A_1(3s)$	6.28	6.70	−0.42	141.016	2.43	2.19	0.021
$2^1B_2(3p_x)$		7.21	0.14	166.537	0.89	2.42	0.008
$3^1A_1(3p_y)$		7.35	−0.29	169.527	−5.26	2.49	0.009
$2^1B_1(3p_z)$		7.45	0.31	158.845	0.26	2.55	0.001
$4^1A_1(3d_{z^2})$		7.95	−0.22	212.750	−3.40	2.93	< 0.001
$5^1A_1(3d_{x^2-y^2})$		7.99	−0.19	214.279	−6.25	2.96	0.011
$3^1B_2(3d_{xy})$		7.93	0.30	220.047	−7.67	2.91	< 0.001
$3^1B_1(3d_{yz})$		8.15	0.41	219.972	−7.29	3.13	0.002
$2^1A_2(3d_{xz})$		8.13	0.52	221.017	−3.52	3.11	–

[a] See legend of table 3

[b] Effective quantum number

Table 9. Phosphabenzene, Rydberg states ($R_{n,l}$, $n = 3$, $l = 0,1,2$)[a]

State	ΔE exp.	ΔE calc.	E_{corr}	$\langle r^2 \rangle$	$\langle \mu \rangle$	n_{eff}^{b}	f
$b_1 \rightarrow R_{n,l}$ *excited states*							
$2^1B_1(3s)$		6.19	−0.06	163.08	−3.72	2.19	0.004
$3^1A_2(3p_x)$		6.75	0.00	184.10	0.81	2.44	–
$3^1B_1(3p_y)$		6.91	0.11	194.54	0.34	2.53	0.04
$4^1A_1(3p_z)$		6.60	−0.53	183.02	−1.00	2.36	0.03
$4^1B_1(3d_{z^2})$		7.07	−0.18	219.52	0.52	2.63	0.008
$7^1B_1(3d_{x^2-y^2})$		7.48	0.17	237.91	6.70	2.96	< 0.001
$4^1A_2(3d_{xy})$		7.15	−0.04	213.09	−0.83	2.69	–
$8^1A_1(3d_{yz})$		7.32	−0.39	237.90	1.16	2.82	0.02
$6^1B_2(3d_{xz})$		7.22	−0.42	225.63	0.88	2.74	0.05
$a_2 \rightarrow R_{n,l}$ *excited states*							
$2^1A_2(3s)$		6.57	−0.07	163.08	−2.15	2.15	–
$5^1B_1(3p_x)$		7.13	−0.01	187.24	0.31	2.39	0.01
$5^1A_2(3p_y)$		7.35	0.04	193.04	−0.95	2.50	–
$3^1B_2(3p_z)$		7.03	−0.49	177.97	−1.86	2.33	0.10
$6^1A_2(3d_{z^2})$		7.76	0.10	216.21	1.64	2.78	–
$7^1A_2(3d_{x^2-y^2})$		7.94	0.13	235.60	11.2	2.93	–
$8^1B_1(3d_{xy})$		7.66	−0.04	221.07	3.52	2.70	< 0.001
$7^1B_2(3d_{yz})$		7.79	−0.42	246.32	4.11	2.80	0.05
$9^1A_1(3d_{xz})$		7.67	−0.48	233.75	0.97	2.71	0.05
$a_1 \rightarrow R_{n,l}$ *excited states*							
$5^1A_1(3s)$		6.66	0.18	163.00	1.72	2.22	0.05
$5^1B_2(3p_x)$		7.21	−0.05	183.90	4.10	2.48	< 0.001
$7^1A_1(3p_y)$		7.25	0.24	195.21	−2.24	2.50	0.04
$6^1B_1(3p_z)$		7.43	0.03	182.81	0.27	2.61	0.003
$10^1A_1(3d_{x^2-y^2})$		7.75	0.31	221.71	−5.41	2.85	0.03
$11^1A_1(3d_{z^2})$		7.81	0.35	232.05	−3.56	2.90	0.005
$7^1B_2(3d_{xy})$		7.72	−0.04	222.49	−9.44	2.83	< 0.001
$9^1B_1(3d_{yz})$		8.05	0.14	240.34	−6.11	3.15	0.005
$8^1A_2(3d_{xz})$		8.02	0.35	237.50	−2.76	3.11	–

[a] See legend of Table 3

[b] Effective quantum number

The Rydberg spectrum of pyridine was studied for the first time by Bolovinos et al. [37], though traces of the 3*s* Rydberg state had been seen earlier in vapor absorption spectra [44] and multiphoton ionization spectra [31]. Recently, the assignment was confirmed by Walker et al. [34]. The first member is observed at 6.3 eV. The quantum defect, δ, for this state is 0.86. The corresponding R_{3p} state is seen at 6.93 eV ($\delta = 0.6$). For symmetry reasons the lowest observed Rydberg state must belong to the $^1A_1$ representation. The second is therefore either a $^1B_1$ or possibly a $^1A_2$ state. In order to interpret the spectra, these authors, however, appear to have used the adiabatic ionization potential (9.26 eV) which is $\approx$0.3 eV lower than the vertical ionization limit.

The computed excitation energies, 6.70($^1A_1$) and 7.25($^1B_1$) eV, differ from the experimental assignments with 0.3–0.4 eV. The tentative assignments are, however, supported by the computed oscillator strength, 0.021 and 0.039, respectively, which

Table 10. Average quantum defects, $\bar{\delta}$, for the Rydberg states ($R_{n,l}$, $n = 3$, $l = 0,1,2$)

Component	$\bar{\delta}$ calc.		$\bar{\delta}$ exp.[a]
Pyridine			
s	0.83		0.86
p_x	0.60	0.54	
p_y	0.50		0.45 and 0.60
p_z	0.52		0.35 and 0.52
d_{z^2}	0.12	0.05	
$d_{x^2-y^2}$	< 0.01		
d_{xy}	0.10		0.22
d_{yz}	< 0.01		
d_{xz}	< 0.01		
Phosphabenzene			
s	0.81		
p_x	0.56	0.54	
p_y	0.49		
p_z	0.57		
d_{x^2}	0.23	0.18	
$d_{x^2-y^2}$	0.20		
d_{xy}	0.26		
d_{yz}	0.08		
d_{xz}	0.15		

[a] Experimental data are taken from Refs. [34, 31]

are the strongest oscillators for all computed states. However, in contrast to the present study Bolovinos et al. and Walker et al. used the adiabatic ionization potential (9.26 eV) to interpret their results, which is 0.28 eV lower than the computed vertical IP. Only two Rydberg states have been assigned experimentally (and with great uncertainty). The present results, which should be accurate to about 0.2 eV, provide a basis for future analysis of the Rydberg states in the pyridine and phosphabenzene electronic spectra. Nothing is known experimentally about the Rydberg excited states in the latter molecule.

We also computed the quantum defect using the theoretical data. As can be seen from Table 10 our computations reproduce the values found in experiment. It is also interesting to note that the quantum defect for the R(3d) series in phosphabenzene is larger than for pyridine.

Summary

The CASSCF/CASPT2 method has been used to predict electronic excited states of pyridine and phosphabenzene. The calculations included basis sets designed to describe Rydberg states. In these calculations all except the atomic core electrons were correlated. The study comprises 43 states for each molecule, 8 singlet and 8 triplet excited valence states as well as 27 Rydberg states.

By comparing the computed data with experiment we were able to establish error bars for the calculations on pyridine. An accuracy of 0.15 eV or better is achieved in predicting the $\pi \rightarrow \pi^*$ singlet excited states. The error bar is somewhat

larger, ≈0.25 eV for the $n \rightarrow \pi^*$ singlet excited states, which in part is due to experimental difficulties in locating the vertical transition. A similar pattern is found for the triplet excited valence states. Only two Rydberg states have been observed in the spectra of pyridine. The computed transition energies are overestimated by ≈0.35 eV. The agreement has to be regarded as satisfactory since the experimental spectra were interpreted on the basis of adiabatic ionization potentials.

To the authors knowledge only three electronic transitions of phosphabenzene have been characterized experimentally. Thus, the present calculations are of predictive character. The accuracy of the results is comparable to those on pyridine as suggested by the few comparison that can be made. To a large extent, the spectrum of phosphabenzene resembles that of pyridine. In general, the excitation energies are shifted to lower values and the state separations are smaller. There is, however, one significant difference between the two spectra. In pyridine, the lowest excited state is of $n \rightarrow \pi^*$ type, while the first state in phosphabenzene is $\pi \rightarrow \pi^*$ with the first $n \rightarrow \pi^*$ state 0.3 eV higher in energy.

The predicted transitions in pyridine are in agreement with the data reported earlier [9] using the same theoretical approach. This is an important result in view of the technical differences involved. For the present study, the basis sets used to describe the valence electrons are somewhat smaller than previously. On the other hand, the basis sets were extended by including functions designed to represent Rydberg states. As pointed out at several occasions and demonstrated also in this report it is important to include such diffuse functions in order to control the intruder state problem which is largely due to the mixing of close lying valence and Rydberg states.

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