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Theoretical Study of the Electronic Spectra of Cyclopentadiene, Pyrrole, and Furan

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Abstract: The electronic spectra of the title molecules have been studied using a newly proposed quantum chemical approach for *ab initio* calculations of dynamic electron correlation effects in molecular systems: multiconfigurational second-order perturbation theory (CASPT2). For cyclopentadiene and furan, the calculations comprise three valence excited singlet states and, in addition, the $1a_2 \rightarrow 3s$, 3p, and 3d Rydberg states, thus providing a full assignment of the spectra in the energy range below 8.0 eV. For pyrrole, the $2b_1 \rightarrow 3s$, 3p, and 3d components of the Rydberg series have been added. The four lowest triplet states have also been studied in all three molecules. The computed excitation energies deviate from experiment by less than 0.17 eV in all cases where an assignment is possible. It is shown that the two main features in the spectra are caused by the valence excited states $^1B_2$ (5.27, 5.92, 6.04 eV) and $^1A_1^+$ (7.89, 7.46, 7.74 eV), where the calculated energies for the two states in the three molecules are given in parentheses. In addition, the $^1A_1^-$ state has been determined to appear near 6 eV in all three molecules. These results differ drastically from earlier theoretical predictions but are in agreement with experimental data. A number of new assignments of the Rydberg states are suggested.

1. Introduction

The interpretation, both qualitatively and quantitatively, of the electronic spectra of the heterocyclic pentadienes 1,3-cyclopentadiene (CP), pyrrole, and furan has remained a challenge for both experiment and theory ever since the first calculations were performed and the first UV spectrum was measured. The difficulties are caused by the appearance of a number of strongly allowed Rydberg series, which overlap some broad and diffuse bands usually assumed to arise from π–π^* valence-type excitations. The general features of the spectra are very similar in the three molecules, with two intense peaks, one centered around 5–6 eV and the second, more intense, between 7 and 8 eV. Overlaid on these bands is a rich structure of Rydberg-type excitations. On the basis of molecular orbital (MO) arguments, one would assign the first feature to a $^1B_2$ valence excited state and the second to a $^1A_1^+$ state of the same type. Such an assignment has been made for cyclopentadiene from an analysis of the spectrum, but the situation is less clear in pyrrole and furan. In addition, a weak $^1A_1^-$ transition is expected to appear in the same energy range as the $^1B_2$ transition.

Theoretically, the early CNDO calculations by Del Bene and Jaffé[1] support this interpretation. In contrast, the *ab initio* studies performed so far give a completely different picture. The most comprehensive treatment is probably the symmetry-adapted-cluster (SAC) CI calculations performed by Nakatsuji *et al.*[2] They find the $^1B_2$ state at energies more than 1 eV above the maximum of the first intense peak and locate the $^1A_1^-$ transition at energies above 7 eV in all three molecules. The intense $^1A_1^+$ state is not found at all. Other theoretical studies have given similar results (for details see the section on pyrrole). On the other hand, these theoretical studies have allowed the calculation of a number of Rydberg states with reasonably good accuracy.

A number of studies reported in the literature illustrate the difficulties involved in computing the vertical excitation energies of valence excited states in conjugated π-electron systems using *ab initio* quantum chemical methods. As we see it, there are three major sources for the difficulties. First of all, extended basis sets are needed in order to account for the diffuse character of some of the excited states and for differential correlation effects. Some of the very large errors obtained in the early studies are most certainly due to the limited basis sets that could be afforded (Nakatsuji *et al.*[2] used a double-ζ (DZ) basis with added diffuse s-, p-, and d-type Rydberg orbitals). Second, electron correlation effects play a crucial role in determining the excitation energies. Especially important is the dynamic polarization of the σ-orbitals in excited states, which are dominated by ionic valence structures. Typical examples are the V-state in ethene[3] and the E_{1u} state in benzene.[4,5] The inability to fully account for these differential correlation effects is the reason for most deviations between calculated and experimental excitation energies for valence excited singlet and triplet states. When configuration interaction (CI) based methods are used, it is in practice impossible to include the dynamic polarization effects fully for larger molecules due to the size bottleneck inherent in this approach, as a recent study of the valence excited states in pyrimidine illustrates.[6] Finally, while the effect of dynamic correlation can be large on some valence excited states, it is usually rather small for excited states of the Rydberg type. Normally, a calculation proceeds in two steps. The first step is used to determine the molecular orbitals which are to be used in the subsequent calculation of the electron correlation effects. This step also provides a reference wave function for a multireference (MR) CI calculation or, as in the present study, a treatment based on perturbation theory. Because of the different correlation effects, the reference wave function for a valence excited state often has an energy larger than one or several Rydberg states. This may, in some cases, give rise to an erroneous and too strong interaction between the valence state

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and a Rydberg state, which makes the orbitals of the former state too diffuse. The electron density is then not well described at this level of the calculation, and it may be very difficult to correct this in a subsequent CI calculation. Thus, there is a difficulty involved in defining a proper reference state for the MR-CI calculation if the reference wave function is embedded in a large number of Rydberg states.

For some time, we have attempted to gain insight into the correlation effects on spectral and structural features of aromatic systems through *ab initio* quantum chemical calculations on the electronic spectra of small and medium-size (up to 20 first row atoms) molecules. Recently, we reported on the π–π^* singly excited states of benzene[5] as an illustration of a novel approach that has the aim of being accurate to better than 0.5 eV in calculating excitation energies. We have also reported results for the π–π^* and n–π^* singly excited states of the azabenzenes[7] and for valence and Rydberg excited singlet and triplet states in the short polyenes, ethene, butadiene, and hexatriene.[8] The excitation energies were in all of these cases computed with an accuracy higher than the proposed aim. The largest error among all of the valence excited states in benzene occurred for the $^3E_{1u}$ state and was 0.26 eV.

To compute the excitation energies from first principles, electron correlation has to be treated in a balanced way and all states of the same symmetry that are close in energy have to be considered simultaneously. The most important correlation effects are described by configuration state functions (CSFs) mixing the π-electrons among the π-orbitals. However, to obtain quantitatively correct results, dynamic correlation effects also have to be considered. As pointed out above, these effects are dominated by the dynamic polarization of the σ-electrons, which is described by configurations involving simultaneous σ–σ^* and π–π^* excitations. Typically, large σ-polarization effects are observed for states with strong ionic character, while they are substantially smaller for states dominated by covalent structures and for Rydberg states.

The approach used here is capable of handling these problems and correctly accounting for the different correlation contributions to the excitation energies, as has been shown in earlier applications.[5,7,8] The method has been described in detail in these applications. It is based on the complete active space (CAS) SCF approximation,[9] which has proven to be particularly suited to deal with situations where the electronic structure varies strongly, for example, in the vicinity of transition states or in excitation processes. The CASSCF wave functions will comprise all strongly interacting electronic configurations but will not, to a large extent, account for the dynamic electron correlation effects. They are added in a subsequent step, where the CASSCF wave function serves as the reference function in a second-order perturbation calculation of the correlation energy (CASPT2).[10,11] The validity of a second-order perturbation calculation of the differential correlation effects on excitation energies has been demonstrated in the earlier applications.[5,7,8] The present study gives further support to the effectiveness of the approach.

Details of the approach and the calculations are described in the next section. A discussion of the results for each of the molecules then follows and is summarized in the last section, which also includes a discussion of features common to all three molecules.

Table I. Basis Sets and Active Spaces for Cyclopentadiene, Pyrrole, and Furan

basis set[a]	active space[b]	SCF energy (au)
	Cyclopentadiene	
2s: 0.043 70, 0.017 25	π–π^* states: (0044)	−192.854 731[c]
2p: 0.039 90, 0.015 75	π–σ^* states: (4222)	−192.737 320[d]
3d: 0.028 50, 0.011 25		
	Pyrrole	
2s: 0.045 60, 0.018 00	π–π^* states: (0064)	−208.879 342[c]
2p: 0.041 42, 0.016 35	π–σ^* states: (4232)	−208.754 720[d]
3d: 0.028 50, 0.011 25		
	Furan	
2s: 0.047 12, 0.018 60	π–π^* states: (0064)	−228.701 359[c]
2p: 0.042 56, 0.016 80	π–σ^* states: (4232)	−228.557 150[d]
3d: 0.028 50, 0.011 25		

[a] Exponents of added diffuse functions at the average charge centroid of the $^2A_2$ and $^2B_1$ cations. [b] Symmetry C_{2v}. The active orbitals are labeled according to the symmetry as (a_1, b_2, b_1, a_2). [c] This work. [d] From ref 2. The basis set was C,N,O [4s2p]/H[2s] plus two s-, two p-, and two d-type diffuse functions.

2. Methods and Computational Details

2A. Basis Sets. Generally contracted basis sets of the atomic natural orbital (ANO) type[12,13] are used, which are obtained from C,N,O-(14s,9p,4d)/H(8s,4p) primitive sets. These basis sets are constructed to optimally treat correlation and polarization effects and should be large enough to describe the electronic structure of the valence excited states with the desired accuracy. The contraction used in the present work is C,N,O[4s3p1d]/H[2s1p]. Since the aim here is to describe both valence excited states and Rydberg states, the original basis sets have been supplemented with diffuse functions. In the study of the linear polyenes,[8] these diffuse functions were centered on the different carbon atoms. As a result, a large number of Rydberg orbitals were created, which made it difficult to locate the valence excited states in the CASSCF calculations. The same procedure was also originally attempted here but had to be abandoned since it became impossible to find the valence excited states. Instead, we have followed the procedure suggested by Dunning and Hay[14] and have added diffuse functions in the average charge centroid for the $^2A_2$ and $^2B_1$ states of the cation. The exponents of the diffuse functions are given in Table I. For comparison with earlier work, the calculated SCF energies are also included in the table. All calculations have been performed at the experimentally determined ground-state equilibrium geometries.[15]

2B. CASSCF and CASSI Calculations. Initially, multiconfigurational wave functions were determined at the CASSCF level of approximation. Only the six π-electrons were active (four in CP), with all σ-electrons inactive. The carbon 1s electrons were kept frozen in the form determined by the ground-state SCF wave function and were not included in the calculation of the correlation energy. Only four active electrons were used in CP, since it is reasonable to treat all the CH bonding orbitals on the same footing, that is, as inactive. Such a choice should not affect the results of the calculations, since with the $1b_1$ orbital active its occupation number would anyhow be very close to two. An equivalent description in such a case is obtained with the orbital inactive.

Thus, the excitations treated are of the types π–π^* and π–σ^*, while no excitations out of the σ-orbitals are considered. The choice of the active orbital space is determined by the type of states to be studied, in this case valence excited states and Rydberg excitations to the 3s, 3p, and 3d orbitals. The valence π-orbitals and the nine Rydberg orbitals then constitute the smallest possible active space. We shall label the active spaces (k,l,m,n), where the indices give the number of orbitals in the four irreducible representations of the C_{2v} point group in the order a_1, b_2, b_1, and a_2. Following the recommendation by Mulliken, the molecules are placed in the *yz* plane. Thus, the two last symmetry species refer to π-orbitals. The full active space for CP, with four π-orbitals, is (4243)

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and for pyrrole and furan is (4253). However, only external π-orbitals will be occupied in wave functions of A_1 and B_2 symmetry (π–π^* excited states), yielding the active space (0053) (or (0043) for CP). In the same fashion, it is not necessary to occupy the π-type Rydberg orbitals in calculations on π–σ^* Rydberg states. For states of symmetry B_1 and A_2, the minimum active space is then (4232) (or (4222) in CP). These active spaces were also used in all calculations on B_1 and A_2 states. However, it turned out to be necessary to extend the active space somewhat in the calculations of π–π^* excited states in order to minimize the effect of intruder states in the CASPT2 calculations (cf. the discussion in ref 5 concerning a similar situation in the benzene molecule). The active spaces actually used for these states are given in Table I. As we shall describe later, the problem of intruder states was not completely removed by this extension of the active space. For pyrrole, we have, in addition, performed some test calculations with even larger active spaces (see section 4) in order to control the convergence of the result. Normally, the results are not very sensitive to the size of the active space, as long as the minimum space is covered. This is illustrated in a number of examples below. The problem occurs only when intruder states appear in the CASPT2 wave function, as will be discussed in more detail later.

The molecular orbitals (MOs) have been obtained from average CASSCF calculations, where the averaging is over all states of interest of a given symmetry. In a few cases we have also performed single-state calculations, mainly in order to test whether the averaging procedure introduces additional uncertainties in the results. This was found not to be the case, which is in agreement with our experience from earlier studies. Details can be found in the Results section. Furan constitutes a special case since it was there necessary to include in the averaging procedure more states than desired in order to locate the states of interest. Thus, in $^1A_1$ symmetry, eight states were used in the average CASSCF calculation even though there are only four states of the types defined above. This was necessary in order to locate the upper valence excited state of this symmetry, which appears as state number 4 in the CASPT2 treatment but as state number 8 in the CASSCF calculation. Single-state calculations were also performed for the ground state with both active spaces. The excitation energies were related to these ground states. It should be pointed out, however, that the difference between these CASPT2 excitation energies and those obtained using the state-averaged ground states is small, normally less than 0.1 eV (see section 3 for detailed examples).

The MOs obtained in the different CASSCF calculations are, in general, not the same. Also, CASSCF wave functions, which have been optimized for different states of the same symmetry, are not orthogonal to each other. The CASSCF state interaction (CASSI) method[16] has been developed to compute transition properties from nonorthogonal state functions and is used here to compute the oscillator strengths. In the formula for the oscillator strength, we used the energy differences corrected by the second-order perturbation method (PT2F). This approach for the oscillator strength is by now well documented in a number of applications and has, in a recent study of the pyrimidine molecule, been shown to give results similar to those obtained with the multireference CI method.[6]

2C. The CASPT2 Method. The CASPT2 method[10,11] 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 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 utilizes only the diagonal part of the Fock matrix (called PT2D), and one which also includes the nondiagonal elements (PT2F). The first choice is computationally simpler and in most cases leads to results not very different from PT2F, as illustrated, for example, in the study of the electronic spectrum of the benzene molecule.[5] It should be emphasized, however, that it is only the nondiagonal approach which is invariant to rotations of the molecular orbitals. The full approach must therefore be used in cases where such invariance is important, for example, in calculations of potential surfaces. It was shown in the calculations on the polyenes[8] that the difference between PT2D and PT2F can be substantial for excited states of the Rydberg type, while it is small for valence excited states. The same conclusions can be drawn from the present results, and we shall therefore use only the more consistent PT2F energies in the discussion of the excitation energies.

The CASPT2 equations are formulated exclusively in terms of one-, two-, and three-body densities and are therefore independent of the actual size of the reference function. The limiting factor is not the number of correlated electrons but the number of active orbitals, which determines the size of the density matrices. The current implementation of the CASPT2 method allows a maximum of 14 active orbitals. A larger number is rarely needed in any application and could anyway not be handled by the CASSCF program, except in cases with very few active electrons (or holes).

The CASPT2 program also calculates the weight, ω, of the CASSCF reference in the first-order wave function. This weight is a measure of how large a fraction of the wave function is treated variationally. The relative weight of ω in different states gives a measure of how balanced the calculation is. Normally, one requires ω to be about the same for the ground and the excited states in order for the calculation to be balanced with respect to the treatment of electron correlation. It may happen, however, that interference with nearby electronic states not included in the reference CI space deteriorates this balance for some excited states. Such a situation can be tolerated in cases where the interaction is very weak and consequently the effect on the second-order energy is small. A large coefficient for an interfering Rydberg state (occupying an orbital not included in the active space) then appears in the first-order wave function with only a very small effect on the energy. Such interactions caused some problems in a previous study of the azabenzenes.[7] As will be discussed in detail below, the same situation obtains here for some of the valence excited states. The problem is due to large differential dynamic correlation effects, which place the valence excited state at energies well above a number of Rydberg states not included in the calculation. Since the interaction elements are small, an appreciable effect on the first-order wave function occurs only when the zeroth-order energy of the valence state happens to coincide with the zeroth-order energy of the Rydberg state. Such situations are completely unpredictable, and at the moment we have no automatic way of handling them. In severe cases, where it is clear that the energy has been affected, two solutions are possible. If the Rydberg orbital in question can be clearly defined, it can be removed from the MO basis set, or it can be included in the active space. In a recent study of the benzene molecule,[17] a 4p Rydberg state appeared as an intruder state of $^1E_{1u}$ symmetry. Both approaches were used to correct the calculation and were found to give identical results. In less clear situations, an extension of the active space normally helps. The intruder-state problem in CASPT2 is, however, an irritation, mainly since it makes the calculations less automatic. We are at present studying alternative ways of formulating the perturbation theory, which hopefully will diminish the problem.

Parts of the calculations have been performed on the IBM 9021/500-2VF computer at the University of Valencia, others on an IBM RS/6000 workstation (Models 550), in all cases using the MOLCAS-2 quantum chemistry software,[18] which includes the CASPT2 program as one module. Some timing data were presented in the recent paper on the benzene molecule.[5]

3. Results

In this section we shall present and discuss the results for each molecule separately and compare the present data with previous *ab initio* results and available experimental data. Such a comparison is not always obvious. As far as possible, we have compared to energies for band maxima, which are generally believed to be close to computed vertical excitation energies, although exceptions to this rule are known. Some experiments give only the energies for the 0–0 transition, however, and the difference to the vertical excitation energy may in some cases be large. For the 2^1A_1 state it is, for example, believed to be larger than 1 eV (*vide supra*). On the other hand, for Rydberg states the 0–0 and vertical transitions are normally very close in energy. Also, the accuracy of measured energies may differ from one experiment to another. This makes it especially difficult to make assignments in cases where several states are close in energy.

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These limitations should be borne in mind when studying the results and judging the accuracy of the calculations.

The five valence-type π-orbitals in the three molecules are in order of energy: $1b_1$, $2b_1$, $1a_2$, $3b_1$, and $2a_2$. The first three of them are occupied with the vertical ionization energies 14.8, 10.7, and 8.6 eV (CP);[19] 12.6, 9.2, and 8.2 eV (pyrrole);[20] and 15.2, 10.4, and 8.9 eV (furan),[21] respectively. From this structure we expect to find three low-lying valence excited singlet states. The excitation $1a_2 \rightarrow 3b_1$ gives rise to one singlet and one triplet state of B_2 symmetry, while the two excitations $1a_2 \rightarrow 2a_2$ and $2b_1 \rightarrow 3b_1$ result in two pairs of states of A_1 symmetry. The corresponding electronic configurations are quasidegenerate and will mix to form A_1^- and A_1^+ states. The minus state has the lower energy and a low intensity, while A_1^+ will be pushed up and will carry most of the intensity. We can also expect a considerable mixing of the doubly excited configuration $(1a_2)^2 \rightarrow (3b_1)^2$ into the minus state analogous with the situation in butadiene (for a recent discussion of the spectrum of this molecule, see ref 8). Thus one is lead to expect the first broad feature in the spectrum to correspond to an excitation to the $^1B_2$ state and the second, more intense band to $^1A_1^+$. The location of the weak $^1A_1^-$ state is more difficult to predict from these simple considerations. Because of its very low intensity, there is still no firm experimental assignment of any band in the spectra of the three molecules to this electronic state. The second state of $^1B_2$ symmetry, corresponding to the excitation $2b_1 \rightarrow 2a_2$, is expected at a rather high energy.

In addition to the valence excited states, the spectra have a rich structure of Rydberg bands arising from excitations out of the $1a_2$ orbital (the R-series). A second series of Rydberg states, excited out of $2b_1$ (the R′-series), appear in pyrrole due to the low value of the second ionization potential. As a result, the pyrrole spectrum has a very complex structure, which makes the assignments of the different bands difficult.

3A. Cyclopentadiene. The electronic spectrum of this molecule has been extensively studied over the years due to its importance as a model compound for the photochemistry of cyclic dienyls.[22-32] Two of the valence excited singlet states have been firmly assigned in the spectrum together with some of the Rydberg series. This is of great value for the present investigation, since the experimental verification of the location of the valence excited states is more uncertain for the other two molecules. A comparison between experiment and theory for CP then gives a measure of the magnitudes of the errors in computed excitation energies.

Table II. Total Energies, Dipole Moments, and Other Properties of the Excited States of Cyclopentadiene

	energy + 192 au					
state	CASSCF	PT2F	$\langle x^2 \rangle^a$	μ^b	ω^c	$n_{states}{}^d$
π–π^* Singlet States (active space (0044))						
1^1A_1	–0.915 278	–1.557 307	24.8	–0.116	0.82	1
2^1A_1	–0.668 018	–1.325 555	25.0	–0.168	0.80	1
3^1A_1	–0.635 016	–1.302 737	83.4	+0.373	0.78	1–5
4^1A_1	–0.509 640	–1.267 412	26.9	–0.736	0.68	1–5
5^1A_1	–0.582 690	–1.256 100	66.2	+0.359	0.78	1–5
1^1B_2	–0.633 151	–1.363 515	29.1	+0.225	0.77	1–3
2^1B_2	–0.679 873	–1.327 726	71.3	+0.361	0.81	1–3
3^1B_2	–0.657 516	–1.305 373	78.3	–0.707	0.81	1–3
σ–π^* Singlet States (active space (4222))						
1^1A_1	–0.916 121	–1.558 170	24.7	–0.108	0.82	1
1^1B_1	–0.689 667	–1.328 587	38.9	+0.033	0.81	1–3
2^1B_1	–0.668 594	–1.305 941	39.2	–0.123	0.81	1–3
3^1B_1	–0.609 526	–1.266 099	43.4	–0.971	0.77	1–3
1^1A_2	–0.704 052	–1.350 426	42.9	–0.345	0.81	1–4
2^1A_2	–0.685 035	–1.326 585	39.6	–0.105	0.81	1–4
3^1A_2	–0.668 639	–1.306 381	52.1	–0.169	0.81	1–4
4^1A_2	–0.666 696	–1.304 230	65.3	+0.355	0.81	1–4
π–π^* Triplet States (active space (0044))						
1^3A_1	–0.727 444	–1.377 166	24.6	–0.066	0.81	1
1^3B_2	–0.791 989	–1.441 693	24.8	–0.056	0.81	1
σ–π^* Triplet States (active space (4222))						
1^3B_1	–0.694 377	–1.328 578	38.8	+0.133	0.81	1
1^3A_2	–0.712 465	–1.351 346	43.2	–0.303	0.81	1

[a] Expectation value (CASSCF) of x^2 (in au^2), where x is the coordinate perpendicular to the molecular plane. [b] Dipole moment in au. [c] The weight of the CASSCF reference function in the first-order wave function. [d] States included in the state-average CASSCF calculation.

CP has not been the subject of many theoretical studies. Semiempirical calculations have been carried out for the valence excited states.[1,33-35] To our knowledge, there exist only two previous *ab initio* calculations of the electronic spectrum of this molecule, the SAC-CI study of Nakatsuji *et al.*[2] and the RPA (random phase approximation) study of Galasso.[36] Neither of these studies was accurate enough to allow a full interpretation of the spectrum.

The results of the present investigation are presented in Tables II and III and are also illustrated in Figure 1. In Table II, we give the total energies (CASSCF and PT2F), the expectation value for x^2 (CASSCF), the dipole moments for all states, and the weight, ω, of the reference state in the first-order wave function.

In all, 14 singlet and four triplet excited states have been considered. The singlet states include three valence states, the $1a_2 \rightarrow 3s$, 3p, and 3d Rydberg states, and, in addition, the $1b_1 \rightarrow 3s$ Rydberg state. The CASSCF calculations were performed as averages over all states of a given symmetry. Independent calculations were, however, performed for the ground state with the two different active spaces. The resulting energies are almost identical, both at the CASSCF and at the CASPT2 levels of treatment. The excitation energies were related to the single-state-optimized ground-state energies obtained with the corresponding active space.

The expectation value of x^2 (the x-coordinate is perpendicular to the molecular plane) can be used to identify the valence excited states. The ground state value is 24.8 au^2, while two excited states of $^1A_1$ symmetry (2^1A_1 and 4^1A_1) have values in the range 25–27 au^2, and $\langle x^2 \rangle$ for the 1^1B_2 state is 29.1 au^2. Thus these states can be clearly identified as valence excited states. The other π–π^* excited states have much larger values and are characterized as Rydberg states.

The weight of the CASSCF reference function (ω) in the first-order perturbed wave function is given in the sixth column of Table II. It is used as an indication of a balanced treatment of electron correlation and should ideally be about the same for all electronic states under consideration. The weight for the ground state is 0.82, and the Rydberg excited states have similar values. The valence excited states have, in general, somewhat smaller weights. In part, this is due to the larger importance of dynamic

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Table III. Calculated and Experimental Excitation Energies and Oscillator Strengths in Cyclopentadiene

	excitation energy (eV)				oscillator strength	
state	PT2F	exptl	deviation[a]	other results	this work	previous
			Singlet States			
1^1B_2 (valence)	5.27	5.26[d–f]	+0.01	6.48,[b] 5.54[c]	0.1475	0.159,[b] 0.115[c]
1^1A_2 ($1a_2 - 3s$)	5.65	5.68[d,f,g]	−0.03	5.76,[b] 5.95[c]		forbidden
1^1B_1 ($1a_2 - 3p\sigma$)	6.24	6.25[d,f,g]	−0.01	6.33,[b] 6.44[c]	0.0306	0.031,[b] 0.057[c]
2^1B_2 ($1a_2 - 3p\pi$)	6.25	6.31[d,f,g]	−0.06	6.42,[b] 6.53[c]	0.0248	0.0044,[b] 0.024[c]
2^1A_2 ($1a_2 - 3p\sigma$)	6.30	6.26[h]	+0.04	6.38,[b] 6.59[c]		forbidden
2^1A_1 (valence)	6.31	6.2[i]		7.81,[b] 8.01[c]	0.0003	0.0193,[b] 0.4235[c]
3^1A_2 ($1a_2 - 3d\delta$)	6.85			7.06[c]		forbidden
3^1B_2 ($1a_2 - 3d\pi$)	6.86	6.80[d]	+0.06	7.25[c]	0.0101	0.0006[c]
2^1B_1 ($1a_2 - 3d\delta$)	6.87			7.09[c]	0.0003	0.0009[c]
4^1A_2 ($1a_2 - 3d\sigma$)	6.91			7.13[c]		forbidden
3^1A_1 ($1a_2 - 3d\pi$)	6.93	7.05[d]	−0.12	7.12,[b] 7.22[c]	0.0208	0.00001,[b] 0.0013[c]
4^1A_1 (valence)	7.89	7.9,[d] 8.0[e]	−0.01	8.80[c]	0.4415	0.2478[c]
3^1B_1 ($2b_1 - 3s$)	7.95	8.03[d]	−0.08	8.17,[b] 8.26[c]	0.0252	0.0202,[b] 0.0005[c]
			Triplet States			
1^3B_2 (valence)	3.15	3.10[d,f]	+0.05	3.52[b]		
1^3A_1 (valence)	4.90	>4.7[d]		5.50[b]		
1^3A_2 ($1a_2 - 3s$)	5.63			5.82[b]		
1^3B_1 ($1a_2 - 3p\sigma$)	6.25			6.36[b]		

[a] Difference between the calculated (PT2F) and experimental excitation energies. [b] SAC-CI results, ref 2. [c] SCF-RPA results, ref 36. [d] Electron impact spectroscopy, ref 26. [e] Optical absorption and electron energy loss spectrum, ref 27. [f] UV absorption data, ref 25. [g] UV absorption data, ref 28. [h] Two-photon resonant multiphoton ionization spectrum, ref 30. [i] Estimate based on experimental data, ref 27.

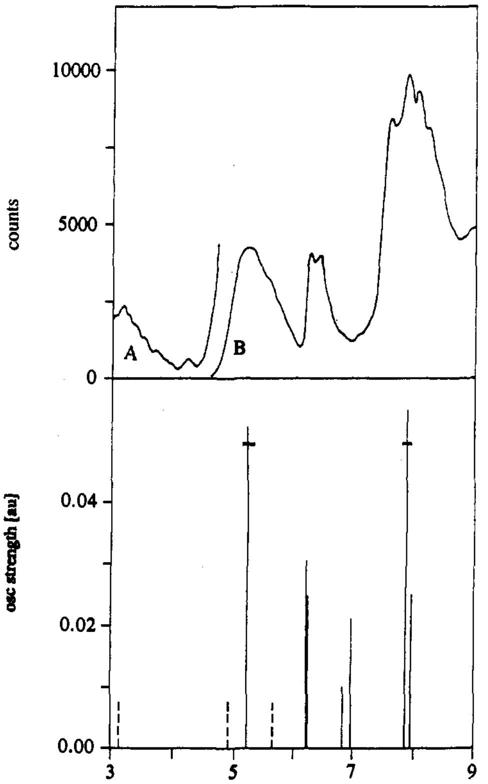

Figure 1. Experimental (top) and theoretical (bottom) excitation spectra of cyclopentadiene. The electron energy loss spectra are copied from ref 26 and measured at $\theta = 20°$, $E = 30$ eV (curve A) and $\theta = 10°$, $E = 50$ eV (curve B), respectively. Curve A is magnified by a factor of 1000, and the dashed theoretical lines mark the position of the triplet states.

correlation in these states, but for the 4^1A_1 state the weight has artificially decreased due to interaction with an intruder state of Rydberg character. The contribution from this state to the second-order energy is, however, small, and therefore it has no effect on the computed excitation energy. A more detailed discussion of the Rydberg intruder problem for valence excited states will be given in the section on pyrrole.

The UV spectrum of CP shows three major features around 5.3, 6.2, and 8.0 eV. From the analysis of the optical absorption and energy loss spectra of the valence[27] and Rydberg states[28,30] made by McDiarmid *et al.* and the electron impact study of Frueholz *et al.*,[26] we get a detailed description of the excited states in the molecule. Below we shall compare these data with the theoretical results and also suggest some new assignments, especially of the 3d Rydberg origins.

Valence Excited Singlet States (1^1B_2, 2^1A_1, and 4^1A_1). The lowest energy singlet–singlet transition in CP gives rise to an absorption band, which begins at about 4.75 eV and extends to 5.90 eV, with an intensity maximum around 5.26 eV.[25–27] All of the experimental data are consistent with a singlet–singlet symmetry-allowed transition and an assignment to the 1^1B_2 state. It has been suggested that the diffuse character of the transition is due to a possible valence–Rydberg mixing.[30,37] McDiarmid[37] has even estimated the Rydberg character to be about 6%. The present value for the excitation energy is 5.27 eV, while the value of $\langle x^2 \rangle$ is 29 au^2, compared with the value of 25 au^2 obtained for the ground state. The corresponding value for the 2^1B_2 Rydberg state is 71 au^2. We conclude that the Rydberg mixing into the 1^1B_2 valence state is small. The computed intensity is 0.15, which places it as the second most intense transition in the spectrum, in agreement with experimental findings and with the result of Nakatsuji *et al.*[2]

The SAC-CI study of Nakatsuji *et al.*[2] gives an energy of 6.48 eV for the 1^1B_2 state. The authors suggest that the error is partly due to the use of a too small basis set (no 3d functions were included), but do not rule out the possibility of a nonvertical nature for the transition. According to our experience, the main reason for the error is an inadequate treatment of electron correlation, especially the dynamic σ–π polarization effects, which in the present calculation lowers the excitation energy by 1.44 eV. Of course, an adequate basis set is needed to describe this effect. The 1^1B_2 state is dominated by the single excitation $1a_2 \rightarrow 3b_1$. It is therefore not so surprising that the RPA energy of Galasso,[36] 5.54 eV, is in reasonably good agreement with experiment.

The next valence excited state is the 2^1A_1 state, which in the present study appears at 6.31 eV. This is the $^1A_1^-$ state. It is a mixture of the configurations $2b_1 \rightarrow 3b_1$ and $1a_2 \rightarrow 2a_2$ but includes a large fraction (about 43%) of the doubly-excited configuration $(1a_2)^2 \rightarrow (3b_1)^2$. The computed intensity is very low, 0.0003. This state has not been found in the spectrum, but McDiarmid has estimated the excitation energy to be about 6.2 eV, in agreement with the present result. The difficulties in finding

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this state in the spectrum are in part due to the appearance of the 3p Rydberg states in the same energy region, with considerably larger intensities.

Shang and Hudson[29] have, however, used the depolarization ratios of resonance-enhanced Raman transitions to demonstrate the presence of two perpendicularly polarized transitions below 6 eV. According to their interpretation, the 2^1A_1 state will fall below the 1^1B_2 state, and they assign the origin to appear at 4.82 eV, which would place this state under the intense 1^1B_2 transition. The separation between the origin and the vertical energy can, however, be expected to be very large in this case. It was calculated to be 1.87 eV in a recent semiempirical study.[38] The difference obtained from our theoretical value for the vertical energy and the value for the origin given by Shang and Hudson is 1.49 eV, which is somewhat smaller than the semiempirical estimate. The state is clearly of valence character ($\langle x^2\rangle = 25$ au^2), and the calculated weight of the reference function, 0.80, does not indicate any difficulties in the correlation treatment. We therefore see no reason why the present result should not be accurate to within a few tenths of an eV and conclude that the difference between the origin and the vertical transition energy is about 1.5 eV.

The RPA calculations[36] place the $^1A_1^-$ transition at 8.01, which is maybe not so surprising, since the method is not expected to work well for a state with a considerable multiconfigurational character, including a large fraction of doubly-excited configurations. The state appears at 7.81 eV in the SAC-CI study[2] with an intensity of 0.0193. In the paper it is assigned to the $^1A_1^+$ state observed at 8.0 eV, but this assignment must be incorrect, since the $^1A_1^-$ state is the first valence excited state of this symmetry and has to occur below the $^1A_1^+$ state.

The third valence excited state represents the most intense feature in the system. The vertical transition energy has been reported as 7.90 eV[26] or 8.0 eV.[27] The calculations place the 4^1A_1 state at 7.89 eV with an intensity of 0.44. This is the $^1A_1^+$ state. The calculated $\langle x^2\rangle$ value is 27 au^2, which clearly demonstrates its valence character. The SAC-CI study[2] does not report this state, and the RPA calculations place it at 8.80 eV with an intensity of 0.25.

$1a_2 \rightarrow 3s$ (1^1A_2). The $n = 3$ Rydberg series of CP has received special attention by Frueholz *et al.*[26] and McDiarmid *et al.*[28,30] A weak feature around 5.68 eV has been characterized as the 1^1A_2 state corresponding to the $1a_2 \rightarrow 3s$ Rydberg excitation. Other experimental results at 5.63 eV[28] and the calculations by Nakatsuji *et al.*[2] (5.76 eV) and Galasso[36] (5.95 eV) confirm the assignment. The present result, 5.65 eV, is in agreement with these earlier predictions.

$1a_2 \rightarrow 3p$ (1^1B_1, 2^1A_2, and 2^1B_2). Between 6.15 and 6.70 eV, the spectrum presents an intense feature with resolvable peaks at 6.28 and 6.31 eV.[26,28] The two discrete transitions have been assigned to $^1B_1$ and $^1B_2$ states. McDiarmid *et al.*[28,30] have performed a careful analysis of the 3p Rydberg states and give the energies 6.25 (B_1), 6.26 (A_2), and 6.31 (B_2) eV. The present results are 6.24, 6.30, and 6.25 eV. Even though the order of the A_2 and B_2 states has shifted, the agreement with experiment must be considered as satisfactory. Derrick *et al.*[32] noted in their analysis that the $n = 3$ member is a doublet with an energy spacing of 0.06 eV, but they have no satisfactory explanation for it. It was argued that the transition at 6.31 eV has a too high quantum defect to be identified with the $^1B_1$ state. The present study shows, however, that the $^1B_2$ and $^1B_1$ states are close in energy and have comparable intensities.

$1a_2 \rightarrow 3d$ (3^1A_2, 3^1B_2, 2^1B_1, 4^1A_2, and 3^1A_1). The first five members of the R(3d) series have been computed to lie in the energy range 6.85–6.93 eV. These states have not been directly observed in the spectrum, but Frueholz *et al.*[26] report two unassigned peaks at 6.80 and 7.05 eV, which could be the two most intense of the five transitions. The 3^1B_2 state at 6.86 eV has an intensity of 0.01 and could correspond to the feature around 6.80 eV, while the 3^1A_1 state, calculated to occur at 6.93 eV with an intensity of 0.02, could be the peak observed at 7.05 eV. The RPA results place these transitions in the range 7.06–7.22 eV.[36] Nakatsuji *et al.*[2] report the energy 7.12 eV for the $^1A_1$ component but give no results for the other states.

$2b_1 \rightarrow 3s$ (3^1B_1). The highest state studied was the first component of the $2b_1$ Rydberg series. The energy has been calculated to be 7.95 eV and could relate to a Rydberg feature described by Frueholz *et al.*[26] at 8.03 eV. The spectrum is, however, dominated in this region by the valence $^1A_1^+$ state at 7.9 eV, and it is difficult to observe any other features. Moreover, the first experimental ionization potential occurs at 8.57 eV. Thus, the other R′ Rydberg series seem energetically too high to be of interest. Nakatsuji *et al.*[2] reported the 3p states at energies around 8.7 eV. Derrick *et al.*[32] have identified two members of this series (based on the spectrum of Price and Walsh[23]) and estimate the 0–0 energy of the $n = 3$ member to be 7.85 eV.

Triplet States. Calculations have been performed for the lowest triplet state in each of the four symmetry species. Two valence excited states occur at 3.15 (1^3B_2) and 4.90 eV (1^3A_1). The lowest energy transition observed in the CP spectrum has an effective Franck–Condon region extending from 2.5 to 3.9 eV, with an intensity maximum occurring at 3.10 eV.[25,26] This band clearly corresponds to the valence excited triplet state 1^3B_2. The SAC-CI treatment[2] overestimates the excitation energy by about 0.4 eV.

Experimentally, the second triplet state has not been directly observed. Frueholz *et al.*[26] suggests that it is hidden behind the singlet valence excitation at 5.2 eV. They estimate the excitation energy to be above 4.7 eV by comparison with other systems, such as *cis*-1,3-butadiene. Our results predicts about the same excitation energy for the 1^3A_1 state in CP and *cis*-butadiene (the computed excitation energy to the 1^3A_1 state in *cis*-butadiene is 4.73 eV).[39]

In addition, we have computed the first two triplet Rydberg excitations. There are no experimental results with which to compare the excitation energies. The computed singlet–triplet splitting is 0.02 eV for the 3s state, while it is –0.01 eV for the 3pb_2 excitation. Negative singlet–triplet splittings (the singlet occurs below the triplet) have also been obtained in the SAC-CI treatment.[2] However, the computed splittings are in the present investigation so small that they are outside the error limits of the calculated energies. The only possible conclusion is then the obvious one, that the singlet–triplet splitting for the lowest Rydberg states are of the order of a few hundreths of an eV.

3B. Pyrrole. The pyrrole molecule gives an interesting example of the difficulties that theory has in providing an understanding and assignment of an electronic spectrum. In spite of numerous calculations employing a variety of computational methods, no complete assignment of the bands in the spectrum is available in the literature. The spectrum itself has been known for a long time,[22,40–42] and recent measurements employing modern techniques have given a very detailed picture[20,43–46] (cf. Figure 2). The main features are two broad bands located at about 6.0 and 7.5 eV. Superimposed on this structure are two sets of Rydberg series arising from excitations out of the highest ($1a_2$) and next

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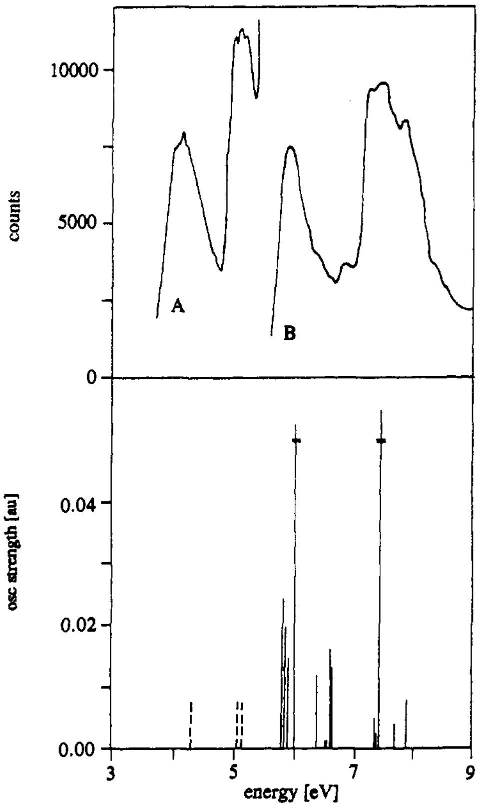

Figure 2. Experimental (top) and theoretical (bottom) excitation spectra of pyrrole. The electron energy loss spectra are copied from ref 43 and measured at $\theta = 70°$, $E = 50$ eV (curve A) and $\theta = 3°$, $E = 50$ eV (curve B), respectively. Curve A is magnified by a factor of 10 000, and the dashed theoretical lines mark the position of the triplet states.

highest ($2b_1$) occupied π-orbitals. In the experimental literature they are labeled R and R′, respectively.

The first attempt to assign the spectrum was made with the aid of semiempirical MO theories. By virtue of the nature of these approaches it was, of course, only possible to consider the valence excited states. Fischer-Hjalmars and Sundbom[47] used semiempirical π-electron theory and arrived at the following excitation energies: $^1B_2$, 5.9 (0.32); $^1A_1^-$, 6.1 (0.06); $^1B_2$, 7.3 (0.90); and $^1A_1^+$, 7.8 (0.31) eV. Oscillator strengths are given in parentheses. This calculation thus explains the two major features of the spectrum, with the exception that the second $^1B_2$ state has a too low energy. Del Bene and Jaffé[1] performed CNDO calculations and obtained the following results: $^1B_2$, 5.0 (0.08); $^1A_1^-$, 5.4 (0.006); $^1B_2$, 7.0 (0.129); and $^1A_1^+$, 7.0 (0.48) eV. By changing the CNDO parameters somewhat, Mullen and Orloff[43] modified these results to: $^1A_1^-$, 5.5 (0.06); $^1B_2$, 5.5 (0.90); and $^1A_1^+$, 7.0 (0.31) eV. The energy of the second $^1B_2$ state was not reported. Mullen and Orloff conclude from these results that the small feature found on the red side of the first major band in the pyrrole spectrum, located at 5.2 eV, should be assigned to the $^1A_1^-$ state. Later experimental and theoretical evidence shows unequivocally that this band is of Rydberg type and corresponds to the excitation $1a_2 \rightarrow 3s$. However, in retrospect it seems clear that these semiempirical studies have been able to give a reasonably satisfactory explanation of the major features of the electronic spectrum of pyrrole. What about *ab initio* methods?

The first attempt to describe the spectrum using *ab initio* methods was made by Tanaka *et al.*,[48] who performed SCF and π-electron CI calculations using a DZ Gaussian-type basis set with additional $2p\pi$ diffuse functions. In the energy range covered (up to about 7.5 eV), they find only one valence excited state, $^1A_1^-$, with an excitation energy of 6.51 eV. Butscher and Thunemann[49] performed SCF plus MRCI calculations using a basis set of about the same quality, now also correlating the σ-electrons. The $^1A_1^-$ state was found at 6.73 eV, and the first valence excited $^1B_2$ state at 7.70 eV. The authors claim that the agreement with experiment is 0.1–0.3 eV, which is somewhat surprising in view of the results. No intensities were computed.

Rawlings and Davidson[50] used the second-order Rayleigh–Schrödinger B_K method and configuration interaction with extrapolation of the energies. The basis set was again of DZ quality with added diffuse functions. The accuracy claimed for the excitation energies is 0.2 eV, but only one valence excited state was found in the energy range 5.25–7.83 eV, the $^1A_1^-$ state, with a computed energy of 6.53 eV and a very small intensity. Thus no explanation of the major features of the spectrum was provided. Finally, Nakatsuji *et al.*[2] in 1985 reported results from a SAC-CI study (the same type of basis set was again used). The $^1A_1^-$ state was found at 7.20 eV. They also located two $^1B_2$ states at 7.52 and 7.59 eV, which were mixtures of a valence ($1a_2 \rightarrow 3b_1$) and a Rydberg ($2b_1 \rightarrow 3d_{yz}$) excited configuration.

Thus, none of the previous *ab initio* calculations have been able to explain the major features of the spectrum. This is probably partly due to the use of too limited basis sets in combination with an insufficient account of the correlation effects between the σ- and π-electrons. We shall return to a more detailed discussion of the Rydberg states later. For these states the earlier calculations have been more successful, which is again not surprising, since the correlation effects are known to be of considerably less importance here.

The results of the present calculations are presented in Tables IV–VI and are also illustrated in Figure 2. Table IV gives the total energies at the CASSCF and the PT2F levels and, in addition, the expectation value for x^2 and the dipole moment. The CASSCF energies and wave functions were obtained from average energy calculations in each symmetry except for the ground state and the triplet states. In all four symmetries the molecular orbitals were determined by averaging over the seven lowest states. Thus four CASSCF calculations were performed for the singlet states and, in addition, two calculations for the ground state, one for each of the two active spaces used. These two calculations can be used as an illustration of the insensitivity of the PT2F energies toward the detailed choice of the active space: the difference in the CASSCF energies is 0.21 eV, which is reduced to 0.13 eV at the PT2F level of approximation. All excitation energies have been related to the ground-state energy obtained with the corresponding active space. In order to control the effect of the averaging procedure, we also did single-state calculations for the lowest excited state in each symmetry. The differences in the calculated excitation energies (PT2F) were in all cases less than 0.01 eV.

The value of $\langle x^2 \rangle$ for the ground state is 25.8 au^2, which can be compared to an experimental estimate[51] yielding the value 27 au^2. Considerably larger values are obtained for the Rydberg states. However, two singlet states of A_1 (2^1A_1 and 6^1A_1) and one state of B_2 symmetry (2^1B_2) have moderately small values (30–40 au^2). These are the valence excited states. The state ordering is different at the CASSCF level, showing the importance of the dynamic correlation effects. This is especially obvious for 2^1B_2, which in the CASSCF calculation appears as the highest of all states considered. One effect responsible for the reordering of the states is the dynamic σ–π polarization, which is especially prominent for states with a large ionic character (see, for example,

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Table IV. Total Energies, Dipole Moments, and Other Properties of the Excited States of Pyrrole

	energy + 208 au					
state	CASSCF	PT2F	$(x^2)^a$	μ^b	ω^c	$n_{states}{}^d$
		$\pi-\pi^*$ Singlet States (active space (0064))				
1^1A_1	–0.955 017	–1.614 589	25.8	–0.695	0.82	1
2^1A_1	–0.689 655	–1.397 146	34.4	–0.451	0.70	1–7
3^1A_1	–0.714 582	–1.374 249	83.5	+0.054	0.81	1–7
4^1A_1	–0.708 477	–1.370 222	69.3	+0.966	0.81	1–7
5^1A_1	–0.683 734	–1.344 183	78.4	–0.854	0.79	1–7
6^1A_1	–0.579 348	–1.340 344	38.9	–1.115	0.59	1–7
7^1A_1	–0.650 192	–1.324 935	67.5	+0.077	0.80	1–7
1^1B_2	–0.736 428	–1.402 299	68.4	+0.987	0.81	1–7
2^1B_2	–0.607 473	–1.393 834	32.2	–0.833	0.68	1–7
3^1B_2	–0.712 117	–1.374 547	83.0	–1.253	0.81	1–7
4^1B_2	–0.681 516	–1.341 410	84.5	+0.026	0.81	1–7
5^1B_2	–0.660 039	–1.330 915	73.4	+1.073	0.80	1–7
6^1B_2	–0.624 712	–1.297 392	70.8	–0.105	0.80	1–7
		$\pi-\sigma^*$ Singlet States (active space (4232))				
1^1A_1	–0.947 153	–1.619 489	25.7	–0.689	0.82	1
1^1B_1	–0.736 591	–1.404 637	38.4	+2.012	0.81	1–7
2^1B_1	–0.750 029	–1.400 213	37.5	+2.872	0.81	1–7
3^1B_1	–0.717 973	–1.384 216	40.7	–1.442	0.81	1–7
4^1B_1	–0.711 668	–1.376 353	43.0	–3.062	0.76	1–7
5^1B_1	–0.693 600	–1.350 682	44.5	–1.885	0.82	1–7
6^1B_1	–0.691 076	–1.347 945	80.0	–0.212	0.81	1–7
1^1A_2	–0.760 456	–1.433 001	36.0	+3.671	0.81	1–7
2^1A_2	–0.740 018	–1.405 245	42.0	–2.000	0.78	1–7
3^1A_2	–0.721 178	–1.383 632	43.4	–1.804	0.81	1–7
4^1A_2	–0.718 151	–1.380 286	80.7	–1.369	0.81	1–7
5^1A_2	–0.707 045	–1.370 864	39.6	+1.354	0.79	1–7
6^1A_2	–0.689 138	–1.350 850	40.4	–1.466	0.81	1–7
		$\pi-\pi^*$ Triplet States (active space (0064))				
1^3A_1	–0.753 126	–1.425 044	26.1	–0.438	0.79	1
1^3B_2	–0.797 865	–1.457 780	25.7	–0.382	0.82	1
		$\pi-\sigma^*$ Triplet States (active space (4323))				
1^3B_1	–0.755 729	–1.405 629	38.7	+1.241	0.82	1
1^3A_2	–0.780 530	–1.434 025	36.5	+3.465	0.82	1

[a] Expectation value (CASSCF) of x^2 (in au^2), where x is the coordinate perpendicular to the molecular plane. [b] Dipole moment in au. [c] The weight of the CASSCF reference function in the first-order wave function. [d] States included in the state-average CASSCF calculation.

Table V. Partitioning of the CASPT2 Correlation Energy (au) for the Valence Excited Singlet States in Pyrrole

state	$\sigma-\sigma$	$\sigma-\pi$	$\pi-\pi$	$\Delta(\sigma-\sigma)^a$	$\Delta(\sigma-\pi)^a$	$\Delta(\pi-\pi)^a$
1^1A_1	–0.3449	–0.2876	–0.0271			
2^1A_1	–0.3545	–0.3028	–0.0502	–0.26	–0.41	–0.63
2^1B_2	–0.3552	–0.3390	–0.0922	–0.28	–1.40	–1.77
6^1A_1	–0.3543	–0.3262	–0.0804	–0.26	–1.05	–1.45

[a] Effect on the excitation energies, in eV.

the discussion in ref 5). For Rydberg states such a reordering occurs only for the first two states of $^1B_1$ symmetry.

The effects of dynamic correlation on the transition energies for the valence excited states are much larger for pyrrole than they have been for any of the molecules previously studied. For butadiene,[8] the excitation energy for the ^1B_u state decreased from 8.54 eV at the CASSCF level to 6.23 eV at the PT2F level. A corresponding effect was found for hexatriene.[8] Here the CASSCF excitation energy for the $^1B_2$ state is 9.46 eV, while the PT2F calculation yields 6.00 eV, a decrease of almost 3.5 eV. A corresponding decrease is found for the 6^1A_1 state. These surprisingly large correlation effects may be one reason why previous calculations have consistently yielded too large excitation energies for these states.

In order to analyze the dynamic correlation effects in more detail, we present in Table V, a partitioning of them into contributions from $\sigma-\sigma$, $\sigma-\pi$, and $\pi-\pi$ electron pairs for the ground state and the valence excited singlet states. These numbers clearly illustrate that there is a large contribution to the excitation energies not only from dynamic $\sigma-\pi$ polarization but also from an increase in the magnitude of the $\pi-\pi$ correlation energy. These numbers are larger than those obtained for any of the other molecules studied with the CASPT2 approach. For example, for benzene we obtained for the most ionic state, $^1E_{1u}$, a contribution to the excitation energy of –1.85 eV from $\sigma-\pi$ polarization but only –0.85 eV from increased $\pi-\pi$ correlation. The difference may be due to the appearance in pyrrole of a π lone pair, which is also affected by dynamic polarization in highly ionic excited states. Similar effects are also obtained for furan, which lends further support to this hypothesis.

Dipole moments have been calculated at the CASSCF level for all of the excited states. The value obtained for the ground state, 0.695 au, is in agreement with the two available experimental estimates, 0.684[52] and 0.708 au.[53]

The Rydberg excited states have the same weight, ω, of the reference function as the ground state. Valence excited states, on the other hand, have somewhat smaller weights, since dynamic correlation effects are of larger importance here. The very low value (0.59) obtained for the 6^1A_1 state is due to the appearance of a nearly degenerate Rydberg state in the first-order wave function, which was not included in the CAS reference space. The contribution of this state to the second-order energy is, however, very small, and thus it has no effect on the resulting correlation energy.

The computed excitation energies for 27 electronic states are presented in Table VI. This table also attempts an assignment of the experimental bands and compares the present results to previous *ab initio* calculations.

The pyrrole spectrum has been extensively studied, starting with the historical electron absorption measurements of Sheibe and Greineisen,[22] Menzel,[40] Horvath *et al.*,[29] and Pickett *et al.*[41] All of them agree on the assignments of the peaks around 6.0, 6.8, and 7.5 eV to singlet–singlet transitions. The UV optical spectrum was studied by Mullen and Orloff[43] and Bavia *et al.*,[44] including a careful study of some possible Rydberg states. The photoelectron spectrum has been measured by Derrick *et al.*,[20] and the results were used in assignments of three Rydberg series. Electron impact spectra were obtained by Van Veen[45] and Flicker *et al.*[46] Robin[54] has completed the studies with some additional assignments. However, in spite of these efforts the experimental assignment of the electronic spectrum of pyrrole is far from complete. It is our hope that the assignments suggested below will give further guidance in this work.

Valence Excited Singlet States (2^1A_1, 2^1B_2, and 6^1A_1). The complex structure of the electronic spectrum of pyrrole with many overlapping Rydberg series in the energy region 5–8 eV has made a precise location of the valence excited states very difficult. Earlier theoretical predictions are also, as mentioned above, in conflict with each other. Several of the experimental discussions avoid the issue completely, and others only mention them as possibilities for the assignments of unresolved structures. At the same time, it is clear from the general appearance of the spectrum (cf. Figure 2) that two intense and broad bands are present, which cannot be completely explained as consisting of only overlapping (and comparatively weak) Rydberg-type transitions. The first band has a maximum near 6.0 eV and the second near 7.5 eV. The former has been discussed by Bavia *et al.*[44] on the basis of both a vapor and a crystal spectrum. The crystal spectrum is of special interest here, since the Rydberg excitations should be much weaker in the crystal. The authors have also identified a band system starting near 5.64 eV and extending to about 6.2 eV which does not belong to the overlapping R(3p) system. Tentatively, they assign this band to a valence excited $^1B_2$ state, possibly with some

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(53) Kofod, H.; Sutton, L. E.; Jackson, J. *J. Chem. Soc.* **1952**, 1467.

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Table VI. Calculated and Experimental Excitation Energies and Oscillator Strengths in Pyrrole

	excitation energy (eV)				oscillator strength	
state	PT2F	exptl	deviation^a	other results	this work	previous
			Singlet States			
1^1A_2 ($^1a_2 - 3s$)	5.08	5.22^{f,g}	–0.14	5.22,^{c} 5.25,^{d} 5.20^e	forbidden	
1^1B_2 ($1a_2 - 3p\pi$)	5.78	5.86^h	–0.08	6.02,^{b} 6.33,^{c} 5.80,^{d} 5.97^e	0.0399	0.0421^e
2^1A_2 ($1a_2 - 3p\sigma$)	5.83			6.03,^{d} 5.95^e	forbidden	
1^1B_1 ($1a_2 - 3p\sigma$)	5.85	5.88^{f,g,i,k}	–0.03	6.05,^{c} 5.63,^{d} 5.85^e	0.0239	0.0322^e
2^1A_1 (valence)	5.92			6.51,^{b} 6.73,^{c} 6.53,^{d} 7.20^e	0.0195	0.0214^e
2^1B_2 (valence)	6.00	5.98^{f,h,l}	+0.02	7.07,^{b} 7.70,^{c} 7.52^e	0.1253	0.0874^e
2^1B_1 ($2b_1 - 3s$)	5.97			6.13,^{c} 5.96,^{d} 6.13^e	0.0006	0.0016^e
3^1B_1 ($1a_2 - 3d\delta$)	6.40	6.43^h	–0.03	6.33^d	0.0117	
3^1A_2 ($1a_2 - 3d\delta$)	6.42			6.62^d	forbidden	
4^1A_2 ($1a_2 - 3d\sigma$)	6.51			6.88^d	forbidden	
3^1B_2 ($1a_2 - 3d\pi$)	6.53	6.50^{f,j}	+0.03	6.97,^{d} 7.59^e	0.0011	0.0930^e
3^1A_1 ($1a_2 - 3d\pi$)	6.54	6.50^{f,j}	+0.04	7.12,^{d} 6.68^e	0.0010	0.0002^e
4^1B_1 ($2b_1 - 3p\sigma$)	6.62	6.78^{f,h,k}	–0.16	6.70,^{d} 6.70^e	0.0161	0.0222^e
4^1A_1 ($2b_1 - 3p\pi$)	6.65	6.78^{f,h,k}	–0.13	6.91,^{d} 6.89^e	0.0127	0.0024^e
5^1A_2 ($2b_1 - 3p\sigma$)	6.77			7.07,^{d} 6.85^e	forbidden	
6^1A_2 ($2b_1 - 3d\delta$)	7.31				forbidden	
5^1B_1 ($2b_1 - 3d\delta$)	7.32	7.26^f	+0.06		0.000 05	
5^1A_1 ($2b_1 - 3d\pi$)	7.36	7.43^f	–0.07	8.18^d	0.0047	
6^1B_1 ($2b_1 - 3d\sigma$)	7.39	7.43^f	–0.04			0.0025
4^1B_2 ($2b_1 - 3d\pi$)	7.43	7.43^f	+0.00	8.10^d	0.0005	
6^1A_1 (valence)	7.46	7.54^f	–0.08		0.3261	
5^1B_2 ($1a_2 - 4d\pi$)	7.72	≈7.4^h			0.0043	
7^1A_1 ($2b_1 - 4d\pi$)	7.88				0.0079	
			Triplet States			
1^3B_2 (valence)	4.27	4.21^{f,j}	+0.06	4.27,^{b} 4.42,^{c} 4.65^e		
1^3A_2 ($1a_2 - 3s$)	5.04			5.25,^{c} 5.17^e		
1^3A_1 (valence)	5.16	5.10^j	+0.06	5.45,^{b} 5.71,^{c} 5.84^e		
1^3B_1 ($1a_2 - 3p\sigma$)	5.82			5.99,^{c} 5.82^e		

^{a} Difference between the calculated (PT2F) and experimental excitation energies. ^{b} SCF plus CI in the π-orbital space, ref 48. ^{c} Selected MRCI calculation, ref 49. ^{d} The RS-Bk method, ref 50. ^{e} SAC-CI results, ref 2. ^{f} Electron impact data, ref 46. ^{g} UV absorption data, ref 43. ^{h} UV absorption data, ref 44. ^{i} UV spectrum, refs 22, 40, 42. ^{j} Electron impact results, ref 45. ^{k} UV absorption data, ref 41. ^{l} UV absorption data, ref 40.

admixture of Rydberg like 3d excitations. This is in perfect agreement with the present results, which locate the valence excited 2^1B_2 state at 6.00 eV with an intensity of 0.125. Further evidence is found in the electron impact (EI) spectrum of Flicker *et al.*,[46] who assign a peak at 5.98 eV to a state of B_2 symmetry. A similar assignment has also been made by Robin[54] and by Platt.[55] The alternative assignment to the origin of the R′(3s) series is unlikely due to the low intensity of this excitation (see below). Earlier theoretical studies have found the $^1B_2$ valence excited state at energies above 7.0 eV.[2,49,50]

The $\langle x^2 \rangle$ value for the 2^1B_2 state is 32.2 au^2, which is somewhat larger than the value for the ground state (25.8 au^2), but considerably smaller than that of the 3dπ Rydberg state 3^1B_2, 83.0 au^2. Thus, we do not see much valence Rydberg mixing in this state, as has been suggested by some authors.

According to the calculation, the 2^1B_2 state is nearly degenerate with the 2^1A_1 valence excited state, which has a computed excitation energy of 5.92 eV, that is, it appears in the same region as the more intense R(3p) transitions. The 2^1A_1 state is not discussed at all in the experimental literature. The present results shows that the band around 6.0 eV is composed of two valence excited states plus a number of Rydberg states, thus giving it a very complex structure. Earlier theoretical treatments place the 2^1A_1 valence excited state in the region 6.5–7.2 eV.[2,48–50] We find no experimental evidence in support of such an assignment.

The wave function of the 2^1A_1 state shows strong similarities to the corresponding state in butadiene. Its major components are the $2b_1 \rightarrow 3b_1$ and $1a_2 \rightarrow 2a_2$ configurations in combination with a large fraction (25%) of doubly excited configurations, predominantly $(1a_2)^2 \rightarrow (3b_1)^2$. The low intensity of the excitation is easily understood from this structure.

The most intense feature in the spectrum is the maximum around 7.5 eV. It is natural to assume that the intensity underlying the many Rydberg series is due to a valence excitation. However, so far there has been no evidence in support of this assumption. Nakatsuji *et al.*[2] in their SAC-CI study obtain the first valence excited state of $^1A_1$ symmetry at 7.20 eV and combinations of Rydberg and a valence excited states of $^1B_2$ symmetry at 7.52 and 7.59 eV. The intensities of all of these transitions are, however, low. The first valence excited state of $^1B_2$ symmetry should, as has been shown above, occur at considerably lower energies. Rawlings and Davidson[47] find, on the other hand, only one valence excited state below 8.4 eV, the 2^1A_1 state at about 6.5 eV.

Experimentally, it is agreed that the most intense features of the spectrum occur in the energy region around 7.5 eV. It is clear that Rydberg states cannot be solely responsible for this intensity as, for example, the oscillator strengths calculated for the R′(3d) states show (cf. Table VI). The most intense peak reported by Flicker *et al.*[46] occurs at 7.54 eV. Similar results are reported by Bavia *et al.*[44] from their vapor UV spectrum. Their crystal spectrum does not extend far enough into the UV region, but they note the onset of an intense and continuous band above 50 000 cm^{-1} (6.2 eV), which they surmise is the start of a valence excited transition.

The present result confirms these observations and locates an intense transition (6^1A_1) at 7.46 eV. The calculated oscillator strength is 0.33, which is 2.6 times larger than that of the second most intense transition, 2^1B_2. The $\langle x^2 \rangle$ value, 38.9 au^2, shows that this is predominantly a valence excited state, even though it may contain some admixture of Rydberg states appearing in the same energy region (for example, R′(3d)).

$1a_2 \rightarrow 3s$ (1^1A_2). This is the first singlet–singlet transition. The calculated excitation energy is 5.08 eV. The weak feature in the UV spectrum of Muller and Orloff[43] found at 5.22 eV (2375 Å) was originally assumed to correspond to a π–π^* transition. The same transition was found in the low-energy region of the EI spectrum of Flicker *et al.*[46] They concluded from an analysis of the angular dependence of intensity ratios that it is a dipole-forbidden spin-allowed transition but again assumed it to be of

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(55) Platt, J. R. *J. Chem. Phys.* **1950**, *18*, 1168; **1951**, *19*, 101.

the π–π^* type (which is inconsistent with the characterization of the state as dipole-forbidden). Bavia *et al.*[44] analyzed the Rydberg series in their VUV spectrum and arrived, by means of a least-squares fit, at the energy 5.0 eV for the $1a_2 \rightarrow 3s$ transition (the very weak system in the spectrum ranges from 4.83 to 5.21 eV). Robin[54] has suggested the same assignment. Earlier theoretical studies[2,49,50] have resulted in excitation energies in the range 5.20–5.25 eV. The nature of the first spin-allowed transition in pyrrole is thus now clearly established.

$1a_2 \rightarrow 3p$ (1^1B_2, 2^1A_2, and 1^1B_1). The intense peak around 6.0 eV contains a number of overlapping bands, and a precise assignment is very difficult. It is generally agreed that the three transitions corresponding to the $1a_2 \rightarrow 3p$ excitations are located in this band and are overlapping a broad valence excitation ($^1B_2$).[44] Our calculated energies for the 3p excitations are 5.78 ($3p\pi$, b_1), 5.83 ($3p\sigma$, a_1), and 5.85 ($3p\sigma$, b_2) eV, respectively. Experimentally, several assignments have been attempted. Mullen and Orloff[43] find a peak at 5.71 eV, which they assign to a $^1B_2$ state. Derrick *et al.*[20] have identified the npb_2 ($^1B_1$) series and assign the peak at 5.87 eV in the spectrum of Mullen and Orloff[43] and Pickett *et al.*[38] to the 3p component. Bavia *et al.*[41] arrive at the alternative $^1B_2$ assignment and give the energy 5.86 eV. They also calculated, by a least-squares fit of higher members to a general formula, the origin of a second 3p series to be 6.08 eV. This value is probably slightly too high, since the computed value for the first series is 6.03 eV, while the measured value is 5.86 eV. The splitting of the two 3p components, 0.05 eV, is probably more accurate. The energy difference between the two dipole-allowed transitions $^1B_2$ and $^1A_1$ is obtained in the present work as 0.07 eV, in agreement with the results of Bavia *et al.*[44] The calculations show that the two states have similar intensities. Finally, Flicker *et al.*[46] find one state at 5.88 ± 0.04 eV but do not suggest any assignment. Cooper *et al.*[56] have studied the Rydberg series in pyrrole and furan using resonance-enhanced multiphoton ionization spectroscopy. They give the energies 5.99, 6.02, and 6.17 eV for three 3p Rydberg states in pyrrole. The bands are, however, broad and diffuse, and the exact energies are uncertain. Especially the last value seems a little bit high. Other theoretical studies have positioned the $1a_2 \rightarrow 3p$ bands in the energy region 5.8–6.3 eV (cf. Table VI for details).

$2b_1 \rightarrow 3s$ (2^1B_1). This is the first member of the second Rydberg series (R′). The results for this state give a transition energy of 5.97 eV and an oscillator strength of only 0.006. Other theoretical studies give 5.96[49] or 6.13 eV.[2,50] Experimentally, the situation is rather confused. Derrick *et al.*[20] assigned a band at 6.23 eV to the first (3s) member of the $2b_1 \rightarrow ns$ Rydberg series. Bavia *et al.*,[44] on the other hand, were able to clearly identify that band as a vibrational progression in the R(3p) series. They find no indication for other transitions in the energy region around 6.2 eV. Flicker *et al.*[46] did not dare to make any detailed assignments in this region of the spectrum. We conclude that this Rydberg series has not been identified experimentally and that the origin lies in the complex region around 6.0 eV.

$1a_2 \rightarrow 3d$ (3^1B_1, 3^1A_2, 4^1A_2, 3^1B_2, and 3^1A_1). The five components of the R(3d) transitions have been computed to lie in the energy range 6.40–6.54 eV. Three of the components are dipole-allowed, but only one of them (3^1B_1 at 6.40 eV) has an appreciable intensity. This is thus the state which should be most easily detectable experimentally. Bavia *et al.*[44] have also found an R(3d) series with the origin tentatively assigned at 6.42 eV, which is in agreement with our energy for the 3^1B_1 state. In the EI spectrum of Van Veen,[45] a maximum around 6.5 eV is assumed to involve many overlapping bands. Two of them could correspond to the 3^1B_2 and 3^1A_1 states, calculated to appear at 6.53 and 6.54 eV with intensities of 0.0011 and 0.0010, respectively. Derrick *et al.*[20] have, on the other hand, suggested an origin at 6.78 eV for the $1a_2 \rightarrow nda_2$ series. We believe, however, that this band is the origin of another Rydberg series (see below). In addition, the second member of the $^1B_2$ series ($1a_2 \rightarrow 4d\pi$) has been computed to have an excitation energy of 7.72 eV. Bavia *et al.*[44] give 7.35 eV for the second member of the $^1B_1$ series. The corresponding $^1B_2$ state should occur at a slightly larger energy. The somewhat too high energy obtained here is certainly due to the lack of enough diffuse functions to describe higher Rydberg orbitals.

Table VII. Total Energies, Dipole Moments, and Other Properties of the Excited States of Furan

	energy + 228 au					
state	CASSCF	PT2F	$\langle x^2 \rangle^a$	μ^b	ω^c	$n_{states}{}^d$
		π–π^* Singlet States (active space (0064))				
1^1A_1	−0.781 135	−1.457 430	24.1	+0.365	0.82	1
2^1A_1	−0.533 617	−1.231 220	24.2	+0.515	0.80	1
3^1A_1	−0.506 625	−1.191 873	83.3	−0.095	0.81	1–8[e]
4^1A_1	−0.390 557	−1.175 839	27.0	−0.146	0.55	1–8[e]
1^1B_2	−0.446 715	−1.235 633	30.2	+0.123	0.65	1–6
2^1B_2	−0.539 287	−1.219 403	66.6	+0.418	0.80	1–6
3^1B_2	−0.516 275	−1.195 285	78.9	−0.564	0.79	1–6
		σ–π^* Singlet States (active space (4232))				
1^1A_1	−0.772 075	−1.462 029	24.0	+0.382	0.82	1
1^1B_1	−0.543 605	−1.225 456	37.8	−0.185	0.81	1–3
2^1B_1	−0.519 708	−1.199 366	39.2	+0.249	0.82	1–3
3^1B_1	−0.501 426	−1.196 968	41.0	−0.953	0.80	1–3
1^1A_2	−0.554 082	−1.245 418	40.7	−0.423	0.81	1–5
2^1A_2	−0.532 736	−1.219 925	37.9	−0.490	0.81	1–5
3^1A_2	−0.518 046	−1.204 609	49.0	+0.108	0.81	1–5
4^1A_2	−0.512 150	−1.196 779	67.5	−0.470	0.77	1–5
		π–π^* Triplet States (active space (0064))				
1^3B_2	−0.633 951	−1.310 763	24.0	+0.526	0.82	1
1^3A_1	−0.581 417	−1.268 104	24.1	+0.444	0.81	1
		σ–π^* Triplet States (active space (4232))				
1^3A_2	−0.565 784	−1.246 675	41.0	−0.336	0.82	1
1^3B_1	−0.549 762	−1.226 167	37.1	−0.061	0.82	1

[a] Expectation value (CASSCF) of x^2 (in au^2), where x is the coordinate perpendicular to the molecular plane. [b] Dipole moment in au. [c] The weight of the CASSCF reference function in the first-order wave function. [d] States included in the state-average CASSCF calculation. [e] The relative weights were 9 for the four states in the table and 1 for the other states.

$2b_1 \rightarrow 3p$ (4^1B_1, 4^1A_1, and 5^1A_2). The three origins of the R′(3p) Rydberg series have been calculated to appear between 6.62 and 6.77 eV. The two allowed transitions have intensities of about 0.015. Other theoretical studies[2] obtain similar results. As new assignments, we propose that the features around 6.78 eV, which occur in both the UV and EI spectra with larger intensities than those around 6.5 eV,[22,44,46] are the origins of the R′(3p) series.

$2b_1 \rightarrow 3d$ (6^1A_2, 5^1B_1, 5^1A_1, 6^1B_1, and 4^1B_2). These Rydberg series (R′(3d)) are calculated to have origins in the energy region 7.31–7.43 eV. The largest intensity, 0.0047, is obtained for the 5^1A_1 state at 7.36 eV. No experiment has identified these series in the spectrum. Flicker *et al.*[46] report, however, a series of five bands in the region 7.26–7.86 eV without attempting any assignment. The two first of these bands, occurring at 7.26 and 7.43 eV, could be identified with the R′(3d) origins. A more detailed assignment is, however, not possible. The second member of the $^1A_1$ series has been computed to appear at 7.88 eV, but the value is rather uncertain.

Triplet States. The first triplet state in each of the four symmetries have been studied. The lowest state is a valence excited state of $^3B_2$ symmetry. The calculated excitation energy, 4.27 eV, agrees with the EI value of 4.21 eV.[45,46] The second valence excited state (1^3A_1) occurs at 5.16 eV. Earlier theoretical studies have placed this state at considerably higher energies.[2,49,50] It has, however, been identified in the EI spectrum of Van Veen[45] to appear at 5.10 eV, in agreement with the present result. In addition, we have also obtained the energies for the $1a_2 \rightarrow 3s$ and $1a_2 \rightarrow 3pb_2$ triplet Rydberg states. The 3s state is predicted to

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Table VIII. Calculated and Experimental Excitation Energies and Oscillator Strengths in Furan

	excitation energy (eV)				oscillator strength	
state	PT2F	exptl	deviation[a]	other results	this work	previous
			Singlet States			
1^1A_2 ($1a_2-3s$)	5.92	5.94[f]	−0.02	5.94,[b] 6.27[c]	forbidden	
1^1B_2 (valence)	6.04	6.06[d,e]	−0.02	7.58,[b] 7.50[c]	0.1543	0.0309[c]
2^1A_1 (valence)	6.16			≈6.9,[b] 7.32[c]	0.0015	0.0044[c]
1^1B_1 ($1a_2-3p\sigma$)	6.46	6.48[e,g]	−0.02	6.52,[b] 6.74[c]	0.0309	0.0426[c]
2^1B_2 ($1a_2-3p\pi$)	6.48	6.48[e,g]	+0.00	6.52,[b] 6.80[c]	0.0471	0.0891[c]
2^1A_2 ($1a_2-3p\sigma$)	6.59	6.61[d,e]	−0.02	6.98[c]	forbidden	
3^1A_2 ($1a_2-3d\delta$)	7.00				forbidden	
3^1B_2 ($1a_2-3d\pi$)	7.13				0.0074	
2^1B_1 ($1a_2-3d\delta$)	7.15				0.0000	
4^1A_2 ($1a_2-3d\sigma$)	7.22				forbidden	
3^1A_1 ($1a_2-3d\pi$)	7.31	7.28[e,g]	+0.03	7.46,[b] 7.59[c]	0.0003	0.0000[c]
3^1B_1 ($2b_1-3s$)	7.21	7.38[e,g]	−0.17	7.27,[b] 7.62[c]	0.0192	0.0309[c]
4^1A_1 (valence)	7.74	7.82[d,e]	−0.08		0.4159	
			Triplet States			
1^3B_2 (valence)	3.99	4.02[e,h]	−0.03	4.08,[b] 4.40[c]		
1^3A_1 (valence)	5.15	5.22[e]	−0.07	5.4–5.8,[b] 5.75[c]		
1^3A_2 ($1a_2-3s$)	5.86			5.82,[b] 6.20[c]		
1^3B_1 ($1a_2-3p\sigma$)	6.42			6.45,[b] 6.68[c]		

[a] Difference between the calculated (PT2F) and experimental excitation energies. [b] MRCI results, ref 61. [c] SAC-CI results, ref 2. [d] UV absorption data, refs 23, 57, 58. [e] Electron impact spectroscopy, ref 46. [f] Assignment based on UV absorption data, ref 54. [g] Assignment based on UV absorption data, ref 59. [h] Electron impact spectroscopy, ref 45.

occur at 5.04 eV, resulting in a very small singlet–triplet splitting (0.04 eV). The same small splitting (0.03 eV) is obtained for the $3pb_2$ state. There is no experimental evidence to which these results can be compared.

3C. Furan. The calculations for furan turned out to be more difficult than for the other two molecules. It was decided to include in the study of the singlet states the three valence excited states, the $1a_2 \rightarrow 3s,3p,3d$ Rydberg states, and the $2b_1 \rightarrow 3s$ Rydberg state. This selection implies that four states of symmetry A_1 should be included in the average CASSCF calculation. However, as it turned out, it was not possible to locate the $^1A_1^+$ state among the resulting wave functions. Not until the number of states was increased to eight was this state found with an (CASSCF) energy 10.6 eV above the ground state. In order to optimize the MOs for the four states of interest, we then repeated the CASSCF calculation, now with the weight of the four desired states increased to 9 times that of the four intruder states. This calculation gave three valence states with $\langle x^2 \rangle$ values in the range 24–27 au^2 (cf. Table VII) and one 3d Rydberg state, as intended. Independent CASSCF calculations were also performed for the first and second states of $^1A_1$ symmetry. The energy difference between these independently optimized states and those obtained in the average calculation was at the PT2F level 0.08 eV for the first and 0.12 eV for the second state. The 2^1A_1 state is thus calculated to lie 6.16 eV above the ground state when independently optimized orbitals are used. With average orbitals, the excitation energy is reduced to 6.11 eV, again illustrating the insensitivity of the CASPT2 method to the detailed choice of the MOs. The singly excited states included in the first-order wave function correct for small deficiencies in the MOs.

Six states were used in the averaging for the $^1B_2$ states, three for $^1B_1$, and five for $^1A_2$. Equal weights were used for all states in these symmetries. The results of the calculations are presented in Table VII. A problematic result is, once more, the low weight obtained for the valence excited states 2^1B_2 and 4^1A_1. As was the case in pyrrole, this is due to the appearance of Rydberg-like intruder states in the first-order wave function. Especially severe is the situation for the 4^1A_1 state, where the weight has decreased to 0.55. A closer analysis shows that the major effect is due to an intruder state corresponding to a Rydberg-type excitation to an orbital of a_2 symmetry, resulting in a state which is nearly degenerate with the CASSCF reference function. The contribution to the second-order energy from this state is 0.20 eV, which introduces an uncertainty in the computed excitation energy of the same order. The calculated transition energy is also smaller than the experimental value: 7.74 eV versus 7.82 eV (cf. Table VIII). The error is, however, well within acceptable limits. We have not tried to extend the calculation and include the intruder orbital into the active space, as was done for pyrrole, since those results showed that it was of minor importance for the excitation energies.

The UV spectrum of furan has been well documented experimentally,[23,45,46,54,57–60] although not so extensively as CP and pyrrole. Due to many overlapping vibrational modes and Rydberg series, certain parts of the spectrum have a complex structure. The assignments of the strong optically-allowed Rydberg transitions have been revised several times. The latest assignments of Derrick *et al.*[59] give support to the Rydberg series $1a_2 \rightarrow np$, $1a_2 \rightarrow nd$, and $2b_1 \rightarrow ns$, with origins at 6.48, 7.28, and 7.38 eV, respectively. Electron impact measurements have given additional information, in particular concerning dipole- and spin-forbidden transitions.[45,46]

Two previous *ab initio* studies are known to us: the SAC-CI calculation by Nakatsuji *et al.*[2] and a multireference CI study by Thunemann *et al.*[61] Both studies find the lowest excited singlet state to be the 1^1A_2 Rydberg state, in good agreement with experiment. The most intense features in the spectrum were related to one Rydberg and one valence state of symmetry $^1B_2$, at low and high energy, respectively. These assignments will be modified in the present work, where both intense peaks will be assigned to valence excited states, in agreement with the results obtained for CP and pyrrole. Table VIII and Figure 3 present our calculated transition energies and intensities and compare them with observed peaks and previous theoretical studies.

Valence Excited Singlet States (1^1B_2, 2^1A_1, and 4^1A_1). As in the other two molecules, we expect to find the two lowest valence excited states, 1^1B_2 and 2^1A_1, in the energy region around 6 eV and the third, $^1A_1^+$, above 7 eV. This presumption is also born out by the calculations. The 1^1B_2 is computed to lie 6.04 eV above the ground state and has an intensity of 0.15. It is clearly related to the second most intense feature in the energy-loss

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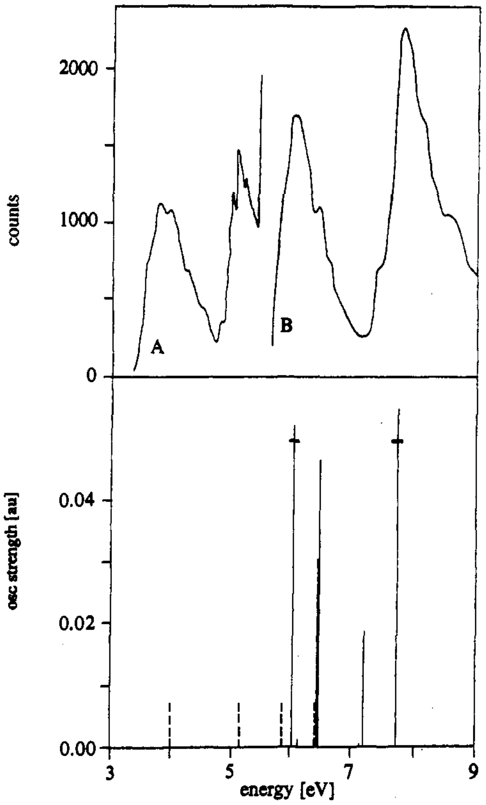

Figure 3. Experimental (top) and theoretical (bottom) excitation spectra of furan. The electron energy loss spectra are copied from ref 43 and measured at $\theta = 50°$, $E = 50$ eV (curve A) and $\theta = 3°$, $E = 50$ eV (curve B), respectively. Curve A is magnified by a factor of 1000, and the dashed theoretical lines mark the position of the triplet states.

spectrum of Flicker *et al.*,[46] which has an intensity maximum at 6.06 eV. The $\langle x^2 \rangle$ value is 30 au^2, which clearly defines it as a valence excited state, even if it is somewhat more diffuse than the ground state ($\langle x^2 \rangle$ = 24 au^2). Previous investigations[2,61] have obtained considerably larger transition energies (around 7.50 eV) and have related this state to the maximum around 7.82 eV,[46] which in the present work will be assigned to the $^1A_1^+$ state.

The second valence excited state is 2^1A_1 ($^1A_1^-$). The calculated transition energy is 6.16 eV, and the intensity is very low, 0.0015. As for the other two molecules, it would be difficult to locate the transition in the spectrum, and there is no experimental evidence which confirms the present result. The value of $\langle x^2 \rangle$ is 24 au^2, which shows its valence character. The ω value, 0.80, shows that there is no problem with intruder states. Also, the similarity between the energies obtained for this state in CP and pyrrole lends further support to the present result. The previous two *ab initio* studies[2,61] placed it at about 7.0 eV but erroneously attempted an assignment to the maximum at 6.06 eV, which belongs to the 1^1B_2 state as shown above. It was argued[2] that the too large energy calculated could be due to the use of a too small basis set, lacking 3d polarization functions, but an assumed nonvertical nature of the transition due to a bond-alternating change in the geometry was also attempted as an explanation. The present results show that such an explanation is not needed. We checked the basis set effect by performing a CASPT2 (0064) calculation using a double-ζ type basis set. The computed excitation energy was 6.60 eV. Thus, basis set deficiencies can explain about half of the error. The major difference between the present and the earlier results is certainly the limitations of the CI-based methods in recovering the large dynamic correlation effects.

The third valence excited state is 4^1A_1 ($^1A_1^+$). It corresponds to the most intense feature of the spectrum with a maximum at 7.82 eV.[24,45,55,57] The calculated transition energy is 7.74 eV, but the appearance of intruder states in the CASPT2 wave function renders an uncertainty of about 0.2 eV to this value, as discussed earlier. The intensity is high, 0.42, and the assignment is therefore clear. None of the earlier theoretical studies have been able to locate this state.

For furan we have also calculated the second valence excited state of $^1B_2$ symmetry. The transition energy is obtained as 8.38 eV with an intensity of 0.27. No experimental assignment is available for comparison.

It might be worth mentioning that the best previous estimate of the valence excitation energies in furan seems to be the CNDO results reported by Del Bene and Jaffé:[1] 5.2 ($^1B_2$), 5.4 ($^1A_1$), 7.3 ($^1A_1$), and 7.3 ($^1B_2$) eV.

$1a_2 \rightarrow 3s$ (1^1A_2). The first excited singlet state in furan is the origin of the R(3d) Rydberg series. The computed transition energy 5.92 eV is in good agreement with the interpretation by Robin,[54] who assigned the weak transition at 5.94 eV superimposed on the N-V$_1$ band to the dipole-forbidden $^1A_2$ Rydberg state. The previous theoretical studies place this state at 5.94 eV[61] and 6.27 eV,[2] respectively.

$1a_2 \rightarrow 3p$ (1^1B_1, 2^1B_2, and 2^1A_2). The components of the 3p Rydberg states have been computed to lie in the energy range 6.46–6.59 eV. The two dipole-allowed transitions (1^1B_1 and 2^1B_2) have rather strong intensities. They have been assigned by Derrick *et al.*[59] to a band located at 6.48 eV. The dipole-forbidden transition 2^1A_2 has not been explicitly assigned, but Flicker *et al.*[46] report a peak at 6.61 eV, which seems to be a good candidate, especially since no other electronic states appear in this energy region. Cooper *et al.*[56] report two bands at 6.47 and 6.48 eV and assign them as members of the 3p triplet.

$1a_2 \rightarrow 3d$ (3^1A_2, 3^1B_2, 2^1B_1, 4^1A_2, and 3^1A_1). The five components of the 3d Rydberg series have been computed to lie in the energy range 7.00–7.31 eV. In all cases the intensities are low, with a maximum for the 3^1B_2 state of 0.0074. Experimentally, one 3d Rydberg state has been located at 7.28 eV[59] and has been assigned to 3^1A_1. The excitation energy for this component has been calculated at 7.31 eV, in agreement with the assignment of Derrick *et al.*[59] This is the only component included in the previous theoretical studies.[2,61] Cooper *et al.*[56] report a value of 7.43 eV for one member of the R(3d) quintet.

$2b_1 \rightarrow 3s$ (3^1B_1). Only the 3s component of the R′ Rydberg series has been located in the present study. The calculated transition energy is 7.21 eV, and the intensity is moderately large, 0.019. Derrick *et al.*[59] have assigned the R′(*ns*) series and arrived at the energy 7.38 eV for the 3s component. The same assignment has been made by Cooper *et al.*[56] We find the difference between theory and experiment distressingly large (compare the corresponding deviations for CP and pyrrole) but cannot suggest an alternative assignment.

Triplet States. As for the other two molecules, we located the four lowest excited triplet states. The first two of them are valence excited, in agreement with the assignments made by Van Veen[45] and Flicker *et al.*[46] The next two states are of the Rydberg type, 3s, and 3pb$_2$. The calculated singlet–triplet splittings are 0.06 eV for 3s and 0.04 eV for 3pb$_2$.

4. Discussion

The excitation energies reported in the previous section are very different from earlier theoretical predictions. In all cases where an unambiguous comparison with experiment is possible, the agreement is excellent. However, it would be more satisfactory if the validity of our results could be confirmed without explicit reference to experiment. A full proof is obviously not possible, since the method is based on second-order perturbation theory and there is no way to estimate the size of higher-order terms explicitly. In a number of small basis set applications it has been possible to compare the CASPT2 result with full CI results.[10,11] The most recent[62] of these calibrations concerns the energy barrier

Table IX. Excitation Energies and Intensities for Valence Excited States[a]

	cyclopentadiene			pyrrole			furan		
state	calcd	exptl	oscillator strength	calcd	exptl	oscillator strength	calcd	exptl	oscillator strength
$^1B_2$	5.27	5.26	0.1475	6.00	(5.98)	0.1253	6.04	6.06	0.1543
$^1A_1^-$	6.31	(6.2)	0.0003	5.92	(5.88)	0.0195	6.16		0.0015
$^1A_1^+$	7.89	7.9–8.0	0.4415	7.46	(7.54)	0.3261	7.74	(7.82)	0.4159
$^3B_2$	3.15	3.10		4.27	4.21		3.99	4.02	
$^3A_1$	4.90	>4.7		5.16	5.10		5.15	5.22	

[a] Excitation energies in eV. Uncertain assignments within parentheses. The numbers given are copied from Tables III, VI, and VIII, where appropriate references are given.

and exothermicity of the reaction F + H_2 → FH + H. The agreement between the CASPT2 and full CI results have been found to be satisfactory in all such tests. Relative energies are reproduced with errors of the order of a few kcal/mol (0.1 eV). Similar results are obtained when CASPT2 is compared to the multireference CI (MRCI) method[10,11] using more extended basis sets. These tests have included a study of the geometry and binding energies of a large number of molecules (the "G1-test").[63] The illustration that binding energies for single bonds could be computed with the same type of accuracy as quoted above may be most relevant for the present discussion. Even more relevant is the comparison between the MRCI and CASPT2 methods for the calculation of the valence excited states in pyrimidine.[6,7] The CASPT2 energies were in all cases in better agreement with experiment than the MRCI results. The main reason for the remaining errors in the MRCI energies was the difficulty in including enough configurations in the reference space for the MRCI wave function. It has been illustrated in a number of applications that it is necessary to saturate the reference space in order to obtain MRCI results of high accuracy. Such a saturation is not always possible due to limitations in the length of the MRCI wave function set by the implementation. The wave functions, in the case of pyrimidine, comprised for some states more than 3 × 10^6 terms, and still the reference space was not saturated. The CASPT2 approach does not suffer from this limitation and therefore often gives more accurate results than MRCI.

Another way of validating the present results, especially for the valence states, is to compare the results for the three molecules. This is done in Table IX. The energies corresponding to assignments which have not been confirmed by the experiments have been put in parentheses. Correlation corrections are similar in the singlet and triplet states. All the triplet states have been found in the spectra and unambiguously assigned (except for the $^3A_1$ state in CP). A comparison with computed values shows that in no case is the error larger than 0.07 eV. The $^1B_2$ state has been firmly assigned in CP and furan. The agreement with the calculations is excellent. The precise location of the $^1A_1^+$ state is uncertain in all molecules, except in CP, while for the $^1A_1^-$ state only speculation about its location can be found in the experimental literature. When the experimental value is confirmed (which happens in eight cases), the agreement with theory is within 0.07 eV. It would be very surprising if the error was considerably larger for the seven other states. Thus, we conclude that the calculations have succeeded to locate the five lowest valence excited states in the three molecules with good accuracy.

Table X. Excitation Energies for Valence Excited Singlet States Obtained with a Minimal Basis Set[a]

	cyclopentadiene		pyrrole		furan	
state	CASSCF	PT2F	CASSCF	PT2F	CASSCF	PT2F
$^1B_2$	9.08	7.38	8.79	8.15	8.89	8.12
$^1A_1^-$	7.18	7.26	6.94	7.04	7.06	7.07
$^1A_1^+$	11.93	10.02	10.53	9.42	10.78	9.46
$^1B_2$	13.98	12.16	10.90	10.16	11.01	10.41

[a] Excitation energies in eV.

Table XI. Calculations on the Valence Excited Singlet States of Pyrrole with the Active Space (0076)[a]

	energy + 208 au					
state	CASSCF	PT2F	$\langle x^2\rangle$	μ	ω	n_{states}
1^1A_1	–0.960 726	–1.614 195	25.8	–0.706	0.82	1
2^1A_1	–0.699 319	–1.395 847	33.5	–0.490	0.80	1–9(4)[b]
6^1A_1	–0.597 891	–1.344 622	29.8	–1.330	0.73	1–9(8)[b]
2^1B_2	–0.620 409	–1.393 278	33.9	–0.691	0.80	1–9(5)[b]

	excitation energy			
state	PT2F	exptl	deviation	oscillator strength
2^1A_1	5.94 (5.92)			0.0179 (0.0195)
2^1B_2	6.01 (6.00)	5.98	+0.03	0.1300 (0.1253)
6^1A_1	7.34 (7.46)	7.54	–0.20	0.3415 (0.3261)

[a] Notation as in Tables IV and VI. [b] The numbers within parentheses correspond to the selected roots. [c] Energies and oscillator strengths from Table VI within parentheses.

Still another way of analyzing the results is to compare the three molecules using a minimal basis (MB) sets. Such a calculation will, of course, not yield accurate excitation energies, but it might be able to show trends. We also know from a number of tests that CASPT2 with a minimal basis set gives results very close to those obtained with the full CI (FCI) method. Intruder states will not be a problem since an MB set does not contain diffuse functions. We have performed such calculations for the valence excited singlet states. The MB set is obtained by keeping only the minimal set in the original basis. The results of these calculations are presented in Table X.

In spite of the large errors, there are many similarities between these and the large basis set results. The CASSCF calculations now correspond to a full CI in the π-orbital space. Thus the CASPT2 corrections account only for interactions with the σ-electrons. These corrections are substantial for the $^1B_2$ and the $^1A_1^+$ states, illustrating the interatomic character of the dynamic polarization (intraatomic correlation cannot be described with an MB set). Obviously, the error in the correlation energy is larger for these states than for the $^1A_1^-$ state, where the correlation energy is much smaller. As a result, the $^1A_1^-$ is the lowest state with the MB set, while the large basis set gives $^1B_2$ as the lowest state, except in pyrrole, where the energies are almost equal. However, the trends of the series CP, pyrrole, furan are the same with both basis sets. Thus $^1B_2$ has its lowest energy in CP, while $^1A_1^-$ and $^1A_1^+$ have larger excitation energies in CP than in pyrrole and furan. These results provide further evidence for the reliability of the large basis set calculations.

One of the most problematic results of the study is the low weights of the reference function in the CASPT2 calculation for some of the valence excited states. As has been already discussed, this is due to interactions with closely lying states of Rydberg character, which should not largely affect the excitation energies. However, the second-order treatment is de facto not valid when large coefficients appear in the first-order wave function. We

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have, in order to check that this has not introduced serious errors in the results, performed CASSCF/CASPT2 calculations for the valence excited singlet states of pyrrole with a larger active space, which includes more orbitals of Rydberg character. The results of these calculations are presented in Table XI. It is immediately clear that the reference weights are now, in all cases, larger and within acceptable limits. The total CASPT2 energies have not changed more than 0.1 eV. The largest change in the excitation energies occurs for the 6^1A_1 state: from 7.46 to 7.34 eV. This state has also become more valence-like, with a decrease of $\langle x^2 \rangle$ from 38.9 to 29.8. This is not so surprising, since the valence Rydberg mixing occurs in the CASSCF wave function, the energy of which is grossly misplaced with respect to the Rydberg states.

5. Summary and Conclusions

A recently proposed[10,11] theoretical method for the calculation of dynamic electron correlation energies has been applied in a study of the lowest valence and Rydberg excited states of the cyclic pentadienes cyclopentadiene, pyrrole, and furan. The model is a two-step procedure with static correlation effects included in the first step, where the molecular orbitals are optimized. Remaining (dynamic) correlation effects are computed in the second step using a second-order perturbation approach. The model has been tested earlier in a study of the excited states in a number of organic molecules,[5,7,8] where it was shown to yield excitation energies with good accuracy. The present study comprises, in total, 61 electronically excited states. The error in the calculated excitation energies is smaller than 0.17 eV in all cases where an unambiguous comparison with experiment is possible. Thus, the present application adds one more example which shows the feasibility of the CASSCF/CASPT2 approach for the calculation of excited states in conjugated systems.

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