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The Electronic Spectrum of Furan

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Abstract: The 30 lowest electronic states of furan have been investigated with theoretical calculations (up to approximately 8.3 eV), and the experimental spectrum scrutinized in the relevant energy region. Electron correlation effects have been examined by performing calculations in a hierarchy of coupled cluster models, and basis set effects have been investigated by carrying out calculations using extensive basis sets. The difference between vertical and adiabatic excitation energies have been calculated. Oscillator strengths, excited-state dipole moments, and second moments of the electronic charge distributions have been used to characterize the calculated electronic transitions and final states. Several reassignments of features in the experimental spectrum have been suggested.

Introduction

The electronic spectrum of furan has been investigated in several experimental[1−12] and theoretical papers.[12−17] It is noteworthy that recent theoretical ab initio studies advocate quite different assignments of several features in the experimental spectrum. The experimental ultraviolet (UV) spectrum[1,2,13] exhibit a few broad and diffuse bands overlapped by a number of Rydberg transitions. Additional information on the electronic spectum have been obtained from multiphoton ionization (MPI)[10,11] and electron impact (EI)[6,7] spectroscopies. The proposed experimental assignments are in some cases contradictory, and, in total, the interpretation is far from straightforward.

Accurate calculation of electronic excitation energies has remained one of the most challenging tasks of ab initio quantum chemistry. The differential nature of the excitation energy makes it compulsary to have a balanced treatment of the two states involved in the excitation process to obtain accurate vertical excitation energies. One of the major sources of errors in the excitation energies is from incompleteness in the one-electron basis set. Most standard basis sets are optimized for ground-state calculations. As excited states are often considerably more diffuse than ground states, extended basis sets are therefore required. A proper treatment of electron correlation is also important for accurate excitation energies, as calculations neglecting electron correlation are often wrong by 1−3 eV. The vertical excitation energies themselves are not experimental observables, and calculations of the 0−0 and other vibronic transitions are therefore more appropriate for comparison with experiment. However, investigation of excited-state potential surfaces is far less well-established in ab initio quantum chemistry than similar studies are for the ground states, and only very recently have efficient techniques been developed for such studies.[18−20]

Different strategies exist for calculation of vertical excitation energies given an appropriate choice of one-electron basis set. In a broad sense, they can be divided into two classes: (1) methods where the total energies of the two states are calculated explicitly and independently and (2) methods focusing directly on the calculation of energy differences. The first class of methods is exemplified by multireference configuration interaction (MRCI)[13,21] and multireference perturbation theory approaches (CASPT2,MRMP);[16,17,22,23] the second by the response theory approach as applied for a Hartree−Fock (HF) or coupled cluster (CC) reference state. In strategy 1, both states and their total energies are calculated and the excitation energy is obtained by subtraction of these energies. In strategy 2, a ground-state calculation is followed by the solution of a response eigenvalue equation giving the vertical excitation energies directly. The excited-state total energy may, in turn, be obtained by addition of the ground-state total energy and the excitation energy. While

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the two strategies are obviously equivalent for exact wave functions, they suggest different approximations for approximate calculations. Another essential difference between the two strategies is that in the state-specific approach a priori physical insight is needed to identify the excited state, whereas in the response function approach, response eigenvalue equations are simply solved for the number of roots representing the desired number of excited states. It therefore becomes exceedingly more difficult to apply the state-specific approach for higher excited states, while no such difficulty exists in the response function approach. In the response function approach, it is straightforward to determine excitations to several Rydberg states or to states where coupling occur between the Rydberg and valence states.

For few-electron systems, multireference configuration interaction (MRCI) calculation has for a long time been an option for obtaining highly accurate excitation energies. However, the factorial growth with the size of the system and the lack of size extensivity of this approach has made such calculations nontractable for larger systems. In multireference perturbation theory methods, a multiconfigurational self-consistent field calculation is initially carried out to obtain a first approximation to the electronic states. Next, the dynamical correlation in both states are accounted for by a (typically second order) perturbational correction. Such calculations rely on physical insight prior to the actual calculation as active spaces needs to be chosen for each state. Improving the accuracy by using higher-order perturbation theory seems bound to fail, as even single reference perturbation theory fails to convergence and behave erratic for many-electron systems.[24,25] Expanding the reference spaces is neither plausible for obtaining increased accuracy because of practical limitations in the size of active spaces that can be treated.

For molecules that have a ground state that is well-described by a single reference state a tractable alternative to the state specific approaches is to use response methods for coupled cluster reference states. We have defined a hierarchy of coupled cluster models, CCS,CC2,CCSD,CC3, that gives excitation energies and molecular properties of increasing accuracy with increasing complexity in the calculations.[26−28] CCS and CCSD denote the coupled cluster singles[26] and the coupled cluster singles and doubles approximation,[29] respectively. In CC2, approximations are introduced to the doubles equations of CCSD.[26] In CC3 the triples equations of the coupled cluster singles, doubles and triples models are approximated.[27,28] For excitation energies we have also introduced CCSDR(3) as a cheap noniterative alternative to CC3.[30] These models in combination with the aforementioned response theory approach gives "black box" methods for calculation of electronic excitation energies. Thus, there is in these models no adaption to the particular system under study. After the one-electron basis set has been chosen, the complete set of excitation energies is defined for each of the coupled cluster models and it only remains to decide how many states to actually investigate.

Initial benchmark calculations against full configuration interaction (FCI) for vertical excitation energies have given very promising results.[31,32] The error in the excitation energies for the lowest excited states of a test suite of small molecules was reduced with about a factor of 3 at each level in the hierarchy, giving a mean (maximum) error of about 0.03 (0.1) eV at the CC3 level.[28,31,32] The same behavior, as in the benchmark calculations, has been found in calculations on several organic molecules, including ethylene and benzene.[28,33] These initial results suggest that the hierarchy of coupled cluster models CCS, CC2, CCSD, and CC3 (or CCSDR(3)) may be as usefull for excited-state studies as self-consistent field (SCF), second-order Møller−Plesset perturbation theory (MP2), CCSD,[29] and CCSD with a perturbative triples correction (CCSD(T))[34] have been for calculation of ground-state properties.[35,36] The accuracy described above for the excitation energies has been obtained only for excitation energies that are single-electron replacement dominated. States such as the so-called elusive E_{2g} state of benzene, where there are significant contributions from double excitations are described less accurately.[28,33] The double-excitation contribution in an excitation process can be monitored by the percentage of single excitation in the solution vectors. If this falls below 90 or so, less accurate results can be expected than described above.

To estimate the basis set error for polyatomic molecules, it is important to carry out calculations using hierarchies of basis sets that converge toward the basis set limit (e.g., in line with the correlation consistent basis sets of Dunning).[37] Large one-electron basis sets must be used in this context, and integral-direct techniques along the lines suggested by Almlöf[38] are often required to make such calculations feasible. Recently, the integral-direct concept was introduced into coupled cluster theory by Koch et al.[39,40] The integral direct algorithm has later been extended to calculation of excitation energies, ground- and excited-state properties, and transition properties.[33,41−43]

By carrying out sequences of calculations using twin-adoption of a hierarchy of coupled cluster models and hierarchies of basis set, it is possible to estimate the accuracy of calculated excitation energies. Calculation of oscillator strengths and excited-state properties are important for the characterization of the excited states, and they also give information that is useful for a

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qualitative assignment of the excited states, for example, in terms of valence and Rydberg states.

Concerning the investigation of excited-state surfaces and calculation of adiabatic and zero-point vibrational energy corrections, it has recently been demonstrated by Stanton and Gauss that this can be done both efficiently and accurately using coupled cluster techniques.[19,20] Furthermore, studies of this kind on *sym*-tetrazine[44] and benzene[45] have demonstrated that it is important to take into account the difference between vertical and adiabatic excitation energies, as well as the differences in zero-point vibrational energies, when discussing an accuracy in excitation energies of a few tenths of an electronvolt.

Calculational Considerations

The electronic configuration of the ground state of furan is $1b_1^2 2b_1^2 1a_2^2 3b_1^0 2a_2^0$ writing out explicitly only the occupancies of the π electrons. A low-lying valence excited state of $^1B_2$ symmetry exists with the principal configuration $1b_1^2 2b_1^2 1a_2^1 3b_1^1 2a_2^0$. We denote this state $^1B_2$. The two valence configurations with nominal π electron occupations $1b_1^2 2b_1^2 1a_2^1 3b_1^0 2a_2^1$ and $1b_1^2 2b_1^1 1a_2^2 3b_1^1 2a_2^0$ give rise to two other valence states of $^1A_1$ symmetry. We denote the lower of these $^1A_1^-$ and the higher $^1A_1^+$. Other valence states, including the one that originates from the $2b_1 \rightarrow 2a_2$ electronic excitation, exist but are found to be somewhat higher in energy. The π electron approximation also predicts correctly that the lowest state of the furan cation has $^2A_2$ symmetry and the second lowest $^2B_1$ symmetry. The experimental ionization potentials are, respectively, 8.883 and 10.308 eV. Accordingly, a number of Rydberg series can be expected to converge toward these values.

In this study, we analyze the electronic spectrum of furan up to around 8.3 eV reporting calculations of about 30 states. These states include, in addition to the valence states $^1B_2$, $^1A_1^-$, and $^1A_1^+$, the $1a_2 \rightarrow nl$ for $n = 3,4$ and $l = 0, 1, 2$ Rydberg states, as well as a number of $1a_2 \rightarrow 5l$ and $2b_1 \rightarrow 3l$ Rydberg states.

Computational Details. We have used the experimental geometry in all of the calculations of vertical excitation energies.[46] For the molecule-centered basis functions, we have used the same center as Serrano-Andres et al.[16] This center was obtained as the average between the centers of the charge centroids of the $^2A_2$ and $^2B_1$ furan cations. We have used the ANO basis of ref 16 in the calculations where we have investigated the convergence with respect to *N*-electron models. The basis set study was performed at the CCSD level, using the ANO basis set and the cc-pVDZ and cc-pVTZ basis sets[37] augmented with both molecule-centered diffuse functions and diffuse functions centered at the atoms. The diffuse atom centered basis functions were (sp/s) and (spd/sp) for the cc-pVDZ and cc-pVTZ, respectively, with exponents taken from ref 47. A series of molecule-centered primitive basis functions was constructed according to Kaufmann et al.[48] and convergence within this series tested for the considered Rydberg states. We have chosen to use a (7s7p7d) set giving the D+7 and T+7 basis sets, comprising, respectively, 177 and 330 basis functions. To demonstrate the convergence with respect to the molecule-centered basis functions, we also give the results for the D+7 basis set extended with one tighter and two more diffuse sets of (spd) molecule centered basis functions. We denote this basis D+10. We describe in more detail the convergence of the excitation energies, with respect to the *N*-electron (subsection B) and the one-electron expansion (subsection C) for some of the lowest states of $^1A_1$ symmetry. Details about these calculations and the calculations of the other symmetry classes can be found in ref 43.

Geometry optimizations have been performed for a number of excited states at the CC2 level. Test calculations indicated that the CC2 level is appropriate at least for the Rydberg states. For example, for the lowest Rydberg state of $^1A_2$ symmetry, the CCS model gave a difference between the vertical and the adiabatic excitation energy of 0.249 eV while the correponding numbers for CC2 and CCSD were, respectively, 0.154 and 0.178 eV. In all of the geometry optimization calculations, we have used the double-ζ basis of ref 49 with polarization functions[50] on all atoms and diffuse functions for the heavy atoms.[51] We denote this basis as DZPR. For the valence states, we also report results obtained without the diffuse functions in this basis, and we denote this basis DZP. All calculations were done using frozen core orbitals. The same basis was also used for the HF calculations on the furan ground state and the two ionized systems.

The calculations were performed using a local version of the Dalton program,[52] including the integral-direct coupled cluster program that recently has been extended to allow integral-direct calculations of excitation energies, transition properties, and ground- and excited-state properties.[33,39−43] The geometry optimizations at the coupled cluster level have been performed using numerical gradients. The HF optimization and frequency calculations were performed using analytical derivatives as included in the Dalton program.

***N*-Electron Convergence on Excitation Energies.** To illustrate the convergence of the excitation energies for the coupled cluster hierarchy, we have displayed in Figure 1 the excitation energies for the lowest states of $^1A_1$ symmetry using the ANO basis. We see good convergence for the excitation energies in the hierarchy of coupled cluster models. The CCS results are in some cases quite erratic, often resulting in a wrong ordering of the states. CC2 is a significant improvement giving results that is within a few tenths of an electronvolt of the CCSD results. Triples corrections lower the excitation energies, and the CCSDR(3) and CC3 results are quite close. For the Rydberg states, the effect of triples is of the order 0.04−0.08 eV. For the valence states, the effect of triples is 0.13−0.25 eV. The largest effect of triples excitations is for the $^1A_1^-$ state. This state has also a slightly larger contribution from doubly replacement electronic configurations, but the single excitation weight is still 91%. The other considered states have a single excitation weight of 94−96%. For an estimate of the accuracy of the excitation energies, we turn to our FCI benchmark calculations.[31,32] Since the coupled cluster response theory

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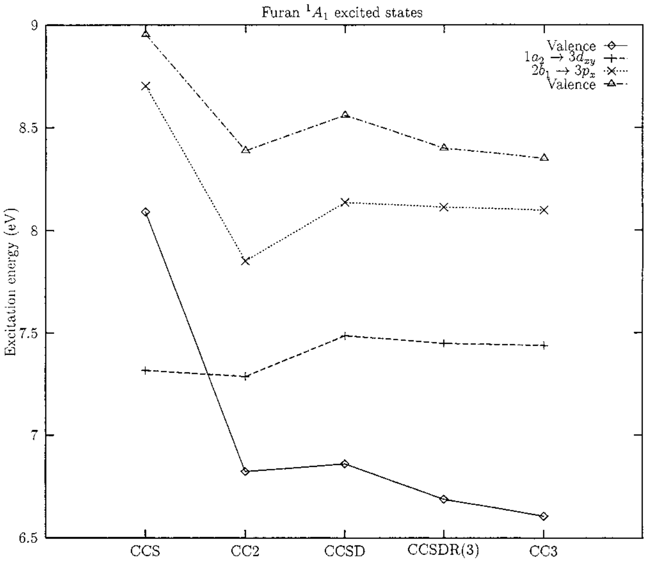

Figure 1. Excitation energies for the lowest states of $^1A_1$ symmetry of furan in different coupled cluster models using the ANO basis set.

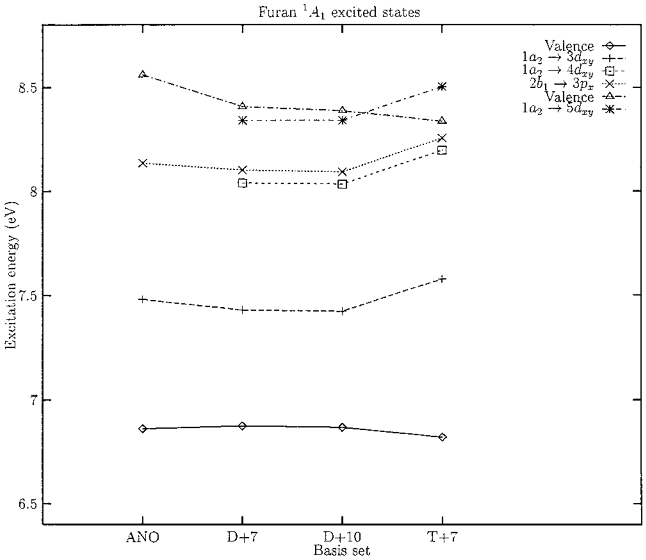

Figure 2. CCSD excitation energies for the lowest states of $^1A_1$ symmetry of furan in different basis sets.

Table 1. One-Electron Properties for the Lowest States of $^1A_1$ Symmetry Calculated at the CCSD/D+7 Level

	$\langle z \rangle$	$\langle x^2 \rangle$	$\langle y^2 \rangle$	$\langle z^2 \rangle$	
1^1A_1	0.273	24.3	134.9	133.3	valence
$^1A_1$	0.367	25.6	136.7	134.6	valence
	−0.037	87.3	193.4	151.0	$1a_2 \rightarrow 3d_{xy}$
	−0.063	215.7	313.8	193.4	$1a_2 \rightarrow 4d_{xy}$
	−0.188	137.1	219.5	167.1	$2b_1 \rightarrow 3p_x$
	0.147	42.2	146.4	146.2	valence
	−0.096	660.1	765.9	341.8	$1a_2 \rightarrow 5d_{xy}$

results scales correct with the size of systems (meaning that results of similar accuracy can be expected for few-electron and many-electron systems) and is a "black box" approach (there is no adaption of the models to the particular system under study), we can gain a good estimate of the reliability of the present results by comparing with these benchmark data. In the benchmark calculation, there is for single excitation dominated states (single excitation weight larger than 90%) a reduction in error by about a factor of 3 at each level in the CCS, CC2, CCSD, CC3 hierarchy. According to this behavior a reasonable estimate of the error in the CC3 results is half the difference between CC3 and CCSD. This gives an error less than 0.1 eV for all states except the two valence $^1A_1$ states, where we estimate that a slightly larger error (0.1−0.2 eV) might be possible. This type of error seems reasonable and conservative in comparison to the mean (maximum) error of about 0.03 (0.1) eV of CC3 in the benchmark calculations. We also point to that on the basis of a similar series of calculations for benzene, the 0−0 excitation energy for the valence $^1B_{2u}$ state was predicted within 0.1 eV. This state was found to contain similar weight of doubles excitations as the $^1A_1^-$ state considered here.

One-Electron Basis Set Convergence on Excitation Energies. The convergence of CCSD excitation energies with extension of the basis set is displayed in Figure 2 for the lowest states of $^1A_1$ symmetry. The basis set effects for the valence states and the Rydberg states are notably different. The $^1A_1^-$ valence state is relatively unaffected by the basis set extension: the T+7 result being lowered by 0.03−0.06 eV compared to the results in the other basis sets. The $^1A_1^+$ state is quite sensitive to the basis. The ANO basis gives an excitation energy about 0.22 eV higher than the T+7 basis, while the D+7 basis result is only 0.07 eV higher than the T+7 result. The ANO basis set is incapable of describing the $n = 4$ Rydberg states. These are described by the D+7 basis set and are insensitive to the further addition of tight and diffuse molecule-centered basis functions, as seen by the D+10 basis set results. The (7s7p7d) molecule-centered basis set is stable within 0.02 eV against inclusion of further molecule-centered basis functions in the sequence of Kaufmann et al.[48] for the electronic states below 8.4 eV. The effect of going from the D+7 to the much larger T+7 basis set is an increase of 0.13 ± 0.04 eV for all Rydberg states. Similar increase in the excitation energies for all Rydberg states going from valence basis sets of double-ζ quality to triple-ζ quality has been found for other molecules (e.g., benzene).[33,41] Experience from test calculations on smaller systems indicates that going from triple- to quadruple-ζ quality basis sets gives only changes of a few hundreth of an electronvolt. Overall, we therefore expect the T+7 basis to give results within a few hundreth of an electronvolt of the basis set saturated result.

Qualitative Assignment of the Excited States. Qualitative information about electronic transitions and the excited states can be obtained in a number of different ways from the ab initio calculations.[53] The qualitative assignments in this paper are based on three such pieces of information. First, the occupied molecular orbitals involved in the primary electronic promotion are identified from the excitation vector. The virtual orbitals have less physical significance, especially when the basis set is enlarged. Second, the oscillator strength for the transition is calculated. Third, excited-state molecular properties as the dipole moment and the second moments of the electronic charge distribution are calculated. The latter can be used to measure the diffuseness of the excited state and is therefore important for the classification into valence and Rydberg states. To illustrate the use of excited-state molecular properties in the assignment of electron transitions, we give in Table 1 the molecular dipole moments and second moments of the electronic charge for the lowest states of $^1A_1$ symmetry in the CCSD/D+7 calculation. We see clearly that some states are selectively compact: these are the valence states. Others are considerably more diffuse, typically with a directional dependency. Together with an analysis of the orbitals from which the primary electron

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Table 2. Excitation Energies (eV) for the Lowest Valence States of Furan

	$^1B_2$	$^1A_1^-$	$^1A_1^+$
CCS/ANO (vert.)	6.32	8.09	8.95
CC2/ANO (vert.)	6.40	6.82	8.38
CCSD/ANO (vert.)	6.49	6.86	8.56
CCSDR(3)/ANO (vert.)	6.38	6.69	8.40
CC3/ANO (vert.)	6.35	6.61	8.35
CCSD/T+7 (vert.)	6.45	6.82	8.34
CC3-CCSD/ANO[a] (vert.)	−0.13	−0.25	−0.21
estimated (vert.)	6.32	6.57	8.13
oscillator strength	0.144	0.000	0.350
CASPT2/ANO (vert.)	6.04	6.16	7.74
MRMP (vert.)	5.95	6.16	7.69
MRCI (vert.)	6.76	6.02	8.32
V-A CC2/DZPR (C_{2v})[b]	0.27	0.41	
V-A CC2/DZP (C_{2v})[b]	0.43	0.44	0.36
V-A CC2/DZP (C_s)[c]	0.43	0.57	0.84
exptl max.	6.04		7.80
exptl range approx.	5.7−6.4		7.5−8.5
refs	1, 13		13

[a] Triples contribution estimated from the difference between CC3 and CCSD using the ANO basis. [b] Difference between vertical and adiabatic excitation energy. Constrained to C_{2v} symmetry. [c] Difference between vertical and adiabatic excitation energy. Constrained to C_s symmetry.

promotion takes place, a qualitative assignments is then made to specific Rydberg transitions. In Table 1, we see how the second electronic moments increase drastically in the $N = 3$, 4, 5 series. A closer analysis of the orbitals from which the electron promotion takes place shows some mixing between the $1a_2 \rightarrow 4d_{xy}$ and $2b_1 \rightarrow 3p_x$ states. This just confirms that the qualitative assignment is indeed only qualitative. The N-electron solutions contain more information than can be contained in an independent-particle description. The calculated molecular properties of the excited states of course have a physical meaning, independent of the qualitative interpretation.

Vertical, Adiabatic, and 0−0 Transition Energies. In Tables 2−4, we have given the difference between adiabatic and vertical excitation energies obtained in CC2/DZPR calculations. These differences are important for all states in view of the accuracy of the calculated vertical excitation energies. For the Rydberg series converging to the $^2A_2$ ionization potential, we find, not surprisingly, very similar effects for all states. The difference between adiabatic and vertical excitation energies is 0.16 ± 0.03 eV for all $n = 3$ Rydberg states. The difference between vertical and adiabatic excitation energies for the Rydberg states with an $^2B_1$ ionic core is smaller.

The importance of zero-point vibrational effects were investigated in exploratory calculations on ionization potentials for the furan $^2A_2$ and $^2B_1$ cations. The results are given in Table 5. We find very small contributions from zero-point vibrations to the ionization potential. Accordingly, we estimate that the zero-point energy contributions to the 0−0 transition energies to be vanishing ($^2A_2$, 0.00 eV) or very small ($^2B_1$, −0.04 eV) for the corresponding Rydberg states. It is interesting to note that for the Rydberg states the differences between the vertical and the adiabatic excitation energies are of similar size and opposite in sign to the effect of increasing the basis set from polarized double-ζ quality to polarized triple-ζ quality.

For the valence states, larger differences are found between vertical and adiabatic excitation energies. The geometry optimizations indicate that the excited valence states are not all of C_{2v} symmetry. The present calculations should only be taken as an order of magnitude estimate of the difference between vertical and adiabatic excitation energies. Furthermore, the zero-point vibrational contributions have not been included for the valence states. It appears to be unnecessary to pursue these aspects further to reliably assign the spectra, as will be discussed in more detail in the next section. We have therefore avoided the rather costly calculations that would be required to significantly improve on the present CC2 results.

The Electronic Spectrum of Furan

Several studies have been reported on the experimental electronic spectrum of furan,[1−12] but a reliable assignment has not been performed for many of the observed electronic transitions. Considering the complexity of the furan spectrum due to a large number of overlapping transitions, it is obvious that experimental assignments are difficult. We demonstrate how some of the ambiguities in the experimental assignment can be resolved on the basis of the coupled cluster electronic spectrum. We consider only assignments of electronic transitions and not the accompanying vibrational structure. A number of previous calculations of vertical excitation energies have been reported[13−17] but will not be discussed in any detail here. For a more detailed comparison between our calculated vertical excitation energies and those previously calculated, we refer the reader to ref 43.

Valence States. While some discussion has occurred over the years, with respect to the two most intense bands in the experimental spectrum, it is now generally accepted that they are due to transitions to the $^1B_2$ and $^1A_1^+$ valence states. The $1^1B_2 \leftarrow 1^1A_1$ transition has been assigned to the band around a maximum of 6.04 eV, while the $^1A_1^+ \leftarrow 1^1A_1$ transition has been assigned to the most intense feature in the spectrum with a maximum around 7.80 eV. These bands are very broad and expanding up to 1 eV. There are no resolved 0−0 transition energy and no assigned vibrational progressions. This makes it difficult to compare the calculated excitation energies with experimental excitation energies. The maxima in the bands is about 0.2−0.3 eV lower than the estimated best vertical excitation energies obtained from the large basis set CCSD results corrected for the effect of triples excitations.

Many theoretical investigations have ignored the uncertainty that exist with respect to obtaining experimental vertical excitation energies and simply assumed that the frequency related to the peak with maximum intensity can straightforwardly be compared with the theoretically calculated vertical excitation energies. This approach can be misleading when subtle issues referring to energy scales of the order of a few tenths of an electronvolt is discussed. As an example, consider the $^1B_{2u}$ valence state of benzene.[33,45] The difference between the vertical excitation energy and the 0−0 transition energy is calculated to be 0.29 eV. Experimentally, the maximum intensity UV peak is about 0.18 eV higher than the 0−0 transition energy. The difference between the vertical and the maximum peak excitation energies is therefore 0.11 eV in this case.

For the furan states studied here, the effect of geometrical relaxation is several times larger than the 0.15 eV in the benzene $^1B_{2u}$ state, and the uncertainty may therefore also be expected to be somewhat larger. The abovementioned agreement is thus as good as can be expected in view of the uncertainty that exists with respect to what the position of the peak intensity really represents and the remaining uncertainty on the order of 0.1 eV in the calculated vertical excitation energies. The present vertical excitation energies, in combination with the calculated

Table 3. Excitation Energies (eV) for the $1a_2 \rightarrow 3l$ Rydberg States

	3s	3p_x	3p_y	3p_z	3d_{xy}	3d_{xz}	3d_{yz}	3d_{z^2}	3$d_{x^2-y^2}$
$1a_2 \rightarrow$ symmetry	$^1A_2$	$^1B_2$	$^1B_1$	$^1A_2$	$^1A_1$	$^1B_2$	$^1B_1$	$^1A_2$	$^1A_2$
CCSD/T+7 (vert.)	6.11	6.94	6.64	6.80	7.58	7.72	7.32	7.12	7.39
CC3-CCSD/ANO (vert.)	−0.07	−0.08	−0.06	−0.07	−0.05	−0.06	−0.06	−0.07	−0.06
V-A CC2/DZPR[b]	−0.15	−0.16	−0.14	−0.17	−0.15	−0.19	−0.15	−0.17	−0.17
estimated 0−0 energy	5.89	6.70	6.44	6.56	7.38	7.47	7.11	6.88	7.16
exptl 0−0[c]	5.91	6.76	6.47	6.61	7.43	7.53	(7.28)		
oscillator strength[d]		0.015	0.035		0.000	0.016	0.001		
CASPT2/ANO (vert.)[e]	5.92	6.48	6.46	6.59	7.31	7.13	7.15	7.00	7.22
MRCI (vert.)[f]	5.95	6.66	6.63	6.41	7.75	7.71	6.99	7.15	7.41
MRMP (vert.)[g]	5.84	6.51	6.40	6.53	7.26	7.18	7.10	6.98	7.18

[a] Triples contribution estimated from the difference between CC3 and CCSD using the ANO basis. [b] Difference between vertical and adiabatic excitation energy at the CC2/DZPR level. [c] In several cases the peaks have been reassigned, see text. See Table 6 for references. [d] Oscillator strength calculated at the CCSD/D+7 level. [e] Reference 16. [f] Reference 13. [g] Reference 17.

Table 4. Excitation Energies (eV) for the $2b_1 \rightarrow 3s,3p$ Rydberg States

	3s	3p_x	3p_y	3p_z
$2b_1 \rightarrow$ symmetry	$^1B_1$	$^1A_1$	$^1A_2$	$^1B_1$
CCSD/T+7 (vert.)	7.52	8.26	8.14	8.11
CC3-CCSD/ANO[a] (vert.)	−0.06	−0.04	−0.06	−0.04
V-A CC2/DZPR[b]	−0.05	−0.05		
ΔO-vib. (HF I.P.)	−0.04	−0.04	−0.04	−0.04
estimated 0−0	7.37	8.13		
exptl 0−0[c]	7.38	8.10		
oscillator strength[d]	0.022	0.016		0.002
CASPT2/ANO (vert.)[e]	7.21			
MRCI[f]	7.14	8.15	7.90	8.04
MRMP[g]	7.31			

[a] Triples contribution estimated from the difference between CC3 and CCSD using the ANO basis. [b] Difference between vertical and adiabatic excitation energy at the CC2/DZPR level. [c] See Table 6 for references. [d] Oscillator strength calculated at the CCSD/D+7 level. [e] Reference 16. [f] Reference 13. [g] Reference 17.

Table 5. Hartree−Fock Ionization Potentials (eV) and Zero-Point Energy Corrections (eV)[a]

	Koopman	vert.	adia.	0-cont.	0−0
$^2A_2$	8.831	7.938	7.660	0.004	7.663
$^1B_1$	10.800	9.779	9.563	−0.036	9.527

[a] HF/DZPR calculation.

relative strength which agrees well with the experimental relative strengths, is sufficient to conclude that the broad 6 eV band is due to $^1B_2$ and the broad 8 eV band is due to $^1A_1{}^+$ beyond reasonable doubt. This assignment was suggested long ago on qualitative grounds.[12] The first ab initio calculation to get this assignment qualitatively correct was the study by Serrano-Andres et al.[16]

There has been some discussion on the assignment of a small feature in the spectrum about 5.80 eV whithin the broad $^1B_2$ band. This feature was found by Roebber et al.[11] and later by Palmer et al.[13] in absorption studies on Jet-cooled furan. Previously the 5.80 eV peak has been assigned to the $1a_2 \rightarrow 3s$ transition; however, Roebber et al. found that it did not behave characteristic for a Rydberg state because it is relatively insensitive to molecular clustering and solution. On the basis of MRCI calculations, Palmer et al.[13] suggested that it should be interpreted as due to the low-lying $^1A_1{}^-$ valence state. The MRCI calculations predicted the vertical excitation energy for the $^1A_1{}^-$ state to be several tenths of an electronvolt below that of the $^1B_2$ state. The vertical excitation energies in all CC models predicts the $^1A_1{}^-$ state to be higher in energy than the $^1B_2$ state. From the large basis set CCSD calculation and the CC3 results we estimate it to be about 0.3 eV higher. Calculations of the vertical excitation energy thus does not support the feature about 5.80 eV to be assigned to the $^1A_1{}^-$ state. On the contrary, the calculated vertical excitation energies predict this state to be more than half an electronvolt higher in energy.

Geometrical relaxation in the $^1A_1{}^-$ state lowers the excitation energy by approximately 0.5−0.6 eV, taking the excitation energy from around 6.6 eV (vertical) into the $^1B_2$ band. The $^1B_2$ 0−0 transition energy is approximately 0.3−0.4 eV lower than the vertical excitation energy. Therefore, the final 0−0 transition energies for these states may indeed become very close, even though the vertical excitation energies differ by ca. 0.2 eV. However, the calculated transition strengths show that the $^1B_2$ transition is at least 2 orders of magnitude more intense than the $^1A_1{}^-$ transition. The $^1A_1{}^-$ transition will therefore most likely be hidden inside the relatively intense $^1B_2$ transition. This probably explains why no secure experimental assignment exist for this state.

In electron transmission on solid furan, broad bands with maximum strengths at 6.40, 6.65, and 8.15 eV were observed,[9] the 6.65 eV peak being only a small shoulder on the high energy side of the 6.40 eV peak. In light of the obvious limitations due to comparison of these results with calculated vacuum excitation energies, we find these transitions to be in fair agreement with the calculated sequence of vertical excitation energies ($^1B_2$, $^1A_1{}^-$, and $^1A_1{}^+$).

Finally, we note that the CASPT2 calculations of Serrano-Andres et al.[16] provide a higher excited valence state of $^1B_2$ symmetry at 8.38 eV. In the coupled cluster calculations, we find the second valence state of this symmetry to be above 9 eV, using the same basis set and geometry. This state is therefore outside of the energy range considered here.

$1a_2 \rightarrow 3s$ Rydberg State. The $a_2 \rightarrow 3s$ Rydberg state is the lowest excited singlet state in our calculations. The calculated excitation energy is 6.11 eV in the large basis CCSD calculations. The triples correction is −0.07 eV. The difference between the vertical and the adiabatic excitation energy is found to be 0.15 eV, and as described above, we estimate the difference in zero-point energy to be small on this energy scale. Thus, we estimate a 0−0 transition energy of 5.89 eV. Roebber et al. assigned a value of 5.91 eV for this transition from multiphoton ionization (MPI) experiments and rejected the previous assignment of the 5.80 eV peak to $a_2 \rightarrow 3s$, as this appeared to be related to a valence state. Though the energy differences are small, our calculations support this reassignment. Furthermore, there is apparently a tendency of our estimated 0−0 energies in Table 3 to be slightly (a few hundreths of an electronvolt) on the low side of the experimental 0−0 transition, as also observed in this case.

$1a_2 \rightarrow 3p$ Rydberg State. The three $1a_2 \rightarrow 3p$ Rydberg states are separated into the symmetry classes B_1 ($3p_y$), B_2 ($3p_x$), and A_2 ($3p_z$). One *p*-type Rydberg state is well-established at a transition energy of 6.47 eV.[1,5,10,13] The associated system is stronger in intensity than the Rydberg transition at 6.76 eV. The latter was assigned to a valence transition by Cooper et al.[10] Later, Robin[12] questioned this and proposed a 3*p* assignment. This was apparently ignored in later comparisons between theory and experiments, probably because the previous theoretical calculations gave very similar excitation energies for the two $^1B_1$ ($3p_y$) and $^1B_2$ ($3p_x$) states,[13,16,17] and, thus, did not support an energy difference of about 0.3 eV. Palmer et al.[13] demonstrated that the experimentally observed vibrational structure in the 6.76 eV transition is similar to the one found in the photoelectron spectrum and also to the one in the 6.47 eV 3*p* Rydberg transition and thus supported the Rydberg 3*p* interpretation. In the coupled cluster calculations the B_1 ($3p_y$) state is predicted to be about 0.3 eV lower than the B_2 ($3p_x$) state and significantly stronger in intensity. This matches the experimentally observed pattern perfectly, and the estimated 0−0 energies are within 0.06 eV of the experimental energies. Palmer et al. assigned the lowest and strongest transition (6.47 eV) to be $^1B_2$ while the other (6.76 eV) was assigned to $^1B_1$. The energies, the energy ordering and the relative oscillator strengths obtained for all CC models indicate that these assignments should be reversed. The assignment to the experimental numbers quoted in Table 3 have been reversed accordingly.

In the electron impact study of Flicker et al.,[6,7] a peak was found at 6.61 eV. This has previously been assigned to the A_2 ($1a_2 \rightarrow 3p_z$) transition, and our predicted value of 6.56 eV supports this assignment.

$1a_2 \rightarrow 3d$ Rydberg State. Three of the five $1a_2 \rightarrow 3d$ excitations (A_1 ($3d_{xy}$), B_1 ($3d_{yz}$), B_2 ($3d_{xz}$), A_2 ($3d_{z^2}$), and A_2 ($3d_{x^2-y^2}$)) are one-photon allowed. In MPI spectra, a Rydberg series with the lowest member being at 7.43 eV has been recorded. A similar peak is apparently not found in the experimental UV spectra. Palmer et al.[13] assumed that the transition was optical forbidden and assigned the 7.43 eV excitation energy to a A_2 (3*d*) transition. However, such an assignment leads to unacceptable large errors compared to our calculated values. A A_1 ($3d_{xy}$) assignment is in better agreement with our theoretical calculations. The one-photon oscillator strength for this transition is very small (less than 10^{-4}), relative to the other Rydberg transitions in the same region. This perhaps explains why it is not observed in UV.

A 7.53 eV peak has been observed and assigned to either A_1 ($3d_{xy}$) or B_2 ($3d_{xz}$). We find that this transition is most appropriately assigned to B_2 ($3d_{xz}$).

A weak absorption was found in the ultraviolet spectrum at 7.28 eV[5,13] and assigned to a Rydberg state; no higher members in this Rydberg series have been observed. Palmer et al. assigned this peak to the $^1B_1$ ($3d_{yz}$) state. A $^1B_1$ assignment leads to a larger deviation (0.17 eV) from the calculated results than for all the other $n = 3$ states (maximum 0.06 eV). However, presently we have no alternative to this interpretation.

Table 6. Calculated Excitation Energies (eV) and Oscillator Strengths for Furan Rydberg States Compared to Experimental Results

	CCSD (vert.)[a]	strength[b]	exptl 0−0	refs	diff.[c]	calcd[d]	assignment
$^1A_1$	7.58	0.000	7.43	10	0.15	0.24	$1a_2 \rightarrow 3d_{xy}$
	8.20	0.004	8.04	10	0.16		$1a_2 \rightarrow 4d_{xy}$
	8.26	0.016	8.10	13	0.16	0.13	$2b_1 \rightarrow 3p_x$
	8.50	0.003	8.34	10	0.16		$1a_2 \rightarrow 5d_{xy}$
$^1B_1$	6.64	0.035	6.47	1, 13	0.17	0.20	$1a_2 \rightarrow 3p_y$
	7.32	0.001	(7.28)	13	(0.04)	0.21	$1a_2 \rightarrow 3d_{yz}$
	7.52	0.022	7.38	13	0.14	0.15	$2b_1 \rightarrow 3s$
	7.90	0.003	7.71	13	0.19		$1a_2 \rightarrow 4p_y$
	8.10	0.002					$2b_1 \rightarrow 3p_z$
	8.17	0.002					$1a_2 \rightarrow 4d_{yz}$
	8.34	0.002	8.19	13	0.15		$1a_2 \rightarrow 5p_y$
	8.42	0.000					$1a_2 \rightarrow 5d_{yz}$
$^1B_2$	6.94	0.015	6.75	13	0.18	0.24	$1a_2 \rightarrow 3p_x$
	7.72	0.016	7.53	13	0.19	0.25	$1a_2 \rightarrow 3d_{xz}$
	7.94	0.001	7.79	13	0.15		$1a_2 \rightarrow 4p_x$
	8.26	0.004	8.01	13	0.25		$1a_2 \rightarrow 4d_{xz}$
	8.36	0.001	8.23		0.13		$1a_2 \rightarrow 5p_x$
	8.52	0.002	8.32	13	0.20		$1a_2 \rightarrow 5d_{xz}$
$^1A_2$	6.11		5.91	10	0.20	0.22	$1a_2 \rightarrow 3s$
	6.80		6.61	7	0.19	0.24	$1a_2 \rightarrow 3p_z$
	7.12					0.24	$1a_2 \rightarrow 3d_{x^2-y^2}$
	7.39					0.23	$1a_2 \rightarrow 3d_{z^2}$
	7.70		7.52	10	0.18		$1a_2 \rightarrow 4s$
	7.93						$1a_2 \rightarrow 4p_z$
	8.03						$1a_2 \rightarrow 4d_{x^2-y^2}$
	8.10						$1a_2 \rightarrow 4d_{z^2}$
	8.14						$2b_1 \rightarrow 3p_y$
	8.26		8.10	10	0.16		$1a_2 \rightarrow 5s$

[a] Large basis (T+7) CCSD vertical excitation energies. [b] Oscillator strength calculated at the CCSD/D+7 level. [c] Difference between CCSD vertical and observed 0−0 energy. [d] Estimated difference between 0−0 energy and calculated CCSD vertical for selected states. Triples corrections as calculated from CC3-CCSD using the ANO basis set results. Geometrical relaxation effects calculated at the CC2/DZPR level.

$2b_1 \rightarrow 3s$ Rydberg State. The $2b_1 \rightarrow 3s$ Rydberg state obviously cannot be expected to behave identical to the Rydberg states with a $^2A_2$ ionic core. Accordingly, we find a diminshed effect of geometrical relaxation in the excited state: 0.05 eV. The large basis set CCSD result of 7.52 eV and a triples correction of −0.06 eV, the afore-mentioned vertical−adiabatic difference, and the zero-vibrational contribution from the HF ionization potential calculations (−0.04 eV) lead us to suggest a 0−0 energy of 7.37 eV. A relatively strong peak has been observed at 7.38 eV[13] and has been assigned to the $2b_1 \rightarrow 3s$ Rydberg transition. This is in good agreement with the estimated 7.37 eV 0−0 energy and a calculated oscillator strength of 0.022.

Higher Rydberg States. For obvious reasons, it becomes rather difficult to give a detailed treatment of all Rydberg states in the system. However, it is also clear from the Rydberg states studied so far that the Rydberg states that converge to the same ionization potential behave similar in a number of different ways. The effect of triple excitations is roughly the same, their behavior, when extending the valence basis, is also approximately the same, and the differences between the vertical and adiabatic excitation energies appear to be roughly the same. For this reason, we compare the experimental and calculated results for the remaining part of the Rydberg series in the following way: In Table 6, we give the calculated large basis set CCSD vertical excitation energies together with experimental 0−0 energies and also the differences between these two values. For the states where we have performed CC2/DZPR geometry optimizations, the expected differences based on calculated triples corrections and the calculated difference between vertical and adiabatic excitation energies are also given. This gives a theoretical method to check the consistency of the assignments. We find that the $1a_2 \rightarrow np_x, np_y$ transition for $n > 3$ follows the same pattern as for $n = 3$, in the sense that the CCSD/T+7

Table 7. Excitation Energies (eV) and Properties (a.u.) for the $1a_2 \rightarrow 3p$ and $1a_2 \rightarrow 4p$ Rydberg States[a,b]

state	CCSD (vert.)	exptl 0−0	strength	$\langle z\rangle$	$\langle x^2\rangle$	$\langle y^2\rangle$	$\langle z^2\rangle$
$1A_1$				0.27	24	135	133
$1a_2 \rightarrow 3p_x$	6.94	6.75	0.012	−2.00	61	141	149
$1a_2 \rightarrow 3p_y$	6.64	6.47	0.036	−0.15	36	180	146
$1a_2 \rightarrow 3p_z$	6.80	6.61		−0.47	38	148	182
$1a_2 \rightarrow 4p_x$	7.94	7.79	0.001	−2.71	240	200	208
$1a_2 \rightarrow 4p_y$	7.90	7.71	0.004	−0.97	93	340	202
$1a_2 \rightarrow 4p_z$	7.93			−0.78	97	202	354

[a] Large basis (T+7) CCSD vertical excitation energies. [b] Oscillator strength and excited-state one-electron properties calculated at the CCSD/D+7 level.

vertical excitation energy is about 0.15−0.20 eV higher than the 0−0 energy. Note that we have again reversed the B_1 and B_2 assignments of Palmer et al. All other transitions are also found to be about 0.15−0.20 eV higher than the 0−0 energy.

The Rydberg series at 7.43, 8.04, and 8.34 eV was assigned as a $R(nd)$ series by Cooper et al.[10] in MPI. We see that this series compares well with a $1a_2 \rightarrow nd_{xy}$ ($^1A_1$) series, while an $^1A_2$ assignment would lead to too large errors, as discussed for the $n = 3$ case.

In Table 7 are given excitation energies and properties for the $1a_2 \rightarrow 3p$ and $1a_2 \rightarrow 4p$ Rydberg states. It is reassuring to see our qualitative expectations confirmed in these calculations. The $n = 4$ states have much larger values for the second electronic moments than the $n = 3$ states, which again is significantly more diffuse than the electronic ground state (see Table 1). The second electronic moments also have a clear directional distortion in agreement with the directional assignment of the Rydberg state. The oscillator strengths for the allowed transitions are reduced by an order of magnitude going from the $n = 3$ to the $n = 4$ Rydberg states. Furthermore, the $n = 4$ states are energetically more close lying than the $n = 3$ series which are split by up to 0.3 eV. The two observed $n = 4$ states are within 0.08 eV of each other. The high reliability in the prediction of trends in the calculations, makes it rather obvious that the unobserved $^1A_2$ ($1a_2 \rightarrow 4p_z$) 0−0 transition should be found a few (1−3) hundreths of an electronvolt below the experimentally observed 7.79 eV $^1B_2$ ($1a_2 \rightarrow 4p_x$) 0−0 transition.

Summary and Concluding Remarks

An important goal of quantum chemistry is to be able to carry out calculations that are accurate enough to explain and predict spectroscopic properties. An essential task is therefore to establish the accuracy of a given calculation. In particular it is important to be able to estimate the errors that are introduced as a result of the two fundamental approximations in the solution of the electronic problem: (1) the use of a finite one-electron basis and (2) the use of approximate N-electron models for describing the electron correlation in the system. Comparison with experimental 0−0 vibronic transitions requires in addition an investigation of the difference between vertical and adiabatice excitation energies, as well as estimates of zero-point vibrational contributions. For the assignment of the experimental spectra, it is also useful to be able to determine the oscillator strength for the transitions. Molecular properties of the excited states may also be useful in characterizing the excited states.

This paper illustrates how state-of-the-art electronic structure calculations can be used to obtain increased accuracy of theoretical predicted electronic excitation spectra and how this accuracy can be used to increase the reliability of the experimental assignments. For the furan molecule investigated in this study, we have thus obtained an overall accuracy of the estimated 0−0 electronic transitions of approximately 0.1 eV. Most of the old assignments have in this way been confirmed, but it has also been necessary to propose several reassignments.

Systematic improvements at the N-electron level have been obtained by carrying out sequences of calculations using the hierarchy of coupled cluster model CCS, CC2, CCSD, and CC3. The performance of these models have been tested with encouraging results in benchmark calculations, where it was found that the errors in the vertical excitation energies are reduced by approximately a factor of 3 at each level, provided the transitions are single replacement dominated. We point out that we have used a "black box" method to calculate the vertical excitation energies. We therefore expect that excited states with equal weight of single excitations are described with equal accuracy and, in particular, that trends for these states are reproduced to very high accuracy. The convergence behavior in the vertical excitation energy calculations of furan is quite similar to the one in the FCI calculations, and this similarity has been used to the discuss the expected accuracy in the predictions. Improvements in the description of the one-particle space have been obtained using large correlation consistent basis sets extended to allow for an accurate description of both valence and Rydberg series. The use of such large basis sets has been made possible for us through the use of integral-direct coupled cluster techniques.

Carrying out systematic sequences of calculations where a still more complete treatment is given both to the one- and N-electron space makes it possible to perform reliable error estimates of the vertical excitation energies. For furan, we expect the estimated vertical excitation energies to be accurate well within one tenth of an electronvolt for the Rydberg and $^1B_2$ valence states and that a slightly larger error may persist for the $^1A_1$ valence states. To estimate 0−0 transitions with similar equal accuracy require that adiabatic corrections to the vertical excitation energies are determined as well as the vibrational frequencies for the ground and excited states. These contributions have been determined for most excitations, although in some cases the estimates are based on rather rudimentary calculations.

High accuracy is required for systematic and reliable studies of electronic spectra. Using state-of-the-art methods, we have shown that for furan theoretical calculations can actually support or challenge experimental assignments and provide reliable insight about the nature of the electronic states and transitions. Though the calculations are presently somewhat expensive, we believe that the methods used in this paper provide valuable tools for reliable assignments of electronic excitation spectra for other polyatomic molecules of similar size.

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